

## Particle-polymer interfaces in foods – using artificial systems to analyze the impact of starch surface functionality

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## Preface

The results and publications of this thesis were produced at the Technical University of Munich, Chair of Brewing and Beverage Technology, Research Group Cereal Technology & Process Engineering from 2014 to 2022

## Publications

The following five peer reviewed publications (shown in chronological order) were generated in the period of this work.

1. Brandner, S., Becker, T., Jekle, M.: **Wheat dough imitating artificial dough system based on hydrocolloids and glass beads.** Journal of Food Engineering 223 (2018), 144–151.
2. Brandner, S., Becker, T., Jekle, M.: **Classification of starch-gluten networks into a viscoelastic liquid or solid, based on rheological aspects - A review.** International Journal of Biological Macromolecules 136 (2019), 1018-1025.
3. Brandner, S., Kratky, T., Holtz, K., Becker, T., Jekle, M.: **Controlling glass bead surface functionality - Impact on network formation in natural edible polymer systems.** Composites Science and Technology 211 (2021), 108864
4. Brandner, S., Becker, T., Jekle, M.: **Impact of the particle-polymer interface on small- and large-scale deformation response in protein- and carbohydrate-based food matrices.** International Journal of Biological Macromolecules 191 (2021), 51-59.
5. Brandner, S., Becker, T., Jekle, M.: **Gluten-starch interface characteristics and wheat dough rheology – insights from hybrid artificial systems.** Journal of food science 87 (2022), 1375-1385.



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## Abbreviations

AACC	American Association of Cereal Chemists
$A_f$	Network strength
Amino-silane	3-aminopropyltriethoxysilane
ANOVA	One-way analysis of variance
BSA	Bovine serum albumin
CLSM	Confocal laser scanning microscopy
Cyano-silane	2-cyanoethyltriethoxysilane
FU	Farino unit
$G^*$	Complex module
HMWG	High molecular weight units
HPC	Hydroxypropyl cellulose
$J_0$	Instantaneous compliance
LMWG	Low molecular weight units
LVE	Linear-viscoelastic
MBS	(N-succinimidyl 3-maleimidobenzoate
Mercapto-silane	Mercaptopropyltriethoxysilane
mNm	Milli-Newton meter
$\eta_0$	Steady state viscosity
NSL	Non-starch lipids
PMPI	N-[p-maleimidophenyl] isocyanate)
propyl-silane	n-propyltriethoxysilane
PVP	Polyvinylpyrrolidone
SDS	Sodium dodecyl sulfate
SGAPs	Starch granule associated proteins
SRC	Solvent retention capacity
XPS	X-ray photoelectron spectroscopy
$z$	Network connectivity

## Summary

Plenty of foods belong to the dispersed systems with particles of soft or rigid character, which are imbedded in a continuous polymeric matrix phase by forming a specific interface between these components. However, in food, and especially cereal science, the knowledge about the rheological impact of this particle-polymer interface is limited. In contrast to synthetic systems, the characterization of the network structures is difficult for natural food systems, such as wheat dough, and led to a large number of different network models. On the one hand, raw material-based fluctuations contribute to this challenging situation, which, on the other hand, is enhanced by the high complexity of the system (dough). A critical review of literature has shown that even the separation into the individual components (e.g. only polymer) and their separate analysis results in different classifications of the network depending on the nature of the raw material and the used analytical approach. Thus, the analysis of complex, native particle-polymer based food systems, is not appropriate for a more detailed analysis of the influence of the particle-polymer interface on the material behavior.

In this context, the complexity of the natural particle-polymer systems was gradually reduced by imitating the particulate component using inert glass particles. Particularly with regard to wheat dough and the ambivalent character of gluten, an imitation of gluten matrix by using standardizable polymers with similar mechanical properties was also necessary, due to the ambivalent character of gluten. The cellulose-based matrix (4 parts HPC, 1 part PVP), which has proven to be suitable for gluten imitation, also enables the consideration of particle-polymer interface in a carbohydrate-based matrix. By the stepwise imitation of wheat dough, the impact of particle-polymer interface can be analyzed, both with protein-based systems (gluten with glass beads, hybrid dough system) and with carbohydrate-based systems (HPC-PVP with glass beads, artificial dough), and thus for the two most common representatives of food matrices. Establishing a defined modification procedure of particulates surface makes it possible to control the surface functionality without inducing further changes. For this purpose, coatings were chosen in order to imitate typical functional groups of the native starch surface: A propyl-silane was used to imitate the hydrophobic, non-polar character of fats (alkyl chains), hydrophilic and polar areas were imitated with cyano-silane, sulfur-containing areas with mercapto-silane, nitrogen-containing areas with amino-silane and covalent interactions by cross-linkers. After the successful validation of surface

functionalization and the characterization of interface characteristics with regard to the adhesiveness and the adsorption mechanism of the polymers, surface functionalization demonstrated already significant differences in the network formation. Depending on the surface functionalization, the required time to develop the maximum network strength, as well as network strength itself, varied between 3.2 and 6.0 minutes, respectively 464 and 874 mNm (protein-based matrix). The following fundamental rheological analyzes were able to show further differences of mechanical network properties depending on surface functionalization, e.g. in the network strength  $A_f$  ranges from  $15250 \pm 2316$  to  $22591 \pm 3481 \text{ Pa s}^{1/2}$  or the fracture strain ranges from 4.4 to 7.0 (protein-based matrix).

In order to transfer the impact of particle-polymer interface to the mechanical properties, native wheat doughs were analyzed using the appropriate rheological methods and compared with the respective properties of the imitating systems. In particular, the importance of an impeded detachment between particle (starch) and polymer (gluten network), in order to increase the deformability of the systems before total structural break down, becomes apparent.

By establishing a new approach of presenting defined glass beads surfaces, which imitate functional groups of starch particle surfaces, the associated standardization contributes significantly to a better understanding of the particle-polymer interface on the mechanical behavior of food matrices. Above all, an understanding of particle-polymer interface characteristics (adhesiveness/adsorption mechanism) has proven to be essential in order to interpret the impact on the mechanical properties.

## Zusammenfassung

Zahlreiche Lebensmittel sind den dispersen Systemen zuzuordnen, welche Partikel mit weicher oder festen Beschaffenheit aufweisen. Diese sind in eine kontinuierliche polymere Matrix eingebettet und bilden dadurch eine spezifische Grenzfläche aus. Jedoch ist in der Lebensmittel- und vor allem der Getreidewissenschaft, das Wissen über den Einfluss der Partikel-Polymer Grenzfläche stark limitiert. Im Gegensatz zu synthetischen Systemen gestaltet sich die Charakterisierung der Netzwerkstrukturen bei natürlichen Lebensmittelsystemen, wie Weizenteig, schwierig und führt prinzipiell zu einer Vielzahl von unterschiedlichen Netzwerk-Modellen. Hierzu tragen einerseits die rohstoffbasierten Schwankungen bei, andererseits stellt die hohe Komplexität der (Teig-) Systeme an sich eine Herausforderung dar. Die kritische Auseinandersetzung mit der Literatur hat gezeigt, dass selbst die Auftrennung in die einzelnen Komponenten (z.B. nur Polymer) und deren separierte Analyse je nach Rohstoffbeschaffenheit und verwendeter Belastungsart/-intensität der Messmethode zu unterschiedlichen Klassifizierungen des Netzwerks führt. Somit erscheint eine Analyse des nativen Gesamtsystems, bestehend aus Partikel und Polymer, als ungeeignet um den Einfluss der Partikel-Polymer Grenzfläche auf das Materialverhalten nähergehend zu analysieren.

Vor dem Hintergrund dieser Problemstellung, erfolgte eine stufenweise Reduzierung der Komplexität der natürlichen Partikel-Polymer Systeme durch die Imitation der partikulären Komponente mittels inerten Glaspartikeln. Speziell in Hinblick auf Weizenteig ist weiterhin, aufgrund des ambivalenten Charakters des Glutens, die Imitation der Glutenmatrix durch standardisiertere Polymere mit ähnlichen mechanischen Eigenschaften notwendig. Die sich hierbei als geeignet erwiesene Cellulose basierte Matrix (4 Teile HPC, 1 Teil PVP), ermöglicht weiterhin die Betrachtung des Einflusses der Partikel-Polymer Grenzfläche in einer kohlenhydratbasierten Matrix. Durch die stufenweise Imitation des Weizenteiges kann der Einfluss der Grenzfläche sowohl bei protein-basierten Partikel-Polymersystemen (Gluten mit Glaspartikeln, hybrides Teigsystem), als auch bei kohlenhydrat-basierten Systemen (HPC-PVP mit Glaspartikeln, künstlicher Teig) und somit für die zwei häufigsten Vertreter lebensmittelbasierter Partikel-Polymersysteme, analysiert werden. Die Etablierung einer gezielten Modifikation der partikulären Oberfläche ermöglicht es die Oberflächenfunktionalität zu kontrollieren, ohne dabei weitere

Veränderungen zu induzieren. Hierfür wurden Beschichtungen so gewählt, dass typische funktionelle Gruppen der nativen Stärkeoberfläche imitiert werden: Zur Imitation des hydrophoben, unpolaren Charakters von Fetten (Alkylketten) wurde ein Propyl-Silan verwendet, hydrophile und polare Bereiche wurden mittels Cyano-Silan imitiert, schwefelhaltige Bereiche mittels Mercapto-Silan und stickstoffhaltige Bereiche mittels Amino-Silan. Um zusätzliche den Einfluss kovalenter partikel-polymer Interaktionen greifbar zu machen, wurden zwei Linker verwendet. Nach der erfolgreichen Validierung der Oberflächenfunktionalisierung und der Charakterisierung der Grenzflächeneigenschaften hinsichtlich der Adhäsivität und des Adsorptionsmechanismus der Polymere konnten bereits bei der Netzwerkentwicklung deutliche Unterschiede in der Entwicklungszeit der Partikel-Polymer Systeme aufgezeigt werden. Je nach Oberflächenfunktionalisierung variierte die notwendige Zeit zur Ausbildung der maximalen Netzwerkstärke zwischen 3,2 bis 6,0 Minuten und 464 bis 874 mNm (proteinbasierte Matrix). Die nachfolgenden fundamental rheologischen Analysen konnten weitere Unterschiede wie z.B. in der Netzwerkstärke  $A_f$  ( $15250 \pm 2316$  bis  $22591 \pm 3481 \text{ Pa s}^{1/2}$ ) oder der Bruchdehnung (4,4 bis 7.0) aufzeigen (proteinbasierte Matrix).

Um eine Deutung über den Einfluss der nativen Stärkeoberfläche in Weizenteigsystemen auf deren mechanische Eigenschaften vornehmen zu können, wurden native Teige mit den entsprechenden rheologischen Methoden analysiert und mit den jeweiligen Eigenschaften der imitierenden Systeme verglichen. Hierbei hat sich vor allem ein verzögertes Ablösen der Polymere (Gluten) von der Partikeloberfläche (Stärke) durch eine hohe Adhäsivität als wichtig herausgestellt um einen frühzeitigen Strukturzusammenbruch unter Deformation zu vermeiden.

Die gezielte Steuerung der partikulären Oberflächenfunktionalität stellt in der Lebensmittelwissenschaft einen innovativen Ansatz dar, welcher durch die Standardisierung wesentlich dazu beiträgt das Verständnis über den Einfluss der Partikel-Polymergrenzfläche auf das Materialverhalten zu vertiefen. Hierbei hat sich vor allem das Verständnis über die Grenzflächeneigenschaften zwischen Partikel und Polymer hinsichtlich der Adhäsivität und des Adsorptionsmechanismus als unabdingbar herausgestellt, um die Effekte auf die mechanischen Eigenschaften interpretieren zu können.

## 1 Introduction

Starch is a very common component of many food systems, whose functional properties allow versatile applications either as particles or as polymers. In the native stage, the granular state of starch enables a particle-based usage. In the presence of water, a temperature increase induces a swelling/breaking of starch granules in combination with the loss of the crystalline structure (gelatinization) and results in the formation of polymeric networks. This property makes starch predestinated for the usage as a thickening and gelling agent since a long time (Maningat et al., 2009). In contrast, the usage of starch as a particle is a relatively new area of application with limited knowledge about the resulting mechanical properties of the particle-polymer interface and its influence on the surrounding matrix phase or the overall particle-polymer system. In general, starch particles offer a broad field for application. For example, they can serve as stabilization agents in Pickering emulsions (Zhu, 2019), as fat-replacers (Chen et al., 2020), as nano-particles in food systems (encapsulation/carrier/releasing agents) or as part of nano-composites in material science (filler reinforcement) (Kumari et al., 2020). To fulfill all of these applications, starch particles often need modifications regarding their size or surface functionality. The natural origin of starch makes it poorly reproducible. In consequence, the applied methods for size or surface modification often result in inconsistent properties that in turn, hamper the understanding of particle-based impact on mechanical properties of the particle-polymer interface, the surrounding matrix phase, as well as the overall particle-polymer system. In particular, particle surface, as part of the interface with the surrounding (polymeric) matrix, is of considerable importance regarding the resulting mechanical properties (Fröhlich et al., 2005); (Bokobza & Rapoport, 2002), since particle surface affects the interactions with the surrounding (polymeric) phase and thus, significantly influence the rheological properties by occurring mechanisms like reinforcement or debonding/delocalization (Payne effect) (Edwards, 1990); (Sternstein & Zhu, 2002). Especially, polymeric matrices with a pronounced viscoelastic character, like gluten, would be affected. However, the impact of these particle-based mechanical mechanisms (e.g. reinforcement, Payne effect), which are well established in material science, are almost unknown, regarding the rheology of viscoelastic food systems, like wheat dough. The unavoidable raw material based fluctuations of natural food systems, such as wheat dough, complicate the understanding of particle-polymer

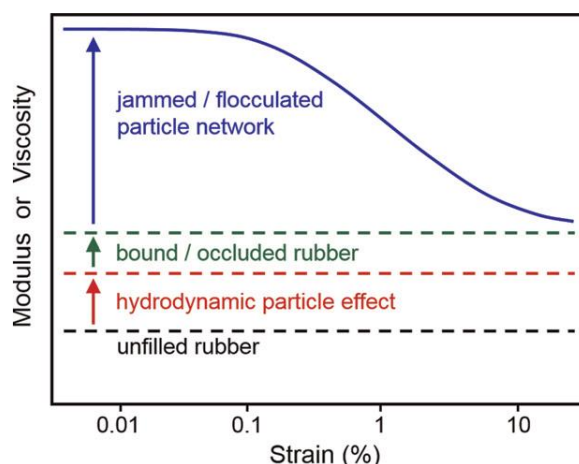


interfaces and their impact on the mechanical behavior, due to their limited degree of standardization. Nevertheless, to gain a more detailed understanding, it requires a reduction of complexity by increasing the standardization of particle-polymer interface in food systems. Using a hybrid artificial approach, consisting of inert particles with a defined coating, offers this standardization and enables a specific assessment of the particle surface located functional groups, regarding the polymeric adsorption mechanism. In combination with a comprehensive rheological analysis, the impact of particle surface on the mechanical properties of viscoelastic food systems can thus be investigated.

In the following section, the general effects of particles (proportion higher percolation threshold) on the mechanical properties of viscoelastic networks is explained. The relevance for food systems and the occurring challenges are discussed by the example of wheat dough, before the thesis outline is presented.

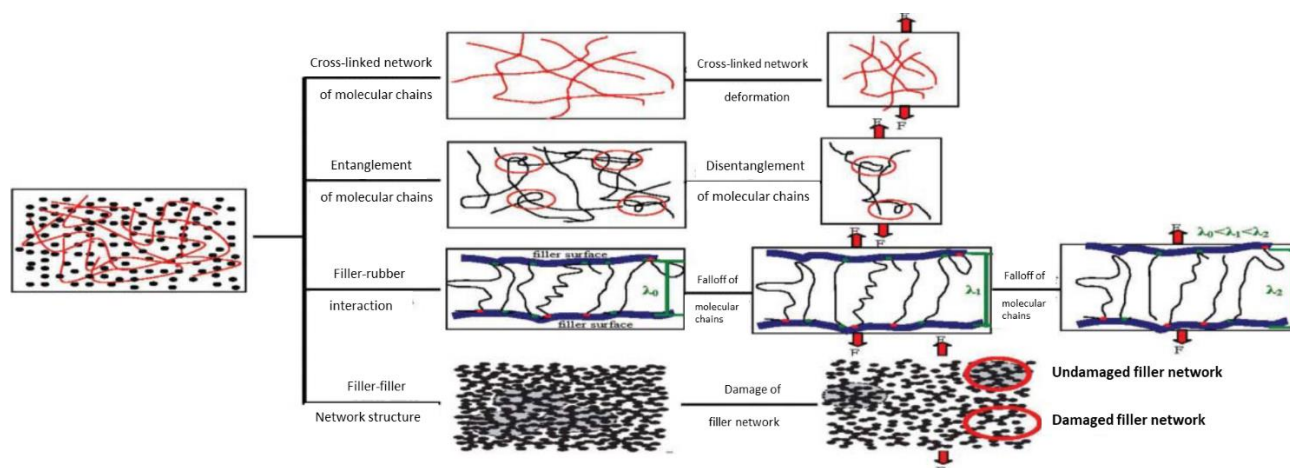
### **1.1 Impact of particles on viscoelastic polymeric matrices**

Adding reinforcements, like particles or fibers, to a viscoelastic polymeric matrix modifies the mechanical properties significantly. Therefore, great efforts are made and are still needed until today, to understand the interacting effects of particles and (polymeric) matrix for designing materials of specific characteristics. The most comprehensive research is probable made in the field of material science of rubber reinforcement. Thus, most of the following explanations are based of rubber/synthetic polymers (or metal-based matrixes), combined with different reinforcements, whose proportion exceeds the percolation threshold. In general, the observed mechanical changes can be summarized by the following terms: mechanical reinforcement, Payne-effect and Mullins-effect. The term mechanical reinforcement describes the general modification of stress-strain behavior. This implies an increase of moduli, tensile strength and elongation at break (Edwards, 1990). The latter terms (Payne- and Mullins-effect) relate to energy dissipation phenomena. Under small deformations, a strong decrease of storage module with a simultaneous increase of loss module occur (compare figure 1). This observation corresponds to the breakdown of particle-particle interactions. Under large deformations, the Mullins-effect becomes visible by a stress softening during a second tensile cycle (Bokobza & Rapoport, 2002); (Srivastava & Mishra, 2018).



**Figure 1: Strain dependent contribution of structural elements of particle reinforced systems on the modulus or viscosity according to (Roland, 2016).**

The level of these mechanical phenomena depends on the properties of the polymeric phase as well as the particular phase and their synergistic effects. As illustrated in figure 2, different structural elements affect the mechanical behavior of the particle-reinforced system.

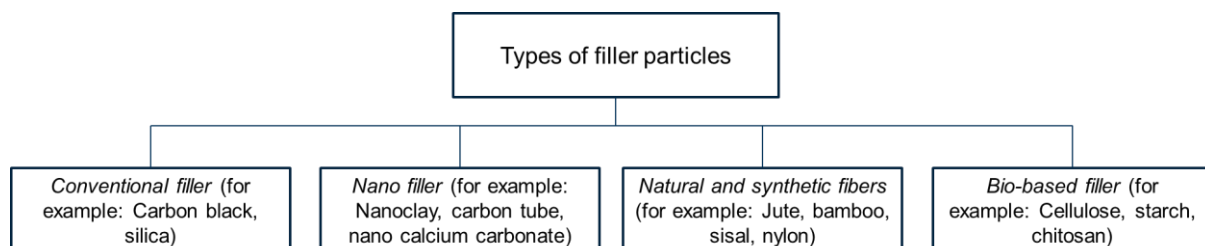


**Figure 2: Impact of mechanical strain on the structural elements of particle-reinforced viscoelastic matrices according to (Fu & Wang, 2016).**

Based on the polymeric network, junctions of covalent or non-covalent character and entanglements contribute to mechanical network properties. Filler particles affect mechanical properties either by an adsorption of polymers or the formation of particle networks. In general, the hydrodynamic effect, which is based on the inclusion of rigid particles, causes an increase of moduli over all strains (Luginsland et al., 2002); (You et al., 2021). This effect strongly depends on the particle volume fraction. If the volume fraction corresponds or exceeds the percolation threshold, particle-particle interactions will affect the moduli (Bokobza & Rapoport, 2002). In general, applying a mechanical

stress to a particle reinforced polymeric network will stress the structural elements at different deformation scales, as illustrated in figure 2 (Roland, 2016). Since the deformability of the polymeric matrix is high, compared to that of rigid particles, the local deformation of polymers, which are located interstitial to particles, will be higher as the overall global deformation. This strain amplification contributes, inter alia, to the reinforcing effect (Song & Zheng, 2016).

Particles used for reinforcement cover a large range of materials and can be classified according to different characteristics (compare fig. 3). Based on the history of usage, carbon black and silica correspond to the conventional types of filler particles, whereas bio-based filler types are used only recently. Beside the time-based characterization, filler particles can be further classified based on their origin (natural vs. synthetic) or their size. Even this classification given by Roy et al. (2020) is quite general and comprise a limited number of characteristics, it illustrates the broadness of used filler types (Roy et al., 2020).



**Figure 3: General classification of filler particles according to (Roy et al., 2020).**

### 1.1.1 Size/-distribution

Beside this large heterogeneity of filler particles, all types have a critical size (Fan et al., 2020) and rigidity in common, which can be considered as a requirement for acting as a reinforcement. The effect of particle size on the mechanical properties will be discussed next. Filler particles can be grouped regarding their size into nano-, micro- and macroscopic particles, with the magnitudes given in figure 4 (Nemati Giv et al., 2018). The smaller the particles, the higher the surface area. In consequence, at a constant volume fraction, smaller particles offer a larger interface for particle-polymer adsorption and thus, making stress transfer mechanisms from polymeric matrix to particles more effective (Nemati Giv et al., 2018). As a result, the modification of stress-strain behavior (reinforcement) is more pronounced for smaller particles (Roy et al.,

2020). In addition, dispersion ability increases with decreasing particles size, which contributes to an increased surface area, too (Fan et al., 2020).

However, reducing the particle size is not always accompanied by a complete change of rheological values. For example, the Young's modulus remains unaffected by a reduction of particle size (Nakamura et al., 1992); (Spanoudakis & Young, 1984); (Lazzeri et al., 2004); (Singh et al., 2002), whereas the tensile strength and fracture toughness shows an unlimited correlation with particle size (Reynaud et al., 2001); (Zhang et al., 2004); (Singh et al., 2002). Therefore, Fu et al. (2008) suggested a critical value for the Young's modulus, which limits the size-based effect on moduli. Above this critical value, a modification of particle size shows no considerable effects anymore. The magnitude of critical particle size depends on the particle itself, the matrix and the particle-matrix adhesion, preventing a predictability (Fu et al., 2008). The different mechanical effects indicate, that beside the particle size, the mobility of particles is important. Gersappe et al. (2002) suppose a function for particle mobility, depending on particle size, attractive forces between particle-polymer and the thermodynamic state of the polymeric matrix (Gersappe, 2002). Furthermore, the aspect ratio (shape) is under debate to affect the mobility and thus the mechanical properties (El Moumen et al., 2015).

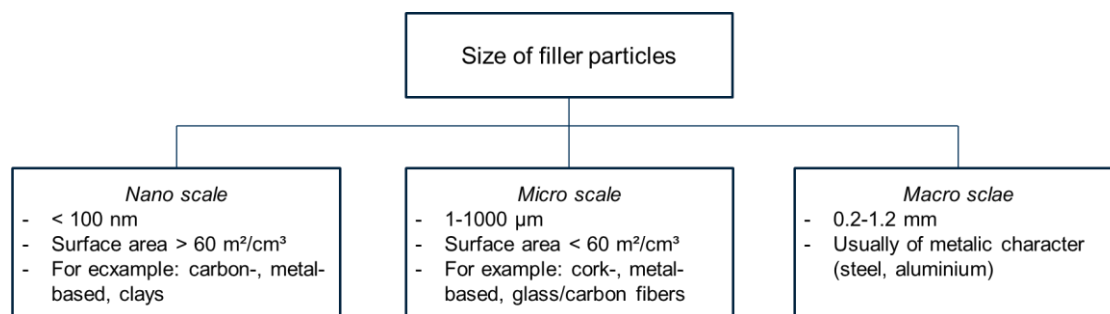


Figure 4: Classification of filler particles based on their size according to (Nemati Giv et al., 2018).

### 1.1.2 Shape

The shape of reinforcements comprises inter alia spherical, ellipsoidal, cylindrical, or fibrous forms. Their shape can be described by the aspect ratio of length to width. In general, for reinforcements with a high aspect ratio (length to cross-sectional diameter), the orientation in respect of the applied load significantly affects the occurring stress fields (Fukuda & Kawata, 1974), (Böhm et al., 2002). However, the literature-based estimation about the contribution of shape on the mechanical properties is quite controversial and ranges from a negligible (Huang et al., 2010) to a

significant (Srivastava et al., 2011) impact. The standard of observation seems to affect the obtained impact of particle shape significantly. For reinforced metal-based matrices a significantly lower ductility and a slightly higher yield strength can be observed with increasing aspect ratio (Song et al., 1996); (Böhm et al., 2002). Despite a deviating character of matrix phase, also hydrogels show an increased stiffness with increasing aspect ratio of reinforcements (Zhang et al., 2019b), which makes the consideration of particle shape reasonable for food matrices. Based on the metal matrices, the differences in mechanical properties correspond with a modified micro stress distribution. Reinforcements with a high aspect ratio (like fibers) bear higher stresses and fluctuations in stress load than those with a smaller aspect ratio (like spherical particles) (Böhm et al., 2002). As a result, deviating failure mechanisms occur. For spherical reinforcements, a void nucleation is supposed, whereas fibrous reinforcements cause a fracture and matrix ligament rupture (Song et al., 1996). Based on the explanations of particle size and shape, it becomes apparent, that a defined analysis of particle surface functionality and their impact on network properties requires particles of constant size/volume and shape.

### **1.1.3 Surface**

Regarding network formation (particle-particle/particle-polymer based), surface activity of reinforcements is a predominant factor, since it determines the interactions between the polymeric and particular phase (Bokobza & Rapoport, 2002). Surface activity can be understood in a chemical sense, based on the chemical groups presented at the surface, or in a physical sense, based on surface energy leading to adsorptions (Fröhlich et al., 2005). There is a general consensus, that the extent of particle-polymer interactions affects the rheological properties significantly. Therefore, the control of particle-polymer compatibility, by using surface modification methods, like coating-/coupling-agents, plasma/heat treatment, (Ramier et al., 2007), is an important topic. The reinforcing effect depends on the effectivity of stress transfer. Consequently, highly adhesive particles increases strength more than poor adhesive particles (Fu et al., 2008). The adhesiveness between particle and polymer also influences the structure of the particle-polymer based system. Based on a given particle-polymer system with a fixed dispersion, the modification of particle surface by coating cause modifications in the network structure, as well as the deformation behavior, as illustrated in figure 5.

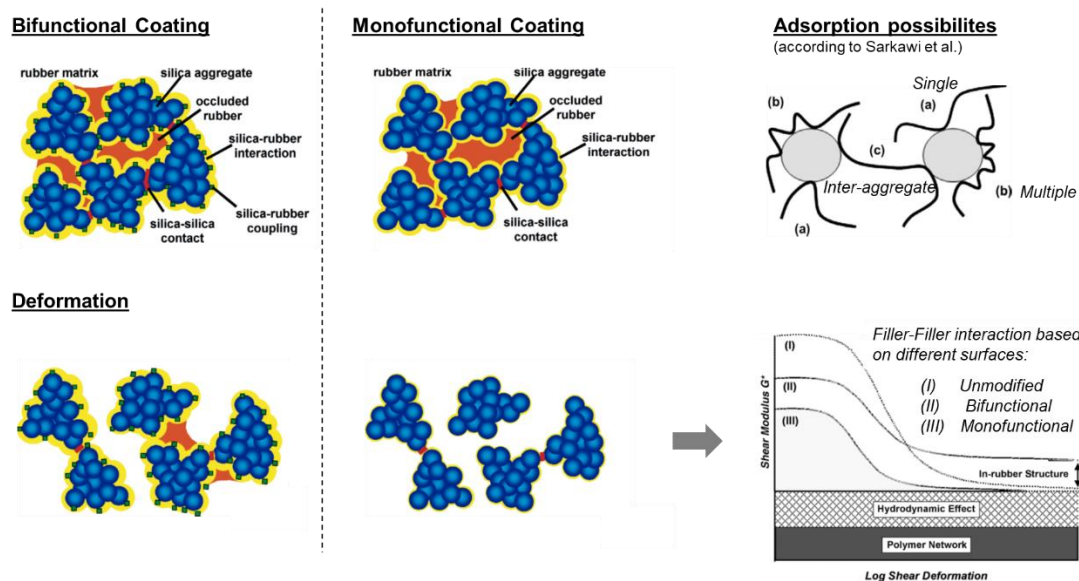


Figure 5: Impact of particle surface activity on the resulting network formation and behavior under deformation according to (Luginsland et al., 2002), respectively (Sarkawi et al., 2014).

In the case of bifunctional coating, which is acting as coupling agent between particle and polymer, a particle-based network and a bound rubber layer are formed. The particle-based network encloses and separates parts of the rubber phase from the overall polymer network (occluded rubber), whereas the bound rubber layer remains accessible for polymer network interactions (Luginsland et al., 2002). The bound rubber phase can be adsorbed loosely or even by strong covalent interactions and in different structures ranging from single, multiple or inter-aggregate attachment (Sarkawi et al., 2014). Using a monofunctional coating, also causes the formation of a particle-based network with enclosed parts of the rubber and an adsorption of polymers at the particle surface. However, the rubber adsorption, as well as the particle-particle interactions are only of weak character. In consequence, the particle-polymer system behaves different under deformation. First, the breakdown of the particle-based network occurs. This is comparable for both coating types and results in the release of the occluded rubber, which promotes a further decrease of modulus. Regarding the adsorbed rubber, a deviating behavior of mono- and bifunctional coating becomes visible. Loosely adsorbed rubber at the monofunctional coating will be detached due to the applied load. A further decrease of modulus results from this detachment. In contrast, the strong (covalent) adsorbed rubber at the bifunctional surface withstand the applied load and results in a lower modulus reduction (Luginsland et al., 2002).

#### **1.1.4 Nature of polymeric matrix**

Reinforced polymer systems belong to the composites. The polymers represent the primary phase of continuous character, whereas the particles belong to the dispersed phase. In general, the character of the matrix phase determines the appropriate applications of the final reinforced system (Jose & Joseph, 2012). For example, the low network strength/viscosity of a particle-reinforced wall paint matrix phase enables an easy application, whereas the high network strength of reinforced metal-based matrices allows high yield strengths. Since each polymeric matrix is very specific regarding the network formation and the mechanical properties, only some general aspects of matrix properties on particle reinforcement are considered in this chapter. A homogenous dispersion of particles is one of the main challenges, since particles have a high surface energy and strong tendency for agglomeration (Rong et al., 2013). The dispersibility can be regarded as a combined effect of enthalpic and entropic interactions (Balazs et al., 2006). The alignment of polymer chains close to the particles cause a reduction of conformational entropy. To maximize entropy, polymers try to repel the particles. As a result, density of polymeric chains can be reduced near the particles. This segregation effect is assumed to be promoted for shorter polymer chains (Crosby & Lee, 2007). In consequence, the effectivity of reinforcements on the mechanical properties depends on the chain length of the polymers. Just small amount of low molecular weight chains induce a significant decrease of elasticity and strength (Sternstein & Zhu, 2002).

#### **1.2 Reinforced viscoelastic food matrices**

Composites are also very common as foods. They are present at different processing steps: in a non-processed form as raw materials, like wheat kernels, in a processed form, like cheese, dough, sausages, or in a highly processed manner as designed foods for specific applications, like nutraceuticals. All of these systems have in common, that a dispersed phase of particular character is embedded in more or less viscoelastic matrix, which is protein or carbohydrate based. However, the rigidity of the particles is very different. In wheat kernels or dough, rigid starch particles are embedded in gluten-based protein matrices, whereas in cheese or sausages soft oil particles are embedded in protein matrices. Despite this difference in particle rigidity, foods containing soft oil droplets are also considered as particle-filled composite materials. Similarly to the rigid particles, the dispersed oil droplets effects structural,

rheological, and sensory properties of foods, too (Gravelle et al., 2019). Consequently, the mechanical effect of soft and rigid particles seems to be comparable and indicates a suitability of rigid particles for fat replacement. Indeed, several studies demonstrate the ability of rigid starch particles for fat replacement in different product types. In low-fat mayonnaise, enzymatically hydrolyzed starch can mimic the fatty mouthfeel due to the rheological properties of the particles (Ma et al., 2006). Further applications of starch particles in fat replacement can be found, for example, in cheese (Montesinos-Herrero et al., 2006), cream (Wang et al., 2013), or ice cream (Aime et al., 2001). Beside spherical particles, fibers are used as well for fat replacement, like inulin fibers in cookies (Rodríguez-García et al., 2013). A second major area of application for reinforced food matrices belongs to the hydrogels. Micro- or nano-gels consist of gel-like particles, which are dispersed in swollen macromolecular networks. Their possibilities for application are versatile. Hydrogels in combination with reinforcements can structure foods and give them the desired textural properties. A stabilizing effect of reinforced hydrogels can increase self-life of metastable products. In nutraceuticals, they serve as delivery systems and ensure the bioavailability of active substances (Li et al., 2021). Moreover, reinforced hydrogels received attention in the field of packaging, either in an edible or non-edible form. Based on the concept of sustainability, the exchange of petrochemical-based packing by biopolymer-based coatings is of large interest (Khalesi et al., 2020). A further contribution to sustainability concerns the limitation of food-spoilage by increasing shelf life. Applying edible films, which contain antimicrobial nanoparticles (like TiO<sub>2</sub>, Ag, ZnO or silicon dioxide), on the surface of fruits and vegetables increases shelf life and thus sustainability (Xing et al., 2019).

Regarding the above-described examples of particles in food matrices, the relevance of a fundamental understanding of particle-polymer interactions on the overall mechanical properties becomes visible. In order to comply with the demand of today's and future human nutrition, some general challenges (see above) can be addressed by reinforced polymer matrices: To prevent an increasing obesity, a reduction of calorie content by particles as fat substitutes can be achieved, food with a therapeutic background can be produced by using reinforced hydrogels as delivery systems, as well as, a general increase of sustainability by replacing petrochemical-based packaging by particle reinforced biopolymer-based packing would be possible. To achieve "new" products with corresponding rheological and textural properties to their

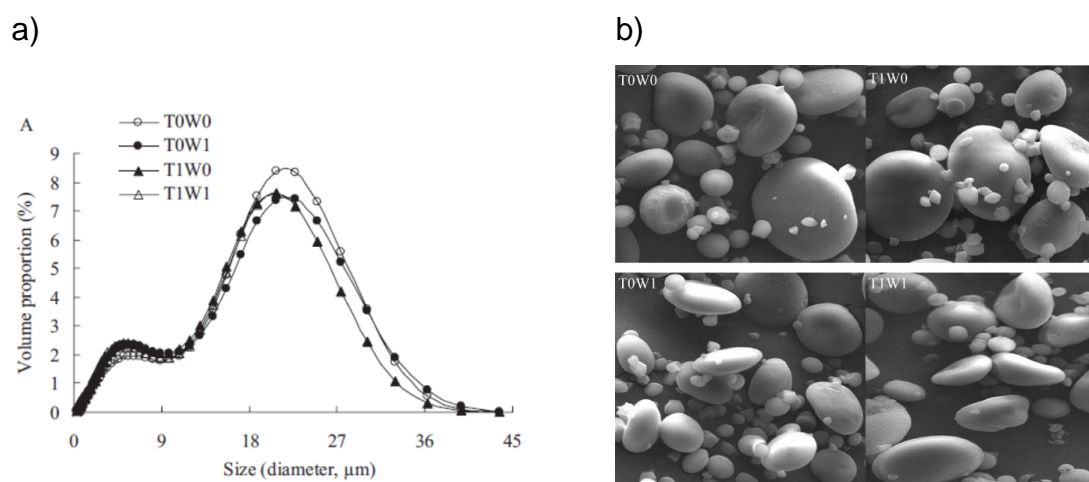


appropriate “original” products, a general understanding of particle-polymer interactions in the original (food) system is necessary. Since starch particles are an often used material in the above described examples, their impact on those natural matrix, gluten, will be explained in the following.

### 1.2.1 Starch reinforced gluten matrices

Starch particles exist together with gluten polymers in wheat kernels. After the milling process and the addition of water and mechanical energy to the flour, a reinforced polymer network, wheat dough, is formed. Similar to reinforced rubber matrices, particles (starch granules) are embedded in the viscoelastic polymer matrix (gluten).

Regarding the particle size, starch granules belong to the micro-scale reinforcements (compare figure 4 and 6). They exhibit a bimodal size distribution (see fig. 6), which can be classified in a smaller fraction of B-type granules with an average size of 3.9 - 4.2  $\mu\text{m}$  and a larger fraction of A-type granules with an average size ranging from 17.0 - 20.2  $\mu\text{m}$ .



**Figure 6: Size distribution and shape of isolated starch granules after different treatments according to (Lu et al., 2014).** Volume distribution (a) and scanning electron micrographs (b) of non-treated (T0W0), and stress treated starch during growing with drought stress (T1W0), heat stress (T0W1) and heat and drought stress (T1W1).

In general, starch granules  $< 10 \mu\text{m}$  belong to the B-type, whereas granules  $> 10 \mu\text{m}$  belong to the A type. Additionally, very small granules ( $< 5 \mu\text{m}$ ) can be classified by the term C-type granule (Maningat et al., 2009). Interestingly, the shape of starch granules depends on their size. Larger A-type granules are lenticular, oblate shaped, whereas smaller B-type granules are spherical (Maningat et al., 2009). In total, larger

A-type granules comprise up to 70 % of volume, but only 10 % of granule number and 20 % of surface area (Lu et al., 2014). As described in section 1.1 the composition/activity of the presented surface area is of great importance regarding the mechanical properties mediated by the filler particles. For wheat starch, proteins as well as lipids are located at the granule surface. The surface located proteins are summarized by the term *Starch granule associated proteins* (SGAPs). Based on their molecular weight, a classification of mainly 10 different proteins with a range of 5 - 149 kDa is possible (Baldwin, 2001). The smaller fraction of SGAPs (~5, 8, 15, 19 und 30 kDa) is directly located at the granule surface, whereas the larger fraction (~60, 77, 86, 95 to 149 kDa) is located within the granules (Schofield, J. und P. Greenwell, 1987). Therefore, only the smaller fraction of SGAPs can contribute to the starch-gluten interface. In particular, the 15 kDa SGAPs (friabilin) gained large attention. Their subunits (puroindoline A and B) can interact via the indole ring of tryptophan with lipids by the formation of hydrogen/hydrophobic bonds and thus, prefer a localization at an interface of non-/polar character (Dubreil et al., 2002). Therefore, Larsson and Eliasson (1997) suggested a control of protein-protein interactions by a separation of the aqueous phase of gluten and starch (LARSSON & ELIASSON, 1997). However, a limitation of the indole ring activity to lipids seems not reasonable and thus, making interactions with the protein matrix also obvious. Beside the SGAPs, lipids are the second prominent component of starch surface. In general, wheat flour lipids can be classified into three groups: Starch-lipids, free non-starch lipids (NSL) and bound NSL. Regarding the particle surface functionality, only the NSL are relevant, since starch-lipids are located within the granule and thus, are not accessible on the surface. NSL contain a broad spectrum of lipid types (~ 60 % non-polar lipids, 25 % glycolipids, 15 % phospholipids). The non-polar lipids belong to the free lipids, whereas glycol- and phospholipids are associated with proteins (bound NSL) (Delcour & Hoseneay, 2010). Phospho- as well as glycolipids have an amphiphilic character and hence, are polar molecules. Their hydrophilic part consists of a phosphate group, respectively a sugar molecule like D-galactose, arabinose or fructose (Kołakowska & Sikorski, 2011). This structure makes an interaction with the vicinal SGAPs obvious. In general, the above made explanations of starch surface composition clearly demonstrate a significant surface activity. Therefore, an active role of starch particles, which would be comparable to that of reinforcements, becomes comprehensible. Since the effect of

reinforcements depends on the character of the polymeric matrix, a brief description of the gluten network is given in the following.

The gluten polymer is composed of monomeric gliadins and polymeric glutenins, which affect the mechanical network properties differently. The viscosity and extensibility of the polymer network is attributed by the gliadins. In contrast, glutenins promote elastic behavior. On a molecular level, gliadins can be classified into  $\omega$ -gliadins,  $\alpha/\beta$ -gliadins and  $\gamma$ -gliadins. Depending on the sulphur content, only the sulphur-rich  $\alpha/\beta$ -gliadins, as well as the  $\gamma$ -gliadins, are linked intramolecular via disulphide bonds (Lindsay & Skerritt, 1999). In contrast, the aggregating glutenin polymers can also interact via intermolecular disulphide bonds. This enables an intermolecular chain elongation by disulphide bonds and results in the formation of large molecules with great differences in molecular weight ranging from 500.000 up to >10 millions Da (Wieser, 2007). Therefore, an additional classification into *high molecular weight units* (HMWG) and *low molecular weight units* (LMWG) is used (Shewry & Tatham, 1997). Based on the molecular structure, the prerequisites for interactions of individual gluten components arise and thus, structure formation on the nanoscopic level. However, network structure of gluten polymers is still not fully understood until today. Lefebvre et al. (2000) describe the structure as a particle-based network with a size of 0.1 -100  $\mu\text{m}$  (Lefebvre et al., 2000). Another theory describes gluten as an entangled polymeric mesoporous hydrogel in the extended polymeric network model (Kontogiorgos, 2011, Kontogiorgos & Dahunsi, 2014). Probably, the most prominent network model is the *Loop and Train Model* of Belton (1999). In this model, proteins arranged in parallel, form the train regions. They are connected via covalent disulphide bonds and non-covalent interactions (Belton, 1999). The formation of loop regions depends, in particular, on the equilibrium of hydrogen bonds between polymer-to-water and polymer-to-polymer. Additional globular proteins associate with the loop and train structure of the HMWGs through non-covalent interactions such as Van der Waals forces, hydrophobic and ionic forces (Shewry & Tatham, 2000). To develop the gluten network the addition of water and mechanical energy (kneading/mixing) is necessary. Simultaneously to network development, starch particles are homogeneously distributed and embedded into the matrix. However, the impact of starch-gluten interface on network formation and behavior might be questionably.

Based on the surface activity of starch granules, adsorption of gluten proteins should be unavoidable and consequently, an impact on network formation and behavior. Nonetheless, the investigation of starch-gluten interactions and their resulting impact on the network properties is very limited and partly quite old. In general it is assumed, that weak physical forces result in an adsorption of proteins (ELIASSON & TJERNELD, 1990). For example, non-polar lipids could interact with the hydrophobic parts of the gluten polymers via hydrophobic forces (McCann et al., 2009). In addition, the possibility of hydrogen bond formation arises from the glutamine-rich domains of gluten polymers and the OH-groups, especially the second or third one, of starch glucose molecules (Bertolini, 2010). Moreover, the polar surface lipids of starch could be involved in hydrogen bond formation with gluten polymers (McCann et al., 2009). Even a basic understanding of gluten adsorption at starch surface exists, the impact on mechanical network properties is mostly of hypothetical character. Based on literature, some general observations can be summarized as follows: A few studies indicate a correlation between network formation and starch-gluten interactions. Yang et al. (2011) analyzed the rheology of reconstituted starch-gluten systems of different ratios. Based on their observations, they suggest an impact of intermolecular starch-gluten interactions on network formation (Yang et al., 2011). Moreover, Watanabe et al. (2002) analyzed reconstituted starch-gluten systems with different amounts of starch and concluded a relation between yielding phenomena and the adhesion strength between starch and gluten (Watanabe & LARSSON, H. ELIASSON, A.-C., 2002). However, by modifying the ratio of particle to polymer content, only the amount, but not the nature, of interface is affected. Consequently, no conclusion regarding the impact of starch-gluten adhesion on the network properties can be made. The ability of starch surface to adsorb gluten polymers by physical or chemical interactions is confirmed by Li et al. (2019). They used adlay instead of wheat starch to produce a gluten-based composite gel and combined rheological with physicochemical analysis. As a result, a gluten polymer adsorption based on hydrogen bonding and hydrophobic interactions is observed (Li et al., 2019). The exchange of starch with a different type of starch is accompanied by a change of particle shape and size distribution. Resulting modifications of rheological properties have to be considered with respect to these factors. Therefore, a clear assessment of particle-polymer adhesion (based on starch-gluten interactions) is restricted. Petrofsky and Hosney (1996) observed an impact of moduli between soft/non-wheat starch and hard wheat starch. They suggested a

different extent of starch-gluten interactions as responsible for the changed moduli (Petrofsky, K.E., Hosney, R.C., 1996). However, also in this case a modified size distribution could affect their observations. In conclusion, the previously described approaches exhibit some basic drawbacks, which hinder a fundamental assignment of starch-gluten adhesion on network properties. In part, the challenges become already visible by the above-described examples (varying size/shape). However, food systems exhibit some additional major challenges in analyzing their particle-polymer interactions, because they are highly complex and simultaneously poorly reproducible.

### **1.3 Determining the rheological impact of particle-polymer interfaces in food matrices**

#### **1.3.1 Challenges in interface analysis**

Despite the availability of highly sensitive methods for analyzing molecular structures, e.g. vibrational spectroscopies, the material-based challenges in analyzing interfaces in food matrices will be illustrated in the following, based on the example of starch reinforced gluten matrices (wheat dough). In general, food exhibits a poor reproducibility regarding its structure and the resulting mechanical properties, due to the natural origin. Therefore, raw material based fluctuations are indispensable. In general, they are caused by climatic conditions (temperature/rainfall) or the availability of nutrients in the soil (nitrogen content). This directly affects the amount and composition of the major components of the raw material, like the ratio of gliadin to glutenin in wheat flour (Daniel & Triboni, 2000), but also minor components, like enzymes, are affected. In case of wheat flour, the varying activity of proteases or amylases results in different degradation levels of gluten, respectively starch (Kawamura & Yonezawa, 2014); (Goesaert et al., 2005). As a result, an instantaneous impact on network structure becomes visible, which will be increasing over time/processing conditions (e.g. temperature), due to the ongoing/promoted activity of enzymes. The occurring modifications, due to enzymatic activity, are often condoned as inevitable side effects, but impede a fundamental understanding of structure-function relationships. In addition to the problem of poor reproducibility and stability, the high complexity of food systems has to be considered. Food systems are constructed of several different components, which, themselves, often comprise again different sub-components. For example, gluten is one major component of wheat flour. Gluten can be divided in several subunits, like the network active components gliadin

and glutenin. This high diversity of components, in combination with the poor reproducibility, results in an almost unlimited number of possible interactions at different structural levels and consequently highly complex structures. Based on these circumstances, the scientific understanding gained by reconstitution experiments is missing accuracy, since many properties are modified at the same time. However, exchanging one component by another of different origin or species, is often used to understand the interplay of two components (Li et al., 2020); (Graßberger et al., 2003); (Zhang et al., 2019a); (Fustier et al., 2008). Consequently, the insights of reconstitution experiments are limited to the general contribution of the whole exchanged component and cannot give deeper insights to the effect of a defined part or functionality of the exchanged component, like, for example, the impact of starch surface activity on the mechanical properties. A further challenge in analyzing food systems persists in their sensibility. Changing ambient conditions will induce a response of a system. Food systems are highly sensitive for every change of ambient condition, whether it is based on temperature, mechanical- or chemical nature. Attempts to induce just one defined modification by a modified ambient condition are therefore highly challenging in a food system, since changing one parameter often results in a necessary adjustment of another one. In the case of wheat starch, a modification of surface activity is achieved by the removal of proteins or lipids by different chemicals. For NSL removal two different types of solvents are necessary: For non-polar lipids, non-polar solvents like hexane and for polar lipids, polar solvents like butanol (Katyal et al., 2020). For protein removal chemicals like sodium dodecyl sulfate (SDS), sodium hydroxide, alkaline protease, or trypsin are commonly used (Zhang et al., 2021). Incubation of wheat flour or starch in these types of chemicals eliminates not only proteins or lipids, but induces additional alterations regarding the porosity or agglomeration properties of the granules (Fustier et al., 2007). In consequence, also modification-based approaches are faced with the problem of unspecific alternations.

### **1.3.2 Opportunities for interface analysis**

Avoiding of unspecific modifications can be attained by model systems. The replacement of natural particles by artificial particles, like glass beads, enables a higher standardization along the whole conditions of food processing, since glass is inert regarding the conditions of food processing, like high temperatures, time, enzymatic or microbiotic activity, etcetera. Despite large differences in rigidity, spherical glass particles can imitate hard, as well as soft particles, like starch (Edwards et al., 2002);

(Brandner et al., 2018) respectively oil droplets (Gravelle et al., 2017; Gravelle et al., 2019). The advantage of particle standardization seems to prevail over the difference in rigidity between oil- and glass-based particles and thus serves as a model system to gain a fundamental understanding. Due to the chemical inertness of glass beads, surface functionalization is possible without inducing other modifications. Edwards et al. (2002) already incorporated glass beads with and without a surface modification into a gluten-based matrix and analyzed the impact on the rheology. However, for surface modification a relatively complex molecule, bovine serum albumin (BSA), is used (Edwards et al., 2002). BSA, as a protein, consists of several amino acids with different functional groups (Rogalinski et al., 2005). In consequence, an undefined surface functionality of glass beads is created, which offers several possibilities for gluten adsorption at the interface. Comparing the rheological results of coated and uncoated glass beads shows considerable differences. In general, this clearly indicates, that the approach of coated glass beads is highly appropriate for analyzing the impact of particle-polymer interface on the mechanical properties. However, the systematic approach and the made assumptions of Edwards et al. (2002) have room for improvement, respectively appear incomprehensible. The uncoated glass bead surface is assumed to be inert with regard to interactions with the gluten matrix (Edwards et al., 2002). Silica glass consists of strong polar Si-O bonds. The polarity of the surface could cause an unspecific adsorption of molecules. Therefore, the statement of no surface interactions with proteins appears indecisive. Moreover, the formation of hydrogen bonds between the BSA coating the gluten protein is assumed (Edwards et al., 2002), but an analytical evaluation is missing. Even if BSA remains its functionality after the adsorption at the glass bead surface, a steric hindrance could limit the degree of hydrogen bond formation with the gluten matrix and the observed rheological changes could just be a result of a modified agglomeration tendency of the particles. In general, BSA coating results in a modified surface functionality of glass beads. However, the effect on the resulting interfacial structure with the gluten proteins remains undefined due to the unspecific coating, which offers several possibilities for gluten adsorption.

To improve the approach of Edwards et al. (2002) a highly defined surface functionality in combination with a detailed analysis of the resulting particle polymer interface is necessary. This combination allows a detailed understanding of the rheological impact of particle polymer interfaces. In material science silanes are established since a long

time for creating defined surface functionalities. The structure of silanes enables a covalent attachment on the glass surface by the formation of covalent siloxane bonds (Si-O-Si) by the hydrolysable groups, whereas the functional group provides the desired functionality. Silanes are commercial available in a wide variety of functionalities (Vistas et al., 2013), thus, choosing an appropriate silane could imitate a functional group of starch surface in a defined way. In combination with an analytical approach for evaluating the resulting adhesiveness between the particle surface and the polymer and the mechanism of adsorption, the impact of particle polymer interface on the mechanical properties of food matrices could be significantly enhanced.



## 1.4 Thesis outline

In food/cereal science, the knowledge about the rheological impact of particle-polymer interface is limited. In contrast to artificial systems, like reinforced rubbers, the characterization of food-based network structures is difficult and lead so far to a large number of different network models. In general, raw material-based fluctuations (protein content/composition, starch quality, enzyme activity, etc.), as well as varying process parameters of network formation and analysis (e.g. various recipes, methodology of network development) contribute to the challenging situation of analyzing food systems. Amidst this situation, a gradual reduction of complexity of the natural particle-polymer systems by imitating the particle-based component by inert glass particles appears reasonable. This thesis takes the approach of a simplified imitating system by providing defined functionalities on the surface of inert particles with a constant size, shape and volume proportion. Thus, the impact of particle-polymer interface on the mechanical properties of protein- or carbohydrate-based matrices can be analyzed in a defined way. Based on the previously outlined challenges and the current state of knowledge the following hypotheses were identified:

- A literature review supported by a critical examination of wheat dough should reveal suitable coatings, which imitate wheat starch surface functionality, as well as suitable polymers, which imitate gluten.
- Coated glass beads bearing a specific functional group can imitate wheat starch and whose surface functionality in a defined way.
- Particle-polymer interfaces are based on different adsorption mechanisms of varying adhesiveness, depending on particle surface functionality.
- The characteristics of particle-polymer interface affects network development, as well as network structure, and thus network properties of food-based matrices.
- The impact of particle-polymer interface on the mechanical properties of food matrices becomes transparent, if adhesiveness between particle and polymer as well as the adsorption mechanism is understood.

To evaluate the above stated hypotheses the following procedures were performed: Initially, it is focused on the challenges in analyzing the mechanical properties of particle-polymer based food systems by the example of wheat flour as a naturally occurring particle reinforced polymer matrix, whose proportion of reinforcements

exceed the percolation threshold. Based on the high material complexity of dough (food) systems, even a separate analysis of individual components (e.g. only polymer) results in different classifications of the network, depending on the nature of raw materials and the experimental setup. Thus, an analysis of native systems, consisting of particles and polymer, appears to be unsuitable regarding a detailed understanding of particle-polymer interfaces and their impact on mechanical behavior.

This leads to a stepwise reduction of complexity by developing a model system, which contains glass beads instead of starch granules. Although glass beads differ from the natural particles in wheat dough (starch) by their perfect spherical shape, the advantage of their consistency (regarding shape and volume) predominates, since a clear focus on particle-polymer interfaces becomes possible. Particularly with regard to wheat dough, the imitation of the gluten matrix by using standardized polymers with similar mechanical properties appears reasonable, due to the ambivalent character of gluten polymers. Such an “optimized matrix” (regarding standardization) would simplify the understanding of particle-polymer interfaces. In addition, a generalization of the particle surface functionality with regard to mechanical properties of reinforced food matrices would be possible through the use of polymers of other origins than proteins, e.g. carbohydrates. By the gradual imitation of the wheat dough, the influence of particle-polymer interface can be analyzed in protein-based particle-polymer systems (gluten with glass particles = hybrid dough system) as well as in “optimized matrix” systems (carbohydrate matrix with glass particles = artificial dough) and thus for the two most common representatives of food-based matrices.

With regard to the polymeric matrix, a specific modification of the particle-based surface activity could be achieved by coating glass beads with silanes bearing specific functional groups. Each of the selected silanes would imitate a functionality of starch surface: The hydrophobic and non-polar character of the alkyl chains of lipids could be imitated by a propyl-functionalized silane, whereas the polar character of amino acids of proteins could be imitated by cyano-functionalized silanes. The amino group or sulfurous amino acids of proteins could be imitated by an amino-functionalized silane respectively a mercapto-functionalized silane. A systematic approach of using varying rinsing steps would allow the analysis of adsorption and desorption kinetics and thus the adhesiveness between particle surface and polymer on a nano- and macroscopic level.

Subsequently, defined and well-characterized particle-polymer interfaces could be analyzed with respect to the overall mechanical properties of the systems. The consideration of mechanical properties at different stress/deformation levels would give more profound insight regarding the impact of particle-polymer adhesiveness and mechanism of polymer adsorption at the particle surface on the rheology of particle-polymer based food systems.

Finally, to enable an evaluation of the influence of native starch surface in wheat dough systems on their mechanical properties, native doughs have to be analyzed using the appropriate rheological methods and compared with the respective properties of the imitating systems.

## 2 Methods overview

A detailed description of materials and methods is given in chapter 3 (results). Briefly, the main methods used in this thesis are summarized as follows:

### 2.1 Surface functionalization

Prior to surface functionalization, surface preparation by heat or chemicals for silicon wafer or rather glass plates/beads was applied. For obtaining a defined particle surface, coatings of different functionalities were used. The selection of coatings reflects the existing functional groups of natural wheat starch surface: n-propyltriethoxysilane (propyl-silane) imitates the hydrophobic and non-polar character of fats (alkyl chains), 2-cyanoethyltriethoxysilane (cyano-silane) imitates hydrophilic and polar/ionic parts, mercaptopropyltriethoxysilane (mercapto-silane) imitates sulphur containing parts and 3-aminopropyltriethoxysilane (amino-silane) imitates amino containing parts. Silylation was carried out at 70 °C for 30 minutes under gentle stirring with a silane concentration of 1 % (v/v) in a 95/5 (v/v) mixture of ethanol/distilled water. In case of 3-mercaptopropyltriethoxysilane-functionalized surfaces, further modifications were achieved by coupling heterobifunctional cross-linker (N-succinimidyl 3-maleimidobenzoate (MBS) rather N-[p-maleimidophenyl] isocyanate (PMPI)) as described by Brandner et al. (2021a). The heterobifunctional cross-linkers enable the polymers to covalently bind to a particle surface and thus, enhance the effects arising from a covalent interaction between functionalized surface and polymer. These functionalized surfaces were used in the third (Brandner et al., 2021a) and fourth publication (Brandner et al., 2021b).

### 2.2 Characterization of interfaces

The interface characteristics between functionalized SiO<sub>2</sub>-surfaces and polymer (gluten rather HPC/PVP) were analyzed on a nano- and macroscopic level by using X-ray photoelectron spectroscopy (XPS) (Leybold-Heraeus LHS 10 spectrometer) and contact angle measurements (Krüss drop shape analyzer DSA25). The functionalized surfaces were incubated in the polymer solvent (gliadin rather HPC/PVP). Subsequently, rinsing steps of different durations (1; 5; 30 min) were applied. Surface composition was analyzed after incubation, rather each rinsing step. The analysis of surface composition after each step enables an evaluation of polymer adhesiveness depending on surface functionality. In addition, the consideration of specific core levels

of the functional groups by XPS gives closer information about the nature (specific/unspecific) of polymer adsorption (Brandner et al., 2021a).

The modification of glass bead surface by surface functionalization was validated by XPS for all samples and fluorescence labeling in combination with confocal laser scanning microscopy (CLSM) (Nikon eclipse Ti-U inverted microscope with an e-C1 plus confocal system) for amino- rather mercapto-functionalized surfaces (Brandner et al., 2021a). Surface/interface characterization was performed in publication three (Brandner et al., 2021a).

### **2.3 Preparation of particle polymer systems**

Particle polymer systems were developed by hydration (non-developed system) or a combination of hydration and mechanical energy (developed system). According to Campos et al. (1996) the non-developed particle-polymer systems were produced by mixing crushed ice particles with the corresponding amount of particle-polymers in a walk-in freezer (Campos, D. T., Steffe, J. F., NG, P. K.W., 1996). Subsequently, network formation was induced by hydration at room temperature for 24 hours (Brandner et al., 2021b). The rheological properties of non-developed particle-polymer systems were compared to developed systems in publication four (Brandner et al., 2021b).

To produce mechanical developed particle polymer systems a z-kneading system or rather a modified glutomatic were used. To reduce raw material consumption, the conventional sieve bottom in a commercial glutomatic (Perten instruments) was replaced by a closed bottom and the automated water dosage system was cut (Döring et al., 2015). This systems allows the production of particle polymer systems in a small scale in publication two (all systems) (Brandner et al., 2018) and four (gluten-based systems) (Brandner et al., 2021b). To observe network development and to determine the required kneading time and appropriate amount of water (according to AACC method 54-70.01) for the reference wheat dough systems, a recording z-kneading system (doughLAB, Perten Instruments) is used in publication two (Brandner et al., 2018) and five (Brandner et al., 2022). Detailed information about the polymers, particles, recipes and kneading times can be found in publication two (Brandner et al., 2018) for systems with native particles, in publication three (Brandner et al., 2021a) for functionalized particles regarding the network formation and in publication four

(Brandner et al., 2021b) for functionalized particles regarding the rheological properties of the particle polymer systems.

## 2.4 Fundamental rheological tests

Fundamental rheological tests were performed with an AR-G2 rheometer (TA instruments) with a 40 mm parallel plate system (upper plate cross hatched) or an MRC 502 rheometer (Anton Paar) with a 25 mm parallel plate system (cross hatched). The AR-G2 rheometer was used for rheological test at a small-scale deformation level, as well as for the deformation sweep in publication two (Brandner et al., 2018). Any other large-scale deformation tests were performed with the MRC 502 rheometer (publication four (Brandner et al., 2021b) and five (Brandner et al., 2022)). All measurements were performed with a sample gap of 2 mm and a temperature of 30 °C. To prevent the samples from drying, the edges were coated with paraffin oil. The second publication (Brandner et al., 2018) uses rheological tests (frequency-sweep, creep-recovery test, deformation sweep) to compare the mechanical properties of the natural dough system with that of the imitating particle-polymer systems (Brandner et al., 2018). In publication four (Brandner et al., 2021b) and five (Brandner et al., 2022) the impact of the different particle surface functionalities on the mechanical properties of particle-polymer systems (publication four (Brandner et al., 2021b)) and their relation to the rheological properties of natural wheat dough was analyzed by frequency sweeps, creep tests within the LVE, creep-recovery test without the LVE, stress-growth tests and flow-relaxation measurements (Brandner et al., 2021b), (Brandner et al., 2022).

Frequency sweeps were analyzed by using the power law. In publication two (Brandner et al., 2018) the storage and loss module are used for fitting, which results in  $K'$  or rather  $K''$  and  $n'$  or rather  $n''$ . Publication four (Brandner et al., 2021b) and five (Brandner et al., 2022) use the complex module for power law fitting, which results in  $A_f$  (network strength) and  $z$  (network connectivity). The creep curve was analyzed by the Burger Model, which results e.g. in  $J_0$  (instantaneous compliance) and  $\eta_0$  (steady state viscosity). Stress-growth curves were evaluated by the height and the deformation level of the maximum stress response of the material and flow-relaxation measurements by the relaxation halftimes (Brandner et al., 2021b).

## **2.5 Statistical Analysis**

For the detection of significant differences, a one-way analysis of variance (ANOVA) with separation of means by the Tukey-Kramer test ( $p < 0.05$ ) was applied.

### 3 Results (Thesis Publications)

#### 3.1 Summary of thesis publications

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<b>1. Classification of starch-gluten networks into a viscoelastic liquid or solid, based on rheological aspects - A review</b>	<b>Pages</b> 34 - 41
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The publication considers the macromolecules gluten and starch in form of wheat dough or gluten networks. Characterization and, in particular, the classification of dough is still challenging. Within this review, the focus is on a clear and neutral assignment of the wheat dough properties based on the rheological, topological, and molecular/thermodynamic properties to the attributes of the network types corresponding to a viscoelastic solid or liquid. Thus, links between classification features for polymers and wheat dough/gluten properties are identified. As a result, the ambivalent character of wheat dough depending on the applied stress/strain level becomes apparent.

The impact of the second major macromolecule (starch) on the dough properties is considered in a second part. Thus, the reinforcing effect of particles on the polymer system becomes visible for wheat dough.

Based on the conclusions of publication one (Brandner et al., 2019), a consideration of the native system, consisting of gluten and starch, appears as inappropriate for analyzing the effect of particle-polymer interfaces on the overall mechanical behavior.

Personal contribution: S. Brandner created the structure of the review article, performed the literature research and manuscript writing. Article structure was critically discussed and improved with co-authors. All authors critically reviewed the article and contributed significantly to the concept of this article.



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<b>2. Wheat dough imitating artificial dough system based on hydrocolloids and glass beads</b>	Pages 42 - 49
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Due to the ambivalent character of gluten networks, as illustrated in publication one (Brandner et al., 2019)., the development of a reference matrix with comparable rheological properties and higher degree of standardization was aspired. The second publication (Brandner et al., 2018) demonstrates the development of a starch-gluten (wheat dough) imitating model system, which offers a simplified and standardized system for a standardized analysis of mechanistic interdependences of particle-polymer interfaces. Due to the limitation of raw materials to hydrocolloids and glass beads, the standardization und simplification of the model system is guaranteed. The main emphasis of imitating starch-gluten (wheat dough) is on the consistency of the viscoelastic properties. Therefore, fundamental rheological tests with different strain levels were used for the adaption process as well as for the characterization of the systems. The results indicate a successful imitation of viscoelastic properties of starch-gluten systems (wheat dough) by the polymers hydroxypropylcellulose (HPC) and polyvinylpyrrolidone (PVP) in a ratio of 4:1 with glass beads of similar particle size as starch. Moreover, coherences of structural elements and the viscoelastic behavior became accessible. Rigid particles enhance the sensitivity to mechanical stress, but simultaneously improve the elastic properties of dough.

The findings of publication two (Brandner et al., 2018) enable a stepwise imitation of wheat dough. Combining gluten polymers with glass beads, allows the analysis of particle-polymer interfaces in hybrid dough systems, those polymer matrix is protein-based. The combination of HPC-PVP with glass beads offers an artificial dough system, those polymer network is carbohydrate-based. Beside this different levels of wheat dough imitation, a general consideration of particle-polymer interfaces for the most common network types of food systems (protein- and carbohydrate-based networks) becomes possible by these systems.

Personal contribution: S. Brandner performed the study conception, conducted the laboratory experiments and data/statistical analysis, as well as literature research, and manuscript writing. All co-authors contributed to the writing of the manuscript.

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<b>3. Controlling glass bead surface functionality - Impact on network formation in natural edible polymer systems</b>	Pages 50 - 58
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Particle-polymer interfaces of food systems are scarcely controllable. This often leads to an indefinite contribution regarding the network properties. By using a hybrid artificial model system, the adhesiveness of two common food-based polymers (protein/carbohydrate) can be evaluated on defined surfaces, functionalized by different coatings. Coatings were chosen to imitate naturally occurring chemical groups on particle surfaces, like hydrophobic parts of lipids or amino groups of proteins. A systematic approach of using varying rinsing steps allows the analysis of adsorption and desorption kinetics on a nano- and macroscopic level. As a result, systems with an adhesiveness ranging from weak unspecific to strong specific adsorptions of polymers were established. Based on the displayed adsorption mechanisms of polymers, a new point of view is available for analyzing the impact of particle surface functionality on network formation of food matrices. Independent of food matrix type, particle adhesiveness influences the mixing time for reaching maximum network strength, thus indicating the ability of particle surface functionality in affecting network formation in food systems. Hereby, the heterogeneity of network junction types enhance the effect of particle surface functionalities. In summary, the presented approach simplifies the challenging analysis of particle-polymer interfaces in food systems and contributes to a deeper understanding of particle-polymer interactions on the overall mechanical properties in food

The assessment of polymer adhesiveness, as well as the mechanism of the polymer adsorption with the different coatings of particle surface, is a prerequisite for understanding those impact on the overall rheological network properties, which are analyzed in publication four (Brandner et al., 2021b).

Personal contribution: S. Brandner performed the study conception and data analysis (except XPS data), as well as literature research, and manuscript writing. K. Holtz contributed by optimizing the experimental design and conducted the laboratory experiments. T. Kratky performed the XPS analysis and coefficient computation. All co-authors contributed to the writing of the manuscript.

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**4. Impact of the particle-polymer interface on small- and large- scale deformation response in protein- and carbohydrate-based food matrices** Pages 59 - 67

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The publication considers varying particle surface functionalities and their rheological impacts on two very common food polymers (protein-based and carbohydrate-based). Silane coated glass beads create a defined particle surface of different functionality (non-/polar, amino/mercapto groups). The variation of particle surface functionality results in different rheological properties at small as well as large deformations for both matrix types. This clarifies the general importance of particle-polymer interface regarding the mechanical properties of food systems. In particular, the adhesiveness between particles and polymers determines the mechanical behavior. Consequently, approved mechanisms of filled rubber systems (like Payne effect) also occur in particle-polymer based food systems. Comparing mercapto with amino coated particles in combination with gluten polymers, demonstrate divergent mechanical properties, despite a comparable adhesiveness. This divergence is attributed to a chain terminating effect of the mercapto coating during polymerization of the protein matrix. In consequence, the adsorption mechanism represents a second important parameter of particle-polymer interfaces, which affects the rheological properties.

Within publication four (Brandner et al., 2021b) the importance of particle surface functionality on the overall mechanical properties of carbohydrate- or protein-based becomes visible. Independent of the polymeric matrix, non-adhesive coatings show the strongest network properties at low stress, but rather the fastest network breakdown under higher stress, whereas coatings with polymer adsorption behave inverse. Since publication four (Brandner et al., 2021b) focus on the impact of particle surface functionality on the rheological properties of food matrices in a general manner, a fifth publication (Brandner et al., 2022) follows for analyzing the impact on wheat dough rheology.

Personal contribution: S. Brandner performed the study conception, conducted the laboratory experiments and data/statistical analysis, as well as literature research, and manuscript writing. All co-authors contributed to the writing of the manuscript.

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<b>5. Gluten-starch interface characteristics and wheat dough rheology – insights from hybrid artificial systems</b>	Pages 68 - 78
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The impact of starch surface on wheat dough rheology is largely unclear. The new perspective, given by the hybrid artificial dough systems with defined particle surface functionalization, can contribute to a better understanding of starch-gluten interfaces and their function in wheat dough. Therefore, the fifth publication (Brandner et al., 2022) discusses the impact of particle surface functionalization in hybrid artificial dough systems on small- and large-scale deformation behavior in relation with the rheological properties of natural wheat dough or rather the effect of starch surface modification reported in literature. Since one coating type imitates the functionality of a certain functional group presented at starch surface, the impact on rheology is clearly assignable.

During network development, starch competes with gluten for intermolecular interactions with the polymer, resulting in lower Farino Units and longer development time. This strong adsorption of starch delays the beginning of non-linearity under large deformations, thus contributing to a high deformability of dough before discontinuities of network structure occur. Consequently, publication five (Brandner et al., 2022) demonstrates a significant impact of starch surface functionality on the mechanical properties, starting from network formation and ending with the thermal fixation of structure.

Personal contribution: S. Brandner performed the study conception, conducted the data/statistical analysis, as well as literature research, and manuscript writing. All co-authors contributed to the writing of the manuscript.

## 3.2 Classification of starch-gluten networks into a viscoelastic liquid or solid, based on rheological aspects - A review

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Review

### Classification of starch-gluten networks into a viscoelastic liquid or solid, based on rheological aspects – A review



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#### ABSTRACT

A material structure determines its processing and product characteristics. Therefore, knowledge on the exact network character is also important in the case of wheat dough to control the process and the product quality. However, the high complexity of wheat dough makes the exact description of the network structure difficult. Several network models, which propose to transfer the observations resulting from rheological or microscopic measurements into structural relationships, exist. This review summarizes the classification features suitable for the characterization of polymer systems, especially food systems, present their typical properties, and verify transferability to wheat dough systems. Thereby, the ambivalent character of dough to behave as solid and liquid becomes evident. As with every polymer network, filler particles have a significant impact on the mechanical properties. Even if the particle content in dough is much higher than the percolation threshold that normally limits the filler usage in reinforced rubbery systems, the general effects of filler particles on the mechanical behavior are also applicable for dough systems.

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#### 1. Introduction

The main functional components of wheat flour are gluten and starch. By themselves, complex network systems, which only need the addition of water and mechanical energy, can be formed. In this system, gluten polymers represent a continuous network phase, while starch granules are dispersed within this network [1,2]. Although starch makes up a larger portion of the two biopolymers, the gluten structure

is mainly responsible for the overall viscoelastic dough properties [3,4]. Gluten is composed of the monomeric gliadin and the polymeric glutenin. The viscosity and extensibility of the dough is determined mainly by gliadin, whereas the elastic properties are subjected to glutenin. On a molecular level, gliadins can be divided into three groups:  $\omega$ -gliadins,  $\alpha/\beta$ -gliadins and  $\gamma$ -gliadins. The  $\alpha/\beta$  and the  $\gamma$ -gliadins form intramolecular disulfide bonds via cysteine groups [3]. In contrast, glutenins are aggregating proteins with cysteine groups at the end and in the middle sequence of the chain [11], which enable intermolecular disulfide bonds and a large range in molecular weight (500,000 to >10 million) [9]. They are subdivided into high molecular weight units

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(HMWG) and low molecular weight units (LMWG). The structure of the individual components of the gluten has not yet been completely clarified. In principle, gluten polymers can interact via different ways, like intra- or intermolecular disulfide bonds, hydrogen bonds, ionic or hydrophobic interactions (for a closer explanation, please see [7–9,69,70]). Based on the molecular structure, specific prerequisites for the interactions of the individual gluten components and thus for the formation of the network structure arise. However, the term “network” is based on a very broad definition and allows many possibilities for interpretations, leading to a large number of network models for gluten/wheat dough. All these models have different focuses, such as rheological or microstructural priorities, resulting in different perspectives of network construction. In contrast, starch granules offer a complete accessible-to-network formation after heating. Prior to heating, starch granules influence the native dough system primarily by their size, shape (larger lenticular vs. smaller spherical grains) [10] and in particular, by their surface functionality acting as a contact point between the filler and the matrix, which determines the interaction with the gluten matrix [11,12]. However, the impact of the particle–matrix interactions on the viscoelastic dough behavior has not been understood in detail. Amemiya and Menjivar suggested that small-scale interactions like hydrogen, hydrophobic or van der Waals interactions lead to an improved elasticity due to starch–starch and starch–gluten interactions [13,14]. The improvement of elasticity caused by small scale interactions can be supported through the observation of an increasing storage module at small strains and a lower linear viscoelastic strain limit by the addition of starch to a gluten matrix [15]. In contrast, reconstitution experiments with starch having a natural or a modified surface (defatted or deproteinized) showed no impact on the viscoelastic properties of raw pasta dough, leading to the conclusion that starch–gluten interactions are limited to a simple physical inclusion [16]. However, further reconstitution experiments have shown a significant influence of the surface functionality of the starch on the dough behavior [71,72]. The overall mechanical behavior of dough systems, which is mainly determined by the gluten network [4], can be easily described by rheological tests; however, the exact determination of the structural arrangement leading to a network remains difficult. The description of the gluten network is mainly based on two perspectives [17]. The first one describes the network cohesion particularly based on disulfide bonds, which undergo certain exchange reactions [1]. Even if no 3D network can be formed in the absence of disulfide bonds, the non-covalent interactions significantly affect the viscoelastic behavior of the gluten network [18]. Therefore, the importance of the non-covalent interactions, especially hydrogen bonds, concerning the network cohesion is often stated (second perspective). As a result of these two perspectives, different network models, which transfer the mechanical dough behavior into the topological properties and relations, have been proposed in the literature. Hamer and van Vliet described the network formation by the hyper-aggregation model in three levels, whereby the network formation arises from the adhering aggregated gluten particles by non-covalent bonds or entanglements. Covalent bonds are only regarded as relevant within the gluten particles [19]. A further common model is the loop and train model of Belton, which describes the elasticity of wheat dough by the formation of train and loop regions in parallel organized gluten molecules [20]. Apart from these two models, a large number of further models exist: the extended polymeric network model of Kontogiorgos et al. described gluten as an entangled polymeric mesoporous hydrogel [5,21]. Lefebvre et al. described gluten as a particle-based network within a size range of 0.1–100  $\mu\text{m}$  [22]. Lefebvre and van Vliet also assumed an aggregated network consisting of insoluble deformable colloidal gluten particles [23]. In conclusion, no consensus of the exact network type of gluten exists [24]. Therefore, the question about the difficulties in describing the type of gluten network arises. Beginning with the raw materials, their fluctuations cause changing properties from dough to dough. Additionally, dough by itself is a dynamic system caused by the enzymatic activity of endogenous proteases and

amylases, which change the network structure, and time dependent hydration effects, which cause an increase of material strength. Finally, the abovementioned variations affect the process and lead to further alterations in the dough properties. Consequently, inconstant and poor reproducible dough systems are the result, making the characterization and, in particular, the classification of dough, challenging. Even if these difficulties are disregarded, the dough structure itself, which consists of a polymer network with two different classes of polymers (i.e., monomeric gliadin and polymeric glutenin) in combination with reinforcing filler particles (starch), contributes to a very complex behavior and description. The overall system consists of several different “subsystems” that determines the material behavior in sum. Therefore, a previous consideration of these subsystems (structural elements) alone is reasonable. Within this review, the focus is on a clear and neutral assignment of the wheat dough properties based on the rheological, topological, and molecular/thermodynamic properties to the attributes of the network types corresponding to a viscoelastic solid or a liquid. Afterwards, the impact of the filler particles will be considered to obtain a clearer overall understanding of the dough behavior.

## 2. Characterization of the network types in polymer sciences

Based on the microstructural level, the common definition is a network is characterized by the network points of a certain functionality  $f$ , which are connected to other network points with  $f$  chains [25]. However, this definition is very general and could comprise materials with completely different properties like a weak gel or a strong duroplastic. Therefore, a variety of closer-defining approaches for the classification of polymers exists. Based on this, polymers can be classified by their physical state (A) by differentiating between amorphous and crystalline (e.g., gelatinized starch and native starch). Based on the architecture (B), linear, branched, or entangled networks can be distinguished, such as polyamide (linear), amylopectin (branched), and gluten (entangled). The degree of crosslinking (C) also enables a differentiation between wide meshed elastomers and narrow meshed thermosets like *Gummi arabicum* vs. epoxy resins. Most foods are characterized as gels or dispersions [26]; hence, some typical classification features of polymer science, apart from the abovementioned ones, like the reaction type of polymerization, are not relevant to the network types in gels. In contrast to the other polymer networks, gels differ in their ability to absorb the surrounding solvent. However, their basic structural elements represent a further network, which can differ in architecture and strength. Based on a network-like structure with a large amount of absorbed water, gels combine the properties of liquid and solid phases, thereby exhibiting a soft rubbery consistency [27]. Materials can generally be classified based on their mechanical behavior into a Newtonian fluid, a viscoelastic fluid, a viscoelastic solid, or a solid. According to this general definition, all categories, except the Newtonian fluid, have a network. Based on the stress independent viscosity of Newtonian fluids, the presence of a network as previously described is impossible because the deformation/disruption of the network points would lead to a change of viscosity. In the case of cereal-based systems, only the differentiation between the viscoelastic liquid and solid is useful because dough neither has the properties of a pure Newtonian liquid nor of a pure solid. However, concerning the classification of wheat dough as viscoelastic solid [28–30] or liquid [15,31,32], no consensus exists in literature. For a classification, the properties of the network-forming elements are essential. In the case of wheat dough, gluten polymers are the network-forming elements, which are mainly responsible for the mechanical behavior. Therefore, and for a reduction of complexity, in a first step, only gluten networks developed by hydration and mechanical energy are considered within this review. The type of considered gluten networks is restricted to ensure a comparability because the network properties strongly depend on the amount of

water and the used energy for polymerization. Therefore, only pure gluten polymerized to a dough-like consistency and gluten networks present in dough in a rubbery state (prepared according to optimum Farinograph water absorption or fixed water absorptions of  $60 \pm 4\%$  of flour weight) are considered. Moreover, for classification, a restriction to characteristics, which are applicable to gluten networks, namely rheological, architecture/topological, mechanical-thermodynamic properties, and the type of chemical bonding, is done. Based on these preassigned characteristics, the properties of a viscoelastic solid or liquid are presented, and their transferability to these gluten networks is assessed.

### 3. Assignment of the polymerized gluten to network types

#### 3.1. Based on the rheological/mechanical behavior

The mechanical behavior of a material described by rheological variables enables a distinction between viscoelastic solid and liquid. A common approach for rheological analysis presents the frequency sweep describing the material behavior by the storage module corresponding to the elastic part, and the loss module corresponding to the viscous part of the material. For viscoelastic liquids, the storage module is smaller than the loss module and approaches nearly zero with an increasing frequency (cf. Table 1, Fig. 1c) because the incorporated energy cannot be stored. In contrast, viscoelastic solids exhibit a greater storage module in the plateau region (cf. Table 1, Fig. 1b) [33]. The high application rate of oscillating stress allows no disentanglement or rearrangement of the polymeric structures because of the fast change of the stress direction resulting in an increased storage module with a flat shape of  $G'$  (plateau region) [34]. Consequently, material properties remained constant within the plateau region until the applied stress achieved a critical limit where structural degradation occurred. For the polymerized gluten networks with a dough-like consistency (50% water w/w), the ratio of gliadin to glutenin significantly affected the proportion of the viscous and elastic parts; however, for all cases, the storage module was higher than the loss module [35]. Moreover, by increasing the frequency, the storage module also increased [36,37] and, for doughs with a high consistency (1000 Brabender units), reached a region with a relatively flat slope (plateau region,  $G' > G''$ ) [13]. In conclusion, at small stress/strain levels, the gluten network clearly behaved as a viscoelastic solid. However, this small stress level did not correspond to the stress occurring during the dough processing. To evaluate the material properties under a higher strain/stress, creep tests are often used. The achievement of an equilibrium compliance under a constant stress is considered as a characteristic for viscoelastic solids, whereas viscoelastic liquids attain only a steady-state compliance [38]. The difference between the viscoelastic solid and liquid by reaching an equilibrium or steady-state compliance is illustrated in Fig. 1a). A steady-state compliance can be achieved in the case of gluten networks present in dough. However, the time necessary for the achievement of a steady-

state compliance varies from a few minutes [39,40] to a few hours [31,41]. In contrast to the assignment of a gluten network to viscoelastic solids at frequency sweeps (small stress level), the observations made in the creep tests at a higher stress level compared to frequency sweeps indicated a liquid-like behavior, clearly indicating the stress-dependent behavior of wheat dough.

A further rheological attribute for the differentiation between viscoelastic liquid and solid represents the ability of viscous flow, which occurs at sufficiently long times for liquids, and not for solids. The observations of the gluten networks after a mechanical energy input led to the conclusion that viscous flow is necessary for the release of elastic stress by structural rearrangements based on thiol-disulfide interchange or hydrogen and hydrophobic bond interchange [42]. However, this viscous flow occurred only by a shift of the thermodynamic equilibrium introduced by a high mechanical stress (kneading). These rearrangements last until rest periods of 3 h, exceeding most process times. Consequently, gluten polymers should be regarded as flowable at least for practical applications, thereby leading to the classifications as a viscoelastic liquid. The capability to flow becomes evident from the good descriptiveness of the mechanical gluten behavior by the Lodge rubberlike model, in which the breaking and the new formation of junctions represents the flowing parts of the system [28,43]. Nevertheless, if a yield point ( $\sigma_{lim}$ ) exists, it would amount to only a few pascals and, therefore, justifies the simplification of  $\sigma_{lim} = 0$  [44]. Table 1 summarizes the rheological properties of the viscoelastic liquid and the solid illustrated and assessed for the gluten network. By summing up the rheological properties, it becomes evident that no clear statement of whether or not gluten polymers should be regarded as a viscoelastic liquid or solid. The classification strongly depends on the stress/strain level used for the measurement: only very small deformations corresponded to the viscoelastic solid-like properties, whereas already moderate stress led to a liquid-like behavior. For most polymeric systems, the sole rheological assessment is insufficient for a clear assignment because architectural properties like the homogenous distribution of the network strands or the formation of clusters are difficult to observe. Therefore, microscopic measurements are used additionally.

#### 3.2. Based on architecture

A clear distinction between different network types can be made by the visualization of the network structures using microscopic measurements and a subsequently network analysis [45]. A characteristic topological feature of gels consisting of high molecular weight polymers in high concentrations represents the formation of entanglements (Table 2, Fig. 2a) for liquids and Fig. 2c) for solids). The entanglements can be formed in polymers with a molecular weight higher than a threshold. This threshold represents the minimum molecular weight necessary for the formation of entanglements, and is characteristic for each polymer. Since glutenin polymers are much bigger than gliadins,

**Table 1**

Summary of the characteristic rheological properties of the viscoelastic liquid and solid and assessment for gluten networks. For illustration, the creep curve and the frequency-sweep curve of a viscoelastic liquid and solid are presented.

Attribute/category	Viscoelastic liquid		Viscoelastic solid	
	Characteristics	i. a. w. <sup>2</sup> gluten network?	Characteristics	i. a. w. gluten network?
Rheological (mechanical behavior)	No equilibrium compliance $J(t)$ , $J(t) \Rightarrow$ infinite [68], cf. Fig. 1a)	✓ Only steady state compliance [39–41]	Equilibrium compliance under constant stress ( $J_e$ ) [68], cf. Fig. 1a)	× Only steady-state compliance [39–41]
	Viscous flow at sufficiently long times	✓ Very limited [28,42,43]	No viscous flow	× Gluten is capable of flow [18]
	$G'(\omega) \rightarrow 0$ with increasing frequency [33], cf. Fig. 1b)	× Storage module increases with increasing frequency [35–37]	$G' > G''$ in the plateau region [33], cf. Fig. 1c)	✓ Plateau region with a relatively flat slope of $G'$ and higher $G'$ than $G''$ [13]
	$G'' > G'$ [68]	× Not for small amplitude oscillatory shear tests [35–37]		

<sup>1</sup> cf. = confer.

<sup>2</sup> i. a. w. = in accordance with.



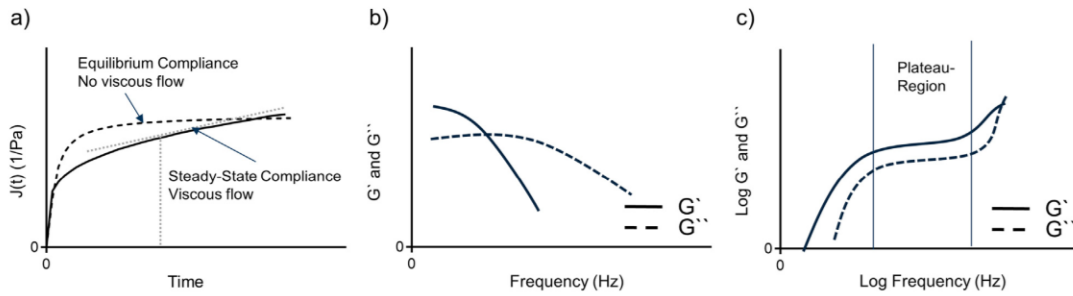


Fig. 1. Illustration of a creep curve a) having an equilibrium or a steady-state compliance for a viscoelastic solid or liquid, a frequency-sweep curve (b) for a viscoelastic liquid/solid and c) with a plateau region of a viscoelastic solid.

entanglements in gluten are expected between neighbouring glutenin polymers. For glutenin entanglements a threshold of 250,000 Da is assumed [46]. Entanglements can be formed in different conformations (compare Table 2). Topological entanglements consist of loops between two different polymer strands, whereas cohesive entanglements form a parallel alignment of two polymer strands [47]. The coupling of the entanglement occurs at a molecular level, whereby small sequences of glutenin interact via physical interactions with the neighbouring molecules [48], mediating an additional strength to the network by an additional fixation of the loop.

In viscoelastic liquids, these architectural elements have apparently the same status as cross-linked elements [49]. Moreover, entanglements can occur in viscoelastic solids. However, their precise effect on the cross-linked system is still controversial [50]. Entanglements, which are present prior to crosslinking reactions, can be incorporated into the network. Subsequently, these entanglements are trapped by the permanent linkages, and may cause an increase of modulus if they are not of a strictly transitory character [51]. In gluten networks, glutenins form entanglements with the neighbouring molecules. These entanglements can generate an additional resistance to flow by acting as transient cross-links. Consequently, a highly viscous system arises. The elasticity is maintained by entanglements, which allow a free slip of polymer chains and prevent the breakage of bonds [48]. In an uncross-linked system, this movement and rearrangement also improved strain hardening through the enhancement of the elastic limit [52]. No clear distinction for gluten networks can be made because of the similar effect of entanglements on the mechanical behavior in the viscoelastic liquids and solids. However, the strong contribution of entanglements to the mechanical behavior, especially strain hardening, supports the assumption to consider entanglements as an independent structural parameter [14] and, consequently, leads to the assignment of a gluten network architecture to a viscoelastic liquid. The polymer networks can be constructed without entanglements (cf. Table 2, Fig. 2b)

and d)). In unentangled systems, the incorporated stress can just only be sustained by elastically active chain strands around the junctions [49]. This applies to viscoelastic liquids and to viscoelastic solids. Therefore, even if this feature is not suitable for classification between viscoelastic liquid and solid, the question of whether or not it makes sense to consider gluten as an unentangled polymer network arises. Lefebvre and Van Vliet argued based on poor solubility of glutenin in water that the polymers should be viewed as colloidal particles [23]. Such a system would be unable to form entanglements. However, this network model was weakened by the argument that the poor solubility arises from protein-protein interactions and not from poor protein-water interactions [34], making the formation of entanglements obvious.

3.3. Based on molecular and thermodynamic properties

The rheological and architectural properties are mainly a result of the chemical/physical junctions between the single structural elements. This molecular basic framework enables a distinction between the viscoelastic liquid and the solid. Liquid-like materials only consist of weak and thermal reversible physical cross-links, including hydrogen bonds, ionic associations, van der Waals-type interactions, stereo-complex formation, or solvent complexation [49]. In contrast, solid-like materials can be formed by temporary physical networks or permanent chemical networks. In the first case, the permanent parts of the network are not completely formed by covalent bonds. Consequently, the removal of one kind of interaction forms individual macromolecules. In the second case, the permanent paths are completely formed by covalent bonds [53]. Gluten networks are capable of forming covalent bonds. Disulfide bonds can be formed at the N and C termini between the glutenin proteins [9]. Additionally, the formation of tyrosine bonds is possible because of the existence of double-tyrosine residues [54]. Disulfide cross-links are regarded as an important element in gluten networks [55], but the formation of free-radicals during kneading

Table 2  
Summary of the characteristic architectural properties of the viscoelastic liquid and solid and assessment for gluten networks on a microscopic level.

Attribute/category	Viscoelastic liquid		Viscoelastic solid	
	Characteristics	i. a. w. <sup>2</sup> gluten network?	Characteristics	i. a. w. gluten network?
Architecture/topology	Entangled: role is similar to the cross-linked junctions (cf. <sup>1</sup> Fig. 2a)) Unentangled: stress is sustained by chain strands [49] (cf. Fig. 2b))	✓ Mediating additional resistance and elasticity	Entangled: increases elasticity, however, their precise effect on the cross-linked system is still controversial [50] (cf. Fig. 2c)) Unentangled: stress is sustained by chain strands [49] (cf. Fig. 2d))	?/(×) Due to the similar effect of entanglements on the mechanical behavior in viscoelastic liquids and solids, no clear distinction for dough systems can be made

<sup>1</sup> cf. = confer.  
<sup>2</sup> i. a. w. = in accordance with.



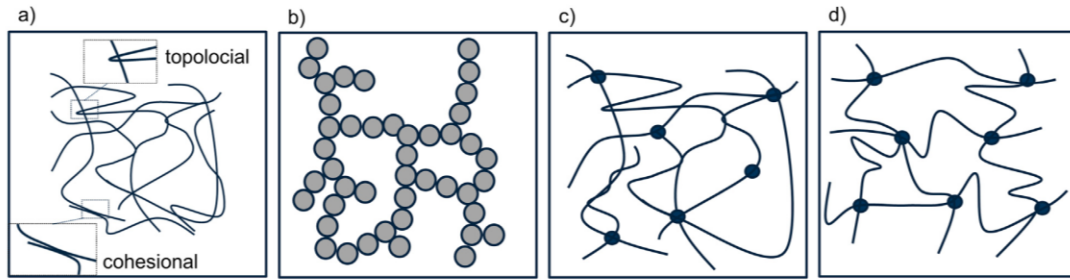


Fig. 2. Illustration of an entangled liquid a), an unentangled liquid b), an entangled solid c) and an unentangled solid d).

leads to sulfhydryl–disulfide interchange reactions during resting times up to 180 min [56]. This exchange of interactions after a mechanical stress can shift the structural balance on a molecular/nanoscale level. Consequently, new arrangements of the polymers corresponding to a movement on this scale can occur. Even if these interchange reactions are only possible in a limited context, an assignment of wheat dough to a permanent chemical network type becomes inappropriate. Moreover, non-covalent interactions are regarded as just as important as disulfide interactions [24]. These relatively weak non-covalent interactions contribute by their high amount to a great strength and stabilize the structure, especially by hydrogen bonding [20]. Therefore, disulfide-linked glutenin polymer could be regarded as a backbone. However, additional non-covalent interactions are needed to explain their characteristics, leading to the assignment of gluten networks to a temporary physical network in the category of viscoelastic solids. As mentioned earlier, the thermodynamic properties are linked to bonding type; therefore, they can serve as a distinctive feature of bonding types or as an independent characteristic for the classification of polymer networks. However, by using thermodynamic properties as a distinctive feature, their characteristics in some cases are predicted by the bonding type (Table 3). Therefore, a permanent covalent network in a viscoelastic solid is non-reversible on thermal fluctuations, whereas physical networks for the liquid- and solid-like types are reversible on thermal fluctuations, at least in parts. This is in accordance with the prior made classification of the gluten network as a non-permanent physical network in the solid-like category because temperature-induced changes can be observed. The strain hardening and failure strain generally decrease with the increasing temperature [57], indicating that the entanglements are weakened by rising temperatures. Based on temperature-dependent relaxation spectra, a decrease in the intensities of short relaxation times occurs, indicating a weakening of the hydrogen bonds. Longer relaxation times corresponding to the stronger part of the network consisting of disulfide bridges and other permanent cross-links show a relative temperature independence [58]. Consequently, with the rising temperatures, the elastic part of the gluten network (hydrogen bonds/entanglements) is weakened, but the rigid part retains its

strength, leading to worse strain hardening properties with the increasing temperatures. However, considering the thermodynamic properties of gluten networks provides no further information for the distinction between viscoelastic liquid and solid because the network properties can be reversible on thermal fluctuations considered as a viscoelastic solid or even as a viscoelastic liquid.

In conclusion, the comparison of the viscoelastic liquid/solid properties in different categories and the assignment to the properties of gluten networks showed that a clear belonging to the viscoelastic solids is only possible for the category “type of bonding”. Concerning the architectural, thermodynamic, and rheological properties, no clear statement is possible. Using rheological tests, the consideration of a gluten network as a critical gel, as proposed by Gabriele et al., is reasonable. In this model, the polymer system consisted of a weak permanent network and a strong temporary one, which would lead to a structure of strong interacting aggregates (as topological points) and easy breakable strands [26]. Based on this model, the theoretically wheat dough can be considered as a viscoelastic solid on a rheological level. However, this is only possible under certain preconditions, excluding mechanical stress input and including long relaxation times. The stress level significantly affects the material properties. Consequently, the gluten network behaves like a viscoelastic solid at very low stress/strain levels, but a small stress input is sufficient to change it to a liquid-like behavior. Additionally, structural relaxation processes after a mechanical stress, whose premise corresponds to a certain mobility of network elements, making the assignment to a viscoelastic solid in consequence inappropriate, last up to 3 h [56]. These described requirements do not correspond to the present conditions during the wheat dough processing. Compared to the desired relaxation times for a solid-like behavior of dough, the single processing steps, where the relaxation could take place before a general change of the network character caused by enzymatic/microbial activity (proofing) or thermal-induced changes (baking) occurs, are short. Based on a practical view, the assessment of dough as a viscoelastic liquid is meaningful. Particularly, the theoretical description/modeling should finally contribute to a better understanding of the process. Moreover, the ability of high deformations without

Table 3  
Summary of the characteristic bonding types and thermodynamic properties of viscoelastic liquid and solid and assessment for gluten networks.

Attribute/category	Viscoelastic liquid		Viscoelastic solid						
	Characteristics	i. a. w. <sup>1</sup> gluten network?	Characteristics	i. a. w. <sup>1</sup> gluten network?	Characteristics	i. a. w. <sup>1</sup> gluten network?			
Type of bonding/linkage	Only physically crosslinked [33]	×	No, even covalent bonds present	Permanent chemical network [33]	×	Non-covalent links are just as important as the disulfide bridges	Temporary physical network [33]	✓	Non-covalent interactions are significantly involved in network formation
Defines	∅			∅			∅		
Thermo-dynamic property	Reversible on thermal fluctuations [49]	×/✓	In part	Non-reversible on thermal fluctuation	/	Not relevant for gluten	Reversible on thermal fluctuations	×/✓	In part

<sup>1</sup> i. a. w. = in accordance with.

a total rupture of the network structure indicates a certain mobility of the network elements. Strain hardening is to be mentioned, which prevents a premature breaking of the covalent bonds by the slippage of the polymer strands. This substantial contribution of the entanglements and the mobility of individual network elements strengthen the classification as a viscoelastic fluid on a practical view.

#### 4. Filler-reinforced networks

Aside from the network-forming gluten polymers, wheat dough consists, to a great extent, of starch granules embedded into the gluten network. A significant impact on the viscoelastic properties must be expected because of the large volume fraction of these particles.

Starch incorporated in the gluten matrix is generally similar to the extensively studied filled polymer systems [14]. Even if the proportion of starch in dough is much higher than that of the filler in rubbery systems, these systems represent a good simplification to observe the general effects of filler particles on the matrix. Mainly, the volume fraction and the size distribution of the particles and the interactions between the particles itself and the matrix [59,60] influence the system's mechanical behavior. Furthermore, the stress level must be considered by analyzing the effect of the filler particles on the polymer matrix. At rest, that means without a mechanical energy input, the addition of particles leads to a raising stiffness of the polymer system [61]. The same effect can be observed for the wheat dough with increasing amounts of starch particles [14,62]. First, this is simply based on the inclusion of rigid particles in a relatively soft matrix. Additionally, the formation of linkages between particle–particle and particle–matrix leads to a reinforcement [63]. As well as the interactions in the polymer network, these linkages can range from weak adsorption effects, like van der Waals forces, to strong chemical reactions [64]; however, they affect the material properties only on a small scale. Nonetheless, the surface functionality of the particles, which determines the possible interactions from the particle site, represents an important material property. Edwards et al. showed that the modification of the surface properties of starch particles altered the overall rheological properties in constituted dough systems [12]. Introducing a deformation or shear stress on a filler-supplemented polymer network revealed an additional energy dissipation process in contrast to the non-supplemented networks [61]. If the local stress is sufficiently high, a separation of the particles from the polymer network occurs, mediating stress softening and a kind of protection of the polymer structure prior to the overall rupture [63,65]. The analysis of the gluten network supplemented with starch granules under deformation/shear indicates a stress softening, too. Increasing the starch content leads to an exponential decrease of the linear strain limit and a lowered elongational viscosity [62]. These observations were also attributed to dissolving particle aggregates [66] or debonding gluten polymer from starch granules [67]. The ability of filler particles to introduce an additional possibility of stress reduction could contribute to the behavior of dough as a critical gel as discussed prior because at rest, the addition of particles leads to an increase of the material strength (solid-like character), but by introducing mechanical stress particles accelerating the system mobility and indicating a more liquid-like behavior. The size distribution of the particles affects the polymer system at rest as well as under deformation. Depending on the size distribution, the filler surface area varied, and the possible contact points for interacting with the polymer matrix. Therefore, smaller particles with a higher surface area improve the reinforcement on a higher level compared to bigger particles with smaller surface areas. For the wheat dough consisting of a greater proportion of small granules (0–10 µm), an increased elastic character could be observed, indicating the stronger interactions with the polymeric matrix [12]. Indeed, starch granules offer no significant network-forming properties. They influence the mechanical behavior to a great extent only by incorporation and interacting to a certain extent with the surrounding matrix. Therefore, a similar effect concerning the protection of the

dough structure against an overall rupture under deformation is mediated by the entanglements introduced by the separation of particles from the network.

#### 5. Conclusion

The analysis of polymer networks by rheological, microscopic, or structure-chemical methods represents an established procedure for material classification and assignment. These methods have long been successfully applied, especially in polymer sciences for material characterization. In addition, gluten or rather wheat dough has long been of major interest. However, an objective assessment of the gluten/wheat dough structure has remained challenging. Gluten represents a very complex polymer system by itself, and the instability over time and under small mechanical stress complicates the coherences even more. By a targeted manipulation of the structural elements, such as addition of reducing/oxidizing substances or manipulation of starch surface functionality by heat treatment, the coherences between structural elements can be understood better, at least in parts. However, even understanding the whole dough system would not change the fact that wheat dough represents a critical behavior between a liquid and a solid-like viscoelastic material. The consideration of wheat dough as a viscoelastic solid is possible under certain conditions (cf. [3], p 10). This view may be useful for a basic understanding of the interactions in the system or the impact modifications of the structural elements on the system because the mechanical-induced rearrangements in the network structure would be completed and result in constant material properties (as far as possible). To enhance this basic understanding, artificial dough components/systems present an interesting approach. The high reproducibility/potential for standardization and the opportunity of a targeted manipulation of artificial components, enables to analyse the effects of specific structural elements on the behavior of the dough system. Thus, as an example, the replacement of starch by inert filler particles seems to be very promising in order to gain a deeper understanding of the impact of starch/particle surface functionality on dough/polymer properties [73,74]. The classification of dough as a viscoelastic fluid is more useful for the “practical” understanding of the dough behavior during processing, since the frequent input of mechanical stress over the entire process or enzymatic/yeast induced changes leads to a constant rearrangement in structure as typical for liquids.

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### 3.3 Wheat dough imitating artificial dough system based on hydrocolloids and glass beads

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## Wheat dough imitating artificial dough system based on hydrocolloids and glass beads



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#### ABSTRACT

Viscoelastic wheat dough properties are a function of processing time, raw material fluctuations, (baking-) process conditions and enzyme/yeast activity. Consequently, varying dough properties complicate analysing mechanisms of structure determining reactions. Therefore, the replacement of wheat dough by an artificial dough system offers a simplified and standardized system, allowing better analysis of mechanistic interdependences in dough systems. To imitate wheat dough, natural and synthetic hydrocolloids were combined with filler particles. These systems were analysed in terms of their ability to mimic wheat dough by using fundamental rheological tests. In total, 106 artificial dough systems were tested and their functional properties compared to that of wheat dough. Particularly, a blend of HPC and PVP showed consistent viscoelastic properties. The slope of the storage module is identical for the artificial system ( $n' = 0.21 \pm 0.01$ ) and wheat dough ( $n' = 0.21 \pm 0.02$ ). Finally, a dough imitating artificial polymer system was developed. It offers the advantages of simplification due to a limitation to the essential network elements and standardization, based on avoided enzyme activity and constant material properties.

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#### 1. Introduction

Wheat dough presents a complex polymer-particle system, whose structure-function relationships are still not fully understood. The difficulties in clarifying the interactions of the structural elements, which contribute to the typical viscoelastic properties of wheat dough, depend on many factors. Both the ingredients and their quality, as well as the processing conditions have a significant influence on dough functionality. The mechanisms behind functional dough properties, which are already significantly changed by the variation of minor ingredients, like yeast, NaCl or sugars, are even more complex compared to a simple flour water dough (Jekle and Becker, 2012), (Wehrle et al., 1997), (Larsson, 2002), (Verheyen et al., 2014), (Salvador et al., 2006). This enhanced complexity is based mostly on the varying properties of the basic dough system (wheat flour and water) from batch to batch and over the resting time of dough, because the observations made, cannot be assigned to either non-reproducible and inconsistent raw material characteristics and/or dough

processing properties or to the examined factor. Wheat flour/dough properties vary, since climatic conditions such as drought/hot or wet/cold (Daniel and Triboi, 2000), as well as location dependent circumstances (such as soil nitrogen content) lead to changing glutenin-gliadin ratio or quantity of sulphurous amino acids, which can result in a changing amount of disulphide bridges (Zhao et al., 1999), (Daniel and Triboi, 2000), (Moss et al., 1981), (Scherer, 2001). Moreover, the enzymatic activities of proteases and amylases change the network structure (Kawamura and Yonezawa, 1982) and lead to a degradation of starch (Goesaert et al., 2005) over the investigation period. Even the use of artificial dough systems consisting of pure isolated starch and gluten, which are often used for analytical purposes (Jekle et al., 2016), (Abdellatif and Rayas-Duarte, 2003), (Wilderjans et al., 2008), (Eliasson and Tjerneld, 1990), cannot avoid some inconsistent dough properties, caused by enzyme activity. Consequently, there is still the need for a standardized dough system. In a simplified view, wheat dough can be considered as a polymer network (gluten), reinforced with a filler (starch) and mainly the interactions of these two components. Hereby, the gluten polymers form a network upon hydration and kneading. The gluten network consists of covalent disulphide bonds, which contribute to the

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plasticity of dough, and elasticity improving non covalent interactions, especially intra- and intermolecular hydrogen bonds, which lead to the formation of loops and trains (Belton, 1999). The starch granules form a particle arrangement. This arrangement is incorporated in the polymer network based on its surface functionality (Schiedt et al., 2013). At a theoretical point of view it should be possible to imitate these viscoelastic wheat dough properties. The combination of network forming polymers with bonding mechanism similar to wheat dough and structuration inducing filler particles should enable the development of a standardized and simplified dough system. This simplified dough system, having the same viscoelastic properties as wheat dough, would offer several advantages. In contrast to real dough systems, yeast activity can, for example, be analysed in a dough like matrix, but independent of raw material fluctuations and enzymatic activity. Thus, questions concerning the impact of viscosity on the availability of nutrients can be investigated in a new way. Moreover, the interaction of the main structural elements (gluten and starch), which form the microstructure and determine the mechanical behaviour of dough, can be identified in more detail by a targeted manipulation of the structural components in the artificial system. Furthermore, a constant and highly reproducible dough-like medium could be used as a testing standard in start-ups of machines/analytical equipment like kneader/mixer systems. The main challenges, in creating such an artificial dough-like system, are to find adequate substitutes for gluten and starch. The substitutes have to fulfil mainly two requirements. First, they must exhibit constant properties, which means that they lack raw material fluctuations and enzymatic activity in order to enable a simplification of coherences and a standardization. Second, they have to comply with the viscoelastic properties of wheat dough at least at a steady state (without processing). Therefore, they have to correspond to the properties of gluten, which means a granular character of gliadin has to be combined with a polymeric character of glutenin, resulting in a deformation depending behaviour. In the following, it will be clarified if it is possible to imitate the viscoelastic dough properties of a simple wheat flour-water dough by starch- (glass beads) and gluten-imitating (hydrocolloids) substitutes. The deformation depending behaviour will be analysed by fundamental rheological tests and compared to real dough by structural rheological models.

## 2. Experimental

### 2.1. Wheat dough preparation

Commercial wheat flour type 550 obtained from Rosenmühle (Landshut, Germany) was determined to contain 13.59 g moisture, 11.49 g protein, and 0.65 g ash per 100 g of sample. The optimum water absorption and kneading time for reaching 500 farino units, were determined in accordance to AACC method 54–21.02 using a doughLAB (Perten Instruments, Hamburg, Germany). For dough preparation 50 g flour (corrected to 14% moisture) and distilled water (water absorption 59.1%), were kneaded for 200 s at a speed of 63 rpm at 30 °C.

### 2.2. Polymer dough preparation

The selection of polymers based on their solubility in cold water in order to enable a dough production process (kneading), similar to that of wheat flour. Moreover, to take into account the different chain lengths of gliadin and glutenin, polymers with a higher viscosity/chain length (HPC, konjac gum, gum traganth, PVP) and a lower viscosity/chain length (gum arabic, PVOH) have been chosen. To guarantee a high degree of standardization, synthetic polymers

should be favoured (Mohanty et al., 2000). However, the selection of cold water soluble synthetic polymers is very limited. Therefore, natural polymers have been taken into account too. Based on the previously made assumptions, polymer dough systems consisted of the natural polymers gum arabic (Kremer Pigmente, Aichstetten, Germany), konjac gum (Salandis GbR, Greifswald, Germany), Hydroxypropylcellulose HPC (Klucel H, Kremer Pigmente, Aichstetten, Germany) or gum traganth (Kremer Pigmente, Aichstetten, Germany), the synthetic polymers Polyvinylpyrrolidone (PVP K 90, VWR, Darmstadt, Germany), Polyvinyl alcohol PVOH (PVA 4-98, Kremer Pigmente, Aichstetten, Germany) with borax (Sigma-Aldrich, Steinheim, Germany) and glass beads (Microperl Sovitec, Schönborn, Germany). The beads are chemically inert and spherical shaped with a smooth surface, as can be seen in Fig. 1 from a scanning electron micrograph (REM-Image), recorded and kindly provided by Hosokawa Alpine (Augsburg, Germany). The particle size of glass beads ranges from 2.60 µm to 19.27 µm, which is similar to that of wheat starch. Due to their size distribution, shape and surface functionality, which allows the formation of non-covalent interactions with the network (DiBenedetto, 2001), glass beads should be suitable to imitate starch in the native dough state.

The polymer dough systems, as shown in Table 1, represent selected blends with the best convergence to wheat dough. To obtain these blends, 106 different polymer blends and water ratios were analysed concerning their fundamental rheological properties in preliminary tests. The water amount was iteratively adjusted to the best accordance between wheat dough and polymer dough. Table 1 summarizes the compositions of the presented blends.

In order to reduce raw material consumption, polymers were mixed with distilled water in a modified glutomatic (Perten instruments, Hamburg, Germany) for 10 min. Within the modification the sieve bottom was replaced by a closed bottom and the water supply was capped. Water was added manually and remains in the mixing system (Döring et al., 2015).

### 2.3. Fundamental rheology

Rheological measurements were performed with an AR-G2 rheometer (TA instruments, New Castle, USA), equipped with

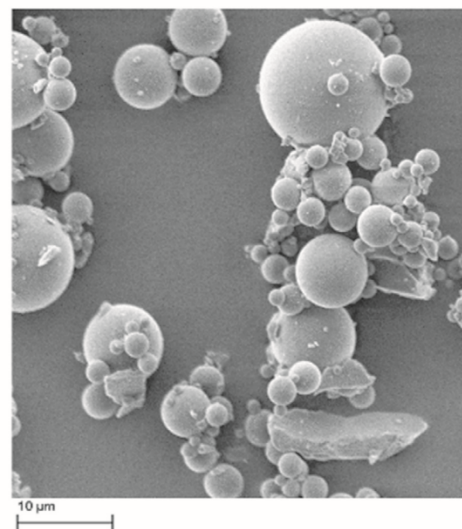


Fig. 1. Scanning electron micrograph (REM) of glass beads in the dry state (powder).

**Table 1**  
Composition of polymer dough systems (indication of quantity in parts).

Nomenclature of polymeric systems	Quantities of polymer/glass beads/water (in parts)								
	Gum arabic	Konjac	HPC	Gum traganth	PVP	PVOH	Borax	Glass beads	Water
PVP	/	/	/	/	1.5	/	/	/	1.0
PVOH with borax	/	/	/	/	/	3.3 (of 2.0 g PVOH dissolved in 48.0 g water)	1	/	/
Gum arabic with konjac	1.0	1.0	/	/	/	/	/	/	1.3
Gum arabic with konjac, HPC	1.0	1.0	1.0	/	/	/	/	/	2.0
PVOH with gum traganth	/	/	/	1.0	/	3.8 (of 24.0 g PVOH dissolved in 48.0 g water)	/	/	/
HPC with PVP	/	/	4.0	/	1.0	/	/	/	4.5
Gum traganth with gum arabic, HPC	1.0	/	1.0	1.0	/	/	/	/	2.5
HPC with PVP, glass beads	/	/	4.0	/	1.0	/	/	3.5	7.0
Gum arabic with konjac, HPC, glass beads	1.0	1.0	1.0	/	/	/	/	2.1	2.75
HPC with PVP, PVOH, glass beads	/	/	4.0	/	1.0	1.0	/	4.2	5.5

parallel plates (4 cm diameter) and a constant gap of 2 mm. The smart sweep peltier plate temperature system ensures a constant temperature of 30 °C for all measurements. The dough sample (spherical 5 g sample) was placed between the upper and lower plate and the gap was set. After removing excess dough edges, the surface was coated with paraffin oil to prevent dehydration and the sample was allowed to relax for 2 min. All tests were determined in triplicate.

2.3.1. Oscillatory measurements

2.3.1.1. Small oscillatory strain tests. All time and frequency sweeps were performed in the linear-viscoelastic region (deformation ≤ 0.1%), which was determined before. Time dependent behaviour was measured under a constant frequency (1 Hz) and deformation (0.1%) over a period of 180 min. The time-dependent fundamental rheological properties of dough samples were evaluated through the complex shear module (G\*). Frequency sweeps were performed in the range of 0.1–10 Hz with a constant deformation of 0.1%. Storage module (G') and loss module (G'') data were fitted according to the power law equation (Equations (1) and (2)) to obtain closer information about network characteristics.

$$G'(\omega) = K' * \omega^{n'} \tag{1}$$

$$G''(\omega) = K'' * \omega^{n''} \tag{2}$$

where ω (s<sup>-1</sup>) is the angular frequency, K', K'' (Pa s<sup>n'</sup>) are equivalent to the intercepts and n', n'' (-) correspond to the slope (Georgopoulos et al., 2004).

2.3.1.2. Deformation sweeps. To imitate a high mechanical stress, as during kneading, a succession of low-high-low deformation steps was used. During the low deformation steps (A) the applied strain was in the linear viscoelastic region (frequency 1 Hz, strain amplitude 0.1%), whereas the high deformation step (B) leads to sharp structural weakening (frequency 1 Hz, strain amplitude 80.0%, 1 min). Thus, dough samples can stabilize during the first low deformation step (A1) and re-construct their structure after the high deformation step (A2). The succession of strain-steps is illustrated in Fig. 2. An oscillating strain was chosen in order to prevent a loss of material in the measurement gap. The ratio of the last value of the first low deformation step and the values at a certain time of the second low deformation step provides a useful expression to evaluate the capacity of structural re-construction for storage module (G'), loss module (G'') and complex module (G\*).

2.4.1. Creep-recovery

Creep-recovery tests were performed subsequently to the

frequency sweeps. A constant stress (100 Pa) was applied for 120 s. After removing the stress, the sample was allowed to recover for 360 s. Creep data was described by creep compliance J(t), which represents the ratio of measured strain γ and constant stress σ. According to Equation (3) the creep phase was analysed with a four parameter Burgers model (Steffe, 1996), (Lazaridou et al., 2007),

$$J(t) = J_0 + J_1 \left[ 1 - e^{-\left(\frac{t}{\lambda}\right)} \right] + \frac{t}{\eta_0} \tag{3}$$

Where J<sub>0</sub> (Pa<sup>-1</sup>) is the instantaneous compliance (pure elastic part), J<sub>1</sub> (Pa<sup>-1</sup>) the visco-elastic compliance, λ (s) the retardation time and η<sub>0</sub> (Pa s) the zero shear viscosity. The parameters J<sub>0</sub>, J<sub>1</sub>, λ and η<sub>0</sub> resulted from fitting the creep compliance to the Burgers model. They are used to describe the viscoelastic response of dough samples to the applied stress. To describe the amount of elastic recovery during the recovery phase, the relationship between minimum compliance at the end of the recovery phase and maximum compliance at the end of the creep phase was used (Equation (4)).

$$rel. Recovery = \frac{J_{min, recovery}}{J_{max, creep}} \tag{4}$$

2.4. Statistical analysis

The statistical analysis was performed with GraphPad Prism 6 (Version 6.01, GraphPad Software Inc. La Jolla, USA). One-way ANOVA with Tukey's multiple comparisons tests were used to confirm the accordance of wheat dough and polymer dough

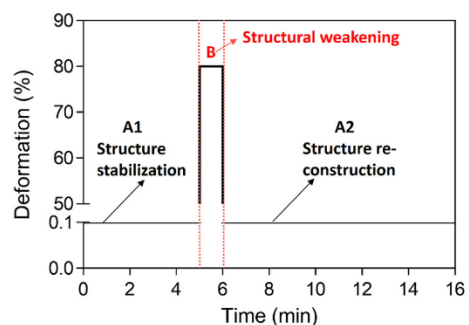


Fig. 2. Illustration of the succession of deformation steps used to observe structure weakening and reconstruction.



samples.

### 3. Results and discussion

#### 3.1. Imitation of the viscoelastic wheat dough properties based on fundamental rheological measurements

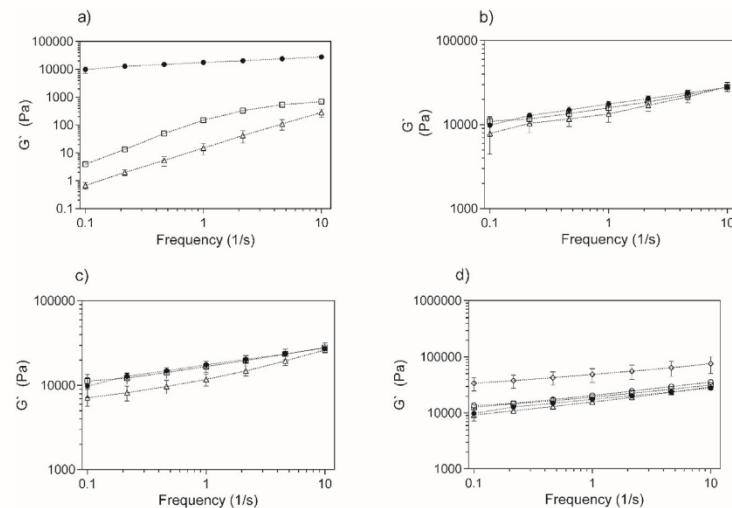
##### 3.1.1. Oscillatory testing - frequency sweep

The mechanical properties of wheat and polymer dough were analysed by fundamental rheological tests. Different deformation and strain ranges were used to respond to different structural elements and levels. The frequency sweep from 0.1 to 10 Hz with a deformation of 0.1%, which is within the linear viscoelastic region for all samples, ensures the maintenance of the structure over the whole measurement. The results of the frequency sweep are divided into four groups according to the composition of the polymer dough systems, with a) synthetic polymers, b) natural polymers, c) mixed systems and d) systems supplemented with glass beads and are shown in Fig. 3. For the storage module  $G'$  and for loss module  $G''$ , see supplementary data.

The frequency dependency of the examined wheat dough reflects typical wheat dough behaviour and is in agreement with literature values compared at a frequency of 1 Hz (Létang et al., 1999) (Lynch et al., 2009). For all samples, except the pure synthetic ones, the weak frequency dependency reflects the physical network character (Yang et al., 2013a), which is typical for wheat dough systems. The purely synthetic polymer systems consisting of linear polyvinyl alcohol (PVOH) chains, which need to be cross linked with borax in order to form a network, and polyvinylpyrrolidone (PVP) do not comply with the wheat dough storage module  $G'$  over the whole frequency range. All data points are significantly lower and in addition, the frequency dependency is higher. Based on these two observations, the synthetic polymer systems can be described as less consolidated (Salvador et al., 2006), with a weaker network character compared to wheat dough. In contrast, no significant differences for  $G'$  exist over the entire frequency range for the natural, the mixed and the glass bead

supplemented systems, with the exception of the blends consisting of konjac with gum arabic, hydroxypropyl cellulose (HPC) and glass beads. For  $G''$ , only the mixed HPC-PVP system and the glass beads supplement systems, without the HPC-PVP-PVOH system, are in accordance to the loss module of wheat dough. To obtain a closer look at the correlation of material properties of wheat and polymer dough systems,  $G'$ - and  $G''$ -data were fitted to a power law equation according to equations (1) and (2). The slopes ( $n'$ ) provide useful information about the network formation, whereby values closer to zero indicate a stronger network (Georgopoulos et al., 2004). Table 3 summarizes the values for  $n'$ ,  $n''$  and  $K'$ ,  $K''$  of the analysed wheat dough and the different types of polymer dough systems. For wheat dough slopes ( $n'$ ,  $n''$ ) ranging from 0.2 to 0.3, as shown in Table 2, depending on wheat varieties, water content and ingredients like salt. The  $n'$  of 0.21 and  $n''$  of 0.20 of wheat dough, examined in this study, can therefore be considered as representative and suitable for evaluating polymer dough systems.

The mixed polymer dough systems consisting of HPC and PVP with and without glass beads show no significant difference with the power law constants  $n$  and  $K$  of wheat dough. Both systems have a high affinity to form hydrogen bonds similar to wheat dough (Dror et al., 2006), (Mezdour et al., 2007). In the case of hydroxypropyl-modified cellulose hydrogen bonds can be formed between OH groups (Bonnet-Gonnet et al., 2001) and for PVP hydrogen bonds can be formed with the nitrogen of the pyridyl group (Malnych et al., 2002). By combining modified cellulose with PVP a 3D-network consisting of hydrogen bonds is formed as shown by Kutsenko et al. (2013), (Kutsenko et al., 2007). In wheat dough, the importance of hydrogen bonds for the viscoelastic behaviour, in particular the elasticity, is already recognised (Kontogiorgos, 2011), (Belton, 1999), (Shewry et al., 2002). Also, in the artificial dough systems the high potential to form hydrogen bonds could explain the good compatibility of the viscoelastic properties of the dough systems and thus, the accordance of power law constants of the storage module. Especially,  $n''$  of the natural and the mixed polymer dough systems are higher compared to  $n'$ . The faster increase of  $G''$  compared to  $G'$  indicates that the



**Fig. 3. Influence of frequency on the storage module  $G'$ .** a) Synthetic polymer system:  $\square$ - polyvinyl alcohol with borax,  $\Delta$ - polyvinylpyrrolidone. b) Natural polymer systems:  $\square$ - gum arabic with konjac and hydroxypropyl cellulose;  $\Delta$ - gum arabic with konjac. c) Mixed systems:  $\square$ - hydroxypropyl cellulose with polyvinylpyrrolidone,  $\Delta$ - Polyvinyl alcohol with gum tragacanth. d) Systems with glass beads:  $\square$ - hydroxypropyl cellulose with polyvinylpyrrolidone,  $\Delta$ - gum arabic with gum arabic and hydroxypropyl cellulose,  $\diamond$ - konjac with gum arabic and hydroxypropyl cellulose,  $\circ$ - hydroxypropyl cellulose with polyvinylpyrrolidone and polyvinyl alcohol. Reference:  $\bullet$ - wheat dough. Means are shown with standard deviation ( $n=3$ ). The scaling of a) is adjusted and differs from b), c) and d).



**Table 2**  
Literature values of power law constants depending on wheat varieties, water content and ingredients.

Variation in dough system	$G'(\omega) = K' \cdot \omega^{n'}$		$G''(\omega) = K'' \cdot \omega^{n''}$		Examined by
	$n'$ (-)	$K'$ (Pa s <sup>n'</sup> )	$n''$ (-)	$K''$ (Pa s <sup>n''</sup> )	
Soft white winter wheat dough	0.28	7810	0.27	4250	Schluentz et al., 2000
Hard red winter wheat dough	0.23	18700	0.22	7910	
Water content 42.6% (w/w)	0.20	Not shown	0.20	Not shown	Georgopoulos et al., 2004
Water content 47.1% (w/w)	0.29	Not shown	0.20	Not shown	
0 g NaCl/kg flour	0.22	1271	0.24	499	Beck et al., 2012
20 g NaCl/kg flour	0.21	1473	0.24	531	
40 g NaCl/kg flour	0.21	1537	0.23	537	

**Table 3**  
Frequency sweep data of  $G'$  and  $G''$  analysed by the power law equation. Goodness of fit to the power law equation is rated by  $r^2$  for each single measurement.

Nomenclature of the polymeric systems	$G'(\omega) = K' \cdot \omega^{n'}$			$G''(\omega) = K'' \cdot \omega^{n''}$		
	$n'$ (-)	$K'$ (Pa s <sup>n'</sup> )	$r^2$	$n''$ (-)	$K''$ (Pa s <sup>n''</sup> )	$r^2$
<b>Reference (wheat dough)</b>						
Wheat dough	0.21 ± 0.02	17277 ± 1680	>0.97	0.20 ± 0.02	6864 ± 154	>0.84
<b>Synthetic polymer dough systems</b>						
PVP	1.26 ± 0.08	16.22 ± 8.39	>0.99	0.94 ± 0.02	207.40 ± 24.15	>0.99
PVOH with borax	0.63 ± 0.02	173.87 ± 5.95	>0.94	0.23 ± 0.01	187.00 ± 5.17	>0.56
<b>Natural polymer dough systems</b>						
Gum arabic with konjac	0.29 ± 0.05	14247 ± 2784	>0.97	0.50 ± 0.02	5708 ± 411	>0.91
Gum arabic with konjac, HPC	0.22 ± 0.00	16310 ± 2000	>0.98	0.39 ± 0.01	6581 ± 823	>0.97
<b>Mixed polymer dough systems</b>						
PVOH with gum tragacanth	0.27 ± 0.09	20308 ± 13772	>0.98	0.47 ± 0.05	6958 ± 1760	>0.99
HPC with PVP	0.21 ± 0.01	17090 ± 2622	>0.98	0.27 ± 0.01	6036 ± 866	>0.98
<b>Polymer dough systems with glass beads (70% from dry matter)</b>						
Gum tragacanth with gum arabic, HPC	0.25 ± 0.00	15981 ± 864	>0.99	0.35 ± 0.01	6733 ± 481	>0.98
HPC with PVP, glass beads	0.20 ± 0.00	19586 ± 1621	>0.99	0.24 ± 0.01	6092 ± 295	>0.96
Gum arabic with konjac, HPC, glass beads	0.18 ± 0.01	49452 ± 14071	>0.99	0.28 ± 0.01	7759 ± 661	>0.98
HPC with PVP, PVOH, glass beads	0.22 ± 0.00	21050 ± 1324	>0.98	0.28 ± 0.04	15388 ± 5555	>0.97

frequency spectra of these dough systems correspond to a transition region. However,  $n'$  and  $n''$  of wheat dough are on the same level. Thus, indicating a plateau (rubbery) region (Georgopoulos et al., 2004). The addition of glass beads leads to an equalisation of  $n'$  and  $n''$ , as can be seen from the HPC-PVP- and the gum arabic-konjac-HPC systems. This indicates a stabilization of the polymer dough systems towards a plateau region and an adjustment to wheat dough. In polymer/rubbery science the reinforcing effect of filler particles, like silica or carbon black, is often reported (Sombatsompop et al., 2004), (Yuan and Mark, 1999), (Edwards, 1990). Based on the large specific surface area of fillers, contacts between filler and matrix occur. Depending on the nature of filler surface and polymer matrix, additional chemical and/or physical interactions are enabled (Bokobza and Rapoport, 2002). In the case of glass, polymers can adsorb to the glass surface by hydrogen bonding, London dispersion or polar forces and acid based interactions (DiBenedetto, 2001). Especially PVP is suited for the immobilization of particles, because it possesses a high affinity to form hydrogen bonds with polar substances or to interact via electrostatic forces. If PVP is deposited on glass, the nitrogen of the pyridyl group interacts with the silanol groups of glass. Depending on the protonation of silanol groups, hydrogen bonds or electrostatic/charge-dipole type interactions are formed (Malynych et al., 2002). Based on the polarity of hydroxyl groups in HPC, hydrogen bonds or electrostatic interactions may also be formed with glass beads. These additional interactions strengthen the network and result in lower  $n'$  and  $n''$ . In addition, the reinforcing effect is visualised by the increased  $K'$ , which can be interpreted as network strength at zero frequency, for the glass beads supplemented systems.

Frequency tests were performed in the linear viscoelastic region

(LVE), and consequently only allow small deformations. However, wheat dough consists of interactions, which are sensitive to different length scales (Schiedt et al., 2013). Therefore, the frequency sweep alone is not sufficient to completely describe the viscoelastic properties. An additional test with higher strain levels, as the creep-recovery test, is necessary.

3.1.2. Creep-recovery test

Creep compliance data were fitted according to equation (3), a four-parameter Burgers model. The results of curve fitting are shown in Table 4. According to the parameters of the Burgers model, the material deformation can be divided into an elastic ( $J_0$ ), a viscoelastic ( $J_1, \lambda$ ) and a viscous ( $\eta_0$ ) part (Steffe, 1996). For wheat dough, the retarded elastic modulus  $J_1$  is higher than the instantaneous elastic modulus  $J_0$ . Thus, the deformation depends mainly on the viscoelastic part. This observation applies to all polymer systems, except the PVOH-borax blend. In general, the Burgers parameters of synthetic polymer systems are incompatible with the wheat dough parameters. However, the natural system (gum arabic with konjac, HPC) has better alignment and the mixed systems supplemented with glass beads correspond best with wheat dough, especially the HPC-PVP system. The instantaneous elastic modulus is slightly smaller in comparison to wheat dough, indicating a smaller part of pure elastic deformation. Conversely,  $\eta_0$  is larger in comparison to wheat dough, reflecting a higher amount of flowing parts. In general, the addition of glass beads decreases  $J_0, J_1$  and  $\lambda$  and increases  $\eta_0$ . The inclusion of a rigid filler increases stiffness (Yang et al., 2013b) and can therefore influence the immediate elastic response. The reduction of retardation time  $\lambda$  indicates a faster relaxation process. This process depends on the efficiency to transport stress (Yang et al., 2013b). Glass beads promote the

**Table 4**  
**Results of the creep-phase, analysed by Burgers model for each single measurement and results of the creep-recovery phase, analysed by relative recovery.** Goodness of fit to the Burgers model is rated by  $r^2$  for each single measurement.

Nomenclature of the polymeric systems	Creep-phase					Creep-recovery phases Relative recovery (%)
	$J_0$ ( $10^{-4}$ 1/Pa)	$J_1$ ( $10^{-4}$ 1/Pa)	$\lambda$ (s)	$\eta_0$ ( $10^5$ Pa s)	$r^2$	
<b>Reference (wheat dough)</b>						
Wheat dough	$0.50 \pm 0.17$	$1.56 \pm 0.14$	$5.27 \pm 2.16$	$4.81 \pm 0.73$	$\geq 0.99$	$41.89 \pm 2.63$
<b>Synthetic polymer dough systems</b>						
PVP	$6.98 \pm 9.19$	$9.92 \pm 0.17$	$17.87 \pm 27.64$	$0.09 \pm 0.10$	$\geq 0.99$	$7.50 \pm 12.87$
PVOH with borax	$0.12 \pm 1.17$	$0.00 \pm 0.00$	$955.03 \pm 459.64$	$0.05 \pm 0.07$	$\geq 0.99$	$0.13 \pm 0.03$
<b>Natural polymer dough systems</b>						
Gum arabic with konjac	$0.17 \pm 0.05$	$0.34 \pm 0.01$	$1.99 \pm 1.19$	$20.60 \pm 3.59$	$\geq 0.97$	$70.44 \pm 37.59$
Gum arabic with konjac, HPC	$0.40 \pm 0.22$	$0.87 \pm 0.45$	$6.30 \pm 1.33$	$10.56 \pm 0.68$	$\geq 0.97$	$54.59 \pm 21.71$
<b>Mixed polymer dough systems</b>						
PVOH with gum traganth	$0.23 \pm 0.09$	$1.55 \pm 0.26$	$2.14 \pm 0.27$	$17.10 \pm 2.59$	$\geq 0.95$	$25.77 \pm 6.15$
HPC with PVP	$1.03 \pm 0.02$	$0.89 \pm 0.04$	$13.80 \pm 2.26$	$10.70 \pm 0.96$	$\geq 0.99$	$26.46 \pm 7.99$
<b>Polymer dough systems with glass beads (70% from dry matter)</b>						
Gum traganth with gum arabic, HPC	$0.56 \pm 0.13$	$1.21 \pm 0.25$	$10.30 \pm 5.63$	$6.86 \pm 0.73$	$\geq 0.98$	$34.45 \pm 8.63$
HPC with PVP, glass beads	$0.31 \pm 0.05$	$0.77 \pm 0.07$	$4.96 \pm 0.86$	$13.30 \pm 0.78$	$\geq 0.89$	$51.00 \pm 1.55$
Gum arabic with konjac, HPC, glass beads	$0.18 \pm 0.06$	$0.23 \pm 0.07$	$1.90 \pm 0.21$	$26.00 \pm 8.17$	$\geq 0.97$	$57.28 \pm 3.76$
HPC with PVP, PVOH, glass beads	$0.34 \pm 0.13$	$1.08 \pm 0.36$	$4.81 \pm 1.75$	$8.76 \pm 2.10$	$\geq 0.98$	$26.86 \pm 16.99$

mobility of the system and thereby lead to a partial desorption of energy (Sohoni and Mark, 1987). Consequently, stress can be reduced faster. Moreover, the higher mobility of the glass bead supplemented systems is apparent in the higher zero shear viscosity  $\eta_0$ . However, the higher amount of flowing parts has no negative effect on the elasticity, as can be seen from the relative recovery. The ratio of re-deformation during relaxation and deformation under creep is higher for glass bead supplemented systems, clearly indicating an improved elasticity. Thus, the results of the creep-recovery test confirmed the reinforcing and mobility improving effects of glass beads, as observed in the frequency tests, on a higher strain level.

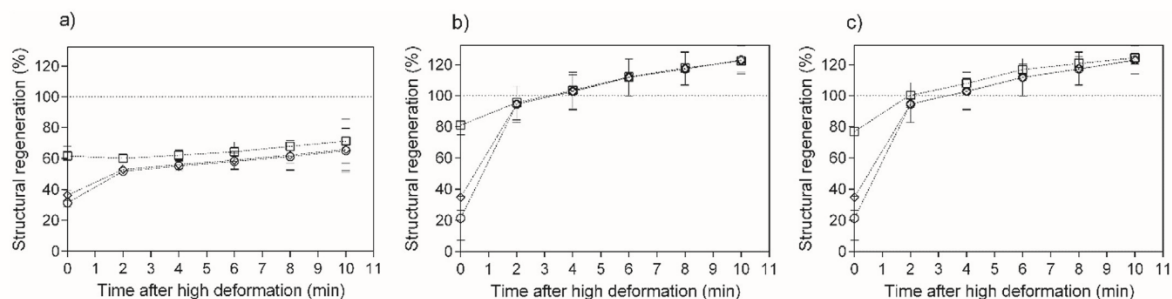
In summary, the mixed system of natural HPC and synthetic PVP with and without GB showed the best concurrence of viscoelastic behaviour in the oscillation and creep-recovery tests. Consequently, for further studies, these two most promising systems were selected. In the second part of the study the viscoelastic properties of the polymer dough systems were analysed under high mechanical strain and over time, in order to assess their suitability to mimic a wheat dough system along the processing steps kneading and resting.

### 3.2. Strain and time depending material behaviour of selected polymer systems analysed by fundamental rheology

#### 3.2.1. Strain depending material behaviour

To simulate a high mechanical stress, as during kneading, a

succession of low-high-low deformation steps in the rheometer is used. Here, an oscillating deformation strain is used, in order to prevent a phase separation and a loss of material in the measurement gap. The deformation during the high deformation step is large enough to achieve a significant loss of structural strength. In contrast, during the low deformation steps, the applied strain is within the viscoelastic limit and the material can regenerate its structure. The structural regeneration in Fig. 4 represents the ratio of the values of storage ( $G'$ ), loss ( $G''$ ) and complex module ( $G^*$ ) before and after the high deformation step at a certain regeneration time. Thus, a structural regeneration of 100% means a complete recovery of the initial structural strength. All Samples show a sharp decrease of structural strength after the high deformation step. Storage and complex module decrease to 20–40% and loss module to 60–80% of their initial values. Wheat dough (a) slowly recovers up to 65–70% of its initial strength within 10 min. However, polymer dough (b and c) quickly recovers completely within 2 min. A large part of the polymer dough structure is based on the formation of hydrogen bonds (Kutsenko et al., 2013). Their formation kinetic depends on the diffusion dynamics (Luzar and Chandler, 1996), which in turn relate to the hydration process. In comparison to wheat dough, polymer dough shows a strong hydration. During hydration, water has to overcome the osmotic pressure inside the absorbents (Zhou et al., 2013). The larger the difference in osmotic pressure, the faster hydration occurs (Liu et al., 2009). Consequently, diffusion dynamics would be higher and hydrogen bonds could be formed faster in the polymer dough than in wheat dough.



**Fig. 4.** Structural regeneration after high deformation of a) wheat dough, b) Hydroxypropyl cellulose with polyvinylpyrrolidone dough and c) Hydroxypropyl cellulose with polyvinylpyrrolidone and glass beads dough. Symbols: -○- storage module  $G'$ , -□- loss module  $G''$  and -◇- complex module  $G^*$ . Means are shown with standard deviation ( $n = 3$ ).

Although, the polymer dough with glass beads should show a slower structure rebuilding based on the lower amount of hydrocolloids, there is no significant difference in the structure regeneration of polymer dough with and without glass beads. Since glass beads promote the mobility of the system (Yang et al., 2013b), the same time frame for structure regeneration could thus be explained. A regeneration over 100% could be an effect of hydration (Baumgartner et al., 2002), (Roy et al., 2010), which leads to an increase of the modules  $G'$ ,  $G''$  and  $G^*$ .

### 3.2.2. Time depending material behaviour

Wheat dough changes its properties over time due to enzymatic activity, hydration, or drying out. These changes are analysed with a time-sweep analysis and compared to polymer dough. It is a requirement that no significant changes over time occur in order to get a simplified and standardized system. However, a strong increase of  $G^*$  over time for the polymer based systems is apparent from Fig. 5. This observation could be a result of two effects. First, a strain induced structure formation could be responsible for the increasing  $G^*$ . Second, swelling of polymers depends on the crosslinking and ionic strength of the polymers. Hydrophilic groups enhance the electrostatic repulsion and thereby strengthen the difference in osmotic pressure as a driving force for swelling (Zhou et al., 2013). Finally, the swelling rate decreases due to the increase of crosslinking density and a lower difference in osmotic pressure (Wang et al., 2007). Consequently, the ongoing hydration leads to an increase of the material strength through the formation of additional hydrogen bonds and increase  $G^*$ . Also, a rise in  $G'$  and  $G''$  as a function of time for a PVP/CMC hydrogel due to the formation of additional hydrogen bonds is observed by Roy et al. (2010). A hydration time of 5 h to reach an equilibrium state is pointed out. Therefore, a previous hydration time could be necessary to reach constant material properties for the artificial dough systems.

In contrast to the increasing strength of the polymer dough systems,  $G^*$  of wheat dough decreases in the first hour of measurement. This observation is caused by two effects. First, structural relaxation after kneading causes a decrease in  $G^*$  during the first 30–45 min (1) (Kim et al., 2008) and second, network degradation, caused by enzyme activity, promotes lower  $G^*$  after longer resting times (2) (Wu and Hosney, 1989).

## 4. Conclusion

To break down the complexity of wheat dough to a simple and constant artificial dough, a system of natural hydroxypropylcellulose (HPC) and synthetic polyvinylpyrrolidone (PVP)

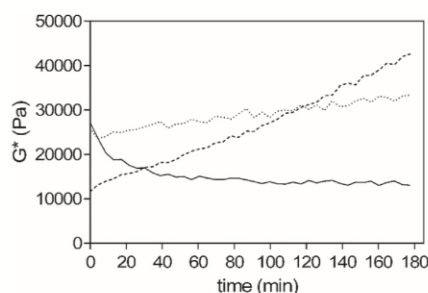


Fig. 5. Influence of time on the complex module  $G^*$  without yeast for wheat dough (—), Hydroxypropyl cellulose with polyvinylpyrrolidone dough (---) and Hydroxypropyl cellulose with polyvinylpyrrolidone and glass beads dough (···). Means are shown without standard deviation ( $n = 3$ ).

supported with glass beads was developed. Based on fundamental rheological tests, the imitation of the viscoelastic wheat dough properties could be verified in frequency and creep-recovery tests (Tables 3 and 4). Therefore, the comparability to natural wheat dough can be ensured and the artificial system represents a useful tool to analyse structural formation reactions in dough systems, as well as a controlled analysis of fermentation properties of yeasts and their impact on the native dough matrix. In further studies temperature effects on viscoelastic properties as well as gas release kinetics during yeast fermentation could be considered.

Concededly, in this study the different network formation mechanisms lead to a divergent behaviour over resting-time and after high mechanical stress. For the polymer dough systems hydrogen bonds seem to be an essential element in network formation. Therefore, the material strength increases over time (Figs. 4 and 5) due to the ongoing hydration. However, these divergent structural mechanistic do not compromise the applicability on the dough system and thus the understanding of structural formation reactions in real dough systems. Typical for filler supplemented systems is a reinforcing effect based on the particles. Those systems simultaneously show a higher sensitivity for stress and an improved elasticity. Thereby, wheat starch as well as glass beads can be considered as reinforcing fillers in the dough matrix. Based on the corresponding attributes, an equivalent effect of starch in wheat dough could be expected. However, the specific filler particle surface exhibits a certain functionality, even if the particles are considered as inert. Consequently, interactions between the particles, like hydrogen bonds or electrostatic interactions, are likely. The formation of an additional weak particle based network, which strengthened the polymer network, could therefore not be excluded. Therefore, the identification and alteration of bonding types between polymer network and particles is elementary for the understanding of microstructure formation. By a gradual increase of filler amount and a specific modification of surface properties, the effect of this structural element of the network formation and the viscoelastic behaviour will be investigated in more detail.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jfoodeng.2017.12.014>.

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## 3.4 Controlling glass bead surface functionality - impact on network formation in natural edible polymer systems

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### Controlling glass bead surface functionality - Impact on network formation in natural edible polymer systems

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## ABSTRACT

Combining particles and polymers provides materials with unique mechanical properties. Hereby, the character of the particle surface is important for the network properties. However, particle-polymer interfaces of food systems are scarcely controllable. This often leads to an indefinite contribution on the network properties. Developing hybrid artificial systems by using inert particles with a well-defined coating represents a new approach in food science. Coating with functionalized silanes enables the imitation of naturally occurring chemical groups. A novel experimental approach involving nano- and macroscopic analytical techniques (X-ray photoelectron spectroscopy and contact angle) sheds light on the nature and the strength of the adsorption. Depending on the presented surface functionality, strong specific to weak unspecific adsorptions arise, e.g. amino-functionalized surfaces show strong interaction with protein, while almost no interaction was observed with an aliphatic surface. Based on these different particle adhesivenesses, the monitoring of network formation discloses a significant impact of particle surface functionality on network development of food matrixes. An increasing network development time (3.2–6.0 min, gluten protein-based) in combination with a decreasing network strength (874–464 mNm gluten protein-based) correlates with an increasing adhesiveness of particles. Thus, using functionalized particles clearly demonstrates the importance of particle surface functionality on network properties in food systems.

#### 1. Introduction

Polymer systems, filled with small particles like carbon black or silica, are widely used in material sciences and applications to improve the mechanical properties by increasing tensile strength or elongation at break [1,2]. These enhanced material properties are mediated by physical and chemical interactions between particle surface and polymer matrix. Beside these designed systems, highly complex particle-polymer systems occur also naturally in foods. Particle-polymer based foods are present at different processing steps: in a non-processed form as raw materials, like wheat kernels, in a processed form, like cheese, dough, sausages, or in a highly processed manner as designed foods for specific applications, like nutraceuticals. For most particle-polymer based food systems, the polymeric matrix consists of proteins or carbohydrates [3], whereas the particles could be of very different character, especially regarding the rigidity. In wheat kernels or dough, rigid starch particles are embedded in gluten-based protein matrices, whereas in cheese or sausages soft oil particles are embedded

in protein matrices. Despite this difference in particle rigidity, foods containing soft oil droplets are also considered as particle-filled composite materials. In general, all these systems have in common, that the analysis of the particle-polymer interface is challenging. In the following, the difficulties in analyzing particle-polymer interfaces of complex food systems supplemented with rigid particles are discussed, using the example of wheat dough, a very frequently processed food pre-product: From a general point of view, particles affect polymer networks mainly by three factors: the particle shape, the size/size distribution and the surface functionality [2,4–6]. Independent of shape and size, surface functionality can be regarded as universal factor, because the surface contributes to the interface between particle and polymer. Therefore, it defines the kind of possible interactions [7]. To analyze the impact of this interface on the network formation, different approaches are used in food science. The most common methods are reconstitution experiments [8] or the modification of a particle (starch) surface by mechanical/chemical treatment [9–11]. However, these methods have several disadvantages. Reconstitution experiments, in

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which polymeric wheat proteins (gluten) and particulate starch (~1–80  $\mu\text{m}$ ) of different origin and nature are mixed in quantities that correspond to wheat flour, modify not only the surface functionality [12] but also the shape and size of starch. In addition, exchanging the starch origin and quality causes different compositions of surface-active proteins and lipids [10,13]. Therefore, the impact of a specific functional group, in mediating a specific interaction, like hydrogen bonds or hydrophobic interactions, can not be identified. Consequently, reconstitution experiments only contribute to the general importance of particle (starch) properties to the overall (food) system, but do not clarify the influence of surface functionality [14]. In addition, modification of a particle (starch) surface by removing lipids or proteins does not offer a clear assignment of the importance of the particle (starch) functionality on the network properties in a rather general manner without delivering any mechanistic relations. These above described problems are highly relevant as they occur in every natural particle-polymer based food system. Therefore, approaches, which enable a target manipulation restricted to the particle surface only, are indispensable for clarifying the impact of the particle surface on the network formation and behaviour in food-based systems. A promising approach relies on the replacement of natural particles by inert artificial microspheres of comparable size and shape. They offer the advantage of a controllable surface functionality [16–18]. In the field of food science, a few studies are available, where natural particles were replaced by artificial particles with modified surface properties based on coatings. Coating surfaces with whole proteins or fats leads to adsorbed structures in an undefined way [16,17]. In contrast, using coupling agents like silanes or cross-linkers, enable the creation of well-defined, homogeneous and stable surfaces bearing just a single functionality. The high amount of commercially available silanes and a well-established synthetic pathway allow for the imitation of nearly every natural occurring functional group of food-based particles. In this study, four different silanes and two heterobifunctional cross-linkers are used to imitate common functional groups of food particle surfaces and their impact on network formation in protein- or carbohydrate-based matrixes. For the imitation of the hydrophobic and non-polar character of fats (alkyl chains), a propyl-functionalized silane is used. Hydrophilic and polar/ionic parts are imitated by a silane bearing cyano groups, sulphur-containing parts by a mercapto-functionalized silane and nitrogen-containing parts by an amino-functionalized silane. In addition, two different heterobifunctional cross-linkers were used to reproduce the possibility of polymers to covalently bind to a particle surface and to enhance the effects arising from a covalent interaction between functionalized surface and polymer. In the following, functionalized surfaces are prepared, validated and analyzed, regarding their interface characteristics, with two common food polymers (protein- and carbohydrate-based). A systematical approach of using varying rinsing steps enables the analysis of adsorption and desorption kinetics on a nano- and macroscopic level within a model system. Based on the revealed adsorption mechanisms and adhesiveness between imitated functional group and polymer, the impact of particle surface functionality and network formation is discussed.

## 2. Experimental

### 2.1. Materials

Glass beads, with a size ranging from 2.60  $\mu\text{m}$  to 19.27  $\mu\text{m}$ , which is comparable to that of microscopic food particles, were purchased from Microperl Sovitec (Schönborn, Germany). Glass plates (microscope slides) were purchased from VWR (Darmstadt, Germany) and silicon wafers were purchased from Wacker Chemie (Munich, Germany). Silane

coupling agents - 3-aminopropyltriethoxysilane (amino-silane, 98%), 3-mercaptopropyltriethoxysilane (mercapto-silane, 98%), *n*-propyltriethoxysilane (propyl-silane, 97%), 2-cyanoethyltriethoxysilane (cyano-silane, 97%) - were purchased from ThermoFisher (Germering, Germany) and Alfa Aesar (Karlsruhe, Germany). For the covalent attachment of mercapto-coated surfaces with the polymeric matrix, two heterobifunctional cross-linkers were purchased from Sigma Aldrich (Taufkirchen, Germany): *N*-succinimidyl 3-maleimidobenzoate (MBS) for the coupling with the protein-based (gluten) polymer matrix and *N*-[*p*-maleimidophenyl] isocyanate (PMPI) for the coupling of the carbohydrate-based (hydroxypropylcellulose) polymer matrix. For the protein-based food matrix vital gluten (Kröner-Stärke, Ibbenbüren, Germany) was used. For the carbohydrate-based food matrix with similar mechanical properties as gluten [18], hydroxypropylcellulose HPC (Kluccel H, Kremer Pigmente, Aichstetten, Germany) as major component (4:1 parts) and polyvinylpyrrolidone (PVP K 90, VWR, Darmstadt, Germany) were used.

### 2.2. Sample cleaning

Glass beads/plates were cleaned by submergence in a freshly prepared piranha solution, consisting of 1.5 parts  $\text{H}_2\text{O}_2$  (30%) and 3.5 parts  $\text{H}_2\text{SO}_4$  (98%) at 95 °C under gentle stirring for 30 min. After a sedimentation time of 120 min, the glass beads were rinsed using ten centrifugations (1500xG for 5 min), replacing the supernatant with distilled water between the steps. Afterwards, a neutral pH value of the supernatant indicated the adequate replacement of piranha solution. Glass beads were stored in distilled water. Glass plates were directly removed from the piranha solution and rinsed with distilled water two times for 5 min each. Si wafer were prepared for coating by annealing at 900 °C for 1 h in air.

### 2.3. Surface functionalization

For coating of the surfaces, 1% (v/v) of silane was hydrolyzed in a 95/5 (v/v) mixture of ethanol/distilled water, adjusted to a pH value of 4.5 by adding hydrochloric acid and stored for 12 h at room temperature. Silylation was carried out at 70 °C for 30 min under gentle stirring. For glass beads, the supernatant was decanted, prior to silylation. After silylation, glass beads were rinsed using four centrifugations (25xG for 6 min), with a replacement of the supernatant with fresh ethanol/distilled water (95/5 v/v) in between the steps to remove unreacted silane. Glass plates were rinsed two times for 5 min each in ethanol/distilled water (95/5, v/v). All samples were dried at 120 °C for >1 h. Functionalized  $\text{SiO}_2$  surfaces were rinsed after drying three times for 5 min in ethanol/distilled water (95/5 v/v).

### 2.4. Attachment of heterobifunctional cross-linkers

The heterobifunctional cross-linker, MBS or PMPI, was attached to mercapto silane-coated samples. Prior to crosslinking, glass beads were soaked in distilled water for 15 min. Subsequently, excess water was removed by centrifugation (15 min at 1000xG). Functionalized Si wafers were directly used. MBS was diluted to a final concentration of 75 mM for glass beads or ~0.02 mM for Si wafers in a 1:1 mixture of DMSO and phosphate buffered saline (PBS). PMPI was diluted to a final concentration of 50 mM for glass beads and ~0.02 mM for  $\text{SiO}_2$ -surfaces in DMSO, respectively. After 1 h of incubation, excess cross-linker was removed by rinsing in the pure solvent. For glass beads rinsing was applied by three centrifugations at 1500xG for 3 min. Between the centrifugations, the supernatant was replaced by PBS for MBS or by DMSO for PMPI. Thereafter, glass beads or functionalized Si wafers were directly used.

### 2.5. Interactions of polymers with functionalized SiO<sub>2</sub> surfaces

To assess the adhesiveness of the silane coatings towards the protein or carbohydrate-based matrix, the functionalized Si wafer were incubated in gliadin/EtOH solution (300 mg/L in 60/40 EtOH/H<sub>2</sub>O dest.) or HPC-PVP/dest. H<sub>2</sub>O solution (1% polymers v/v, with 1 part PVP and 4 parts HPC) at room temperature for 30 min under gentle stirring. Since not the whole gluten polymer is soluble, the ethanol soluble gliadin fraction was used in order to prove the adsorption properties between the wafer and the gluten polymer. After incubation, the adhesiveness between polymer and wafer was analyzed by applying different rinsing intensities (none; 1 min, 5 min, 30 min) in the corresponding solvent of the used polymer. Before analysis, the samples were dried at 60 °C for 1 h.

#### 2.5.1. Contact angle measurements

The functionalized Si wafers (see 2.3–2.5) were analyzed by sessile drop method using a drop shape analyzer (DSA25 Krüss, Germany).

#### 2.5.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded on a Leybold-Heraeus LHS 10 spectrometer using a non-monochromatized Mg K $\alpha$  source (1253.6 eV). All coated glass beads, except propyl, were pressed into cavities and measured as pellets. Functionalized Si wafers were directly mounted on a sample holder. For the detection of the propyl coating on a glass surface, a coated and a reference glass piece were mounted on a sample holder and annealed at 150 °C overnight before measurement. All spectra were recorded in an ultra-high vacuum chamber at a pressure below  $5 \times 10^{-8}$  mbar. The analyzer was operated at a constant pass energy of 100 eV leading to an energy resolution with a full width at half-maximum (fwhm) of  $\sim 1.1$  eV. The energy scale of the spectra was corrected for sample charging by using the Si 2p signal at 103.3 eV (SiO<sub>2</sub>). Core level spectra were deconvoluted by using Voigt functions after linear background subtraction.

### 2.6. Interactions of polymers with functionalized glass bead surfaces

#### 2.6.1. Fluorescence labeling

Based on the ability of amino and mercapto groups to interact with fluorescein-5-isothiocyanat or *N*-(5-fluoresceinyl)maleimide, respectively, the coverage of the glass bead surface by amino or mercapto silanes can be analyzed by confocal laser scanning microscopy (CLSM). For dye labelling, approximately 0.5–1.0 g of coated and uncoated (reference) glass beads were stirred in ethanol with 0.01 g dye per 10 ml for 15 min at room temperature. For amino silane fluorescein-5-isothiocyanat (Merck, Germany) and for mercapto silane *N*-(5-fluoresceinyl)maleimide (Sigma Aldrich, Germany) was used. Labeled samples were washed by centrifugation (6 times at 25 x G for 3 min) with ethanol until the supernatant became colorless. Labeled and washed glass beads were placed onto a hemocytometer, which was used as object carrier. For visualization, an eclipse Ti-U inverted microscope with an e-C1 plus confocal system (Nikon GmbH, Düsseldorf, Germany), a Plan Apo VC 60x/1.40 oil objective and 534 nm and 488 nm lasers was used. Three images of the coated and uncoated glass particles, each with a resolution of 1024 x 1024 pixel (size 215 x 215  $\mu$ m) and at a different position in z-direction, were acquired.

#### 2.6.2. Network formation of food matrices

For analyzing the effect of the particle-polymer interface on the network formation in complex food matrices, different polymer-particle systems were hydrated and mixed (gluten or HPC/PVP-based) by using a recording z-kneading system (DoughLAB, Perten Instruments, Hamburg, Germany). For monitoring the network formation, all systems were mixed for 20 min at a speed of 63 rpm at 30 °C. To produce optimal developed (max. mNm) polymer particle systems, protein-based matrices were mixed for 7 min and carbohydrate-based systems 8 min.

**Table 1**

Food matrix composition and particle proportion. Quantity in parts.

Matrix type	Distilled water	Glass beads	Gluten	HPC	PVP
Protein	1	1.59	0.68	/	/
Carbohydrate	1	0.74	/	0.25	0.07

Table 1 shows the used amounts of polymers and glass beads for the different systems. The amount of water and polymer used is based on a previous study [18].

## 3. Results and discussion

### 3.1. Polymer adsorption on functionalized surfaces

The characteristics of the interface between differently functionalized surfaces and two common food matrices (protein- and carbohydrate-based) are analyzed regarding their adsorption and desorption kinetics (adhesiveness) on a nano- and macroscopic level. Since coating and characterization of an ideally flat and well-defined surface is simplified compared to a heterogeneous spherical surface (particles), SiO<sub>2</sub> surfaces serve as a model system for glass beads. After annealing in air, the atomically flat and single-crystalline surface of a Si wafer is oxidized to SiO<sub>2</sub> and, hence, chemically identical to quartz glass. Therefore, results obtained from this model system are highly comparable to those of functionalized glass beads. In total, 10 different systems were analyzed: Propyl-, cyano-, amino- and mercapto-functionalized SiO<sub>2</sub> surfaces in combination with HPC-PVP and gliadin, respectively, MBS-functionalized SiO<sub>2</sub> surfaces in combination with gliadin, and PMPI-functionalized SiO<sub>2</sub> surfaces in combination with HPC-PVP. Thereby, the protein-based matrix is represented by gliadin and the carbohydrate-based by HPC-PVP. Contact angle measurements monitor surface characteristics at the macroscale, based on the hydrophobicity of the surface. Therefore, modified wetting properties of water droplets are capable to detect functional groups and even adsorbates. In contrast, XPS is a surface-sensitive method, which characterizes the chemical composition on the nanoscale. A successful functionalization of the SiO<sub>2</sub> surfaces was confirmed by XPS and contact angle measurements for all systems. Specific core levels of the functional groups were detected in XPS: C 1s peak for propyl groups (285.2 eV), N 1s peak for cyano and amino groups as well as for the PMPI and MBS cross-linkers (400.0, 399.7, 401.0 and 401.3 eV, respectively) and S 2s peak for mercapto groups (227.3 eV) [25]. In addition, the functionalized SiO<sub>2</sub> surfaces show various contact angles between water droplets and surface, depending on the hydrophobic/hydrophilic character of the coating (compare Fig. 2 a). For the propyl coating, a contact angle of  $99.2 \pm 1.5^\circ$  demonstrates the hydrophobic character. In contrast, mercapto ( $69.7 \pm 5.7^\circ$ ) and cyano ( $64.9 \pm 0.8^\circ$ ) coatings show a lower hydrophobicity due to their lower contact angles. The amino functionalization induces nearly full wetting ( $29.6 \pm 8.8^\circ$ ) due to a strong hydrophilic character. Attaching cross-linkers to the mercapto coating, causes further modifications of the surface; PMPI slightly increases ( $71.1 \pm 2.2^\circ$ ), whereas MBS reduces the hydrophobic character ( $65.8 \pm 1.7^\circ$ ). The experimental approach for the assessment of polymer adhesiveness on differently functionalized SiO<sub>2</sub> surfaces is summarized in Fig. 1. By comparing contact angle and XPS data of the functionalized SiO<sub>2</sub> surfaces before (reference) and after incubation in a polymer solution, the adsorption of the polymers can be analyzed. The subsequent rinsing steps of different durations assess the desorption and, thus, determine the adhesiveness between polymer and functionalized surface.

After incubation in a carbohydrate-based (HPC-PVP) or a protein-based (gliadin) polymer solution, the surface is completely covered by the polymer, independent of the coating. Therefore, contact angles are in a small range between  $31.8 \pm 3.7^\circ$  for HPC-PVP and  $30.8 \pm 6.7^\circ$  for gliadin for every coating. The low standard deviations of 3.4 and 6.7°,



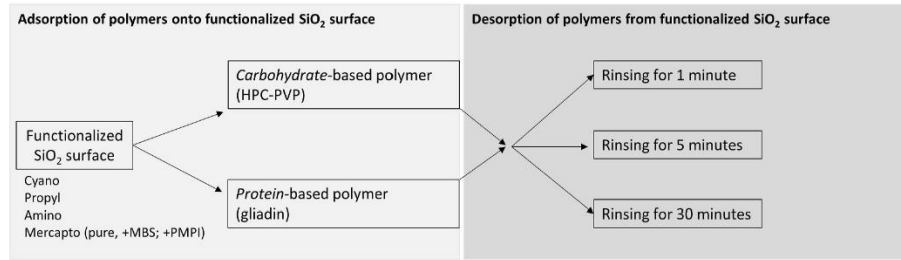


Fig. 1. Experimental approach for analyzing the adsorption and desorption properties of polymers towards differently functionalized surfaces (cyano-, propyl-, amino-, mercapto-, MBS-, PMPI-coated). Contact angle and XPS were measured after each step.

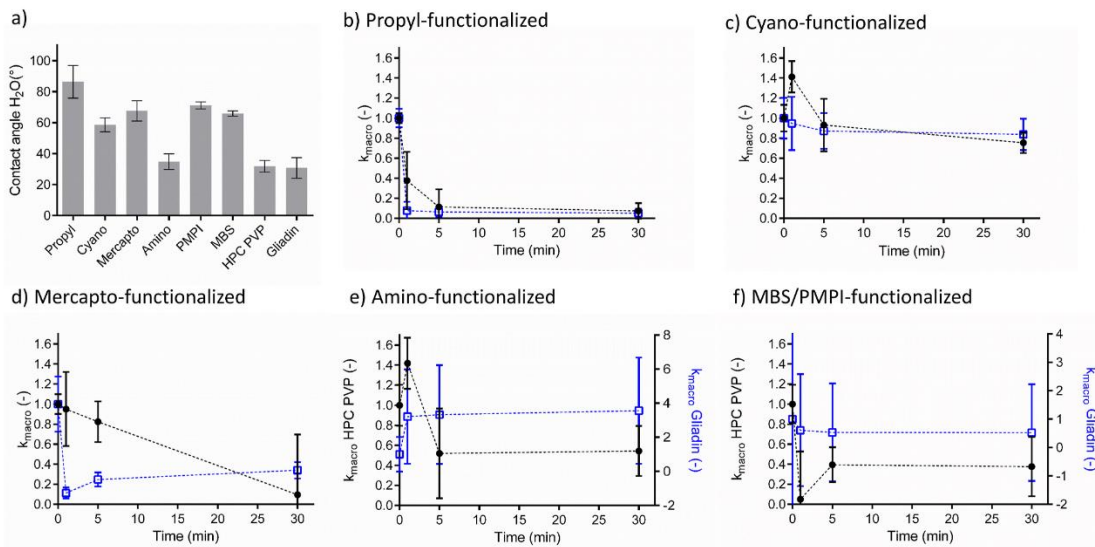


Fig. 2. Evaluation of polymer adhesiveness on functionalized SiO<sub>2</sub> surfaces by contact angle measurements. Coating and incubation in polymer solution in a). Adhesiveness, expressed by  $k_{macro}$ , over rinsing time of HPC-PVP (●) and gliadin (□) in b) - f) depending on surface functionalization: propyl-functionalized surface in b), cyano-functionalized surface in c), mercapto-functionalized surface in d), amino-functionalized surface in e) as well as MBS- (for gliadin) and PMPI- (for HPC-PVP)-functionalized surface in f). For better visualization in c) and f), gliadin is plotted versus a separate y-axis (right side). Means are shown with standard deviation (a) or propagation of error considering the standard deviation (b-f).

respectively indicate the formation of a homogenous polymer layer which covers the surface entirely. XPS confirms these results as the Si 2p peak originating from the SiO<sub>2</sub> surface is almost completely attenuated by a covering adlayer.

3.2. Evaluation of polymer desorption from functionalized surfaces

For the assessment of the polymer adhesiveness, the rinsing induced desorption of the polymers from the functionalized SiO<sub>2</sub> surfaces is evaluated. Due to different functional groups present in the coating, neither absolute values for the contact angle, nor absolute XPS intensities of a single surface, provide reasonable numbers to address the desorption behavior. Hence, we defined macro- and nanoscopic coefficients to evaluate the polymer adhesiveness as a function of the rinsing time by comparing the functionalized surface before and after polymer incubation with the rinsed surfaces. The results and discussion of contact angle and XPS data for every coating and polymer can be found in the supplementary data. The surface modification observed by contact angle measurements, is assessed by the macroscopic adsorption coefficient  $k_{macro}$ , which is defined as follows:

$$k_{macro} = \frac{\alpha_{coating} - \alpha(t)}{\alpha_{coating} - \alpha_0} \tag{1}$$

$\alpha_{coating}$  corresponds to the contact angle measured on a functionalized SiO<sub>2</sub> surface,  $\alpha_0$  to the contact angle directly after polymer incubation and  $\alpha(t)$  to the contact angle after a certain rinsing time. Based on the amount of adsorbed/desorbed polymers on the functionalized surface over rinsing time, the contact angle varies. If  $\alpha(t)$  is equal to  $\alpha_{coating}$ , no polymer is adsorbed anymore and  $k_{macro} = 0$ . In contrast, if  $\alpha(t)$  is equal to  $\alpha_0$ , all polymers remain adsorbed at the surface and  $k_{macro} = 1$ . The error of  $k_{macro}$  was calculated based on the propagation of error considering the standard deviation of the respective contact angles.

$k_{nano}$  was calculated based on XPS data. Characteristic core levels for the coating as well as the polymers were identified. In most cases, distinct components of the C 1s core level could be attributed to either the polymer or the coating. Deconvolution of the signals (see supplementary information) reveals the peak area of each component ( $A_{polymer}$  and  $A_{coating}$ ). We defined  $k_{nano}$  to reflect the amount of polymers adsorbed on the functionalized SiO<sub>2</sub> surface as a function of the rinsing time  $t$  as follows:



$$k_{\text{nano}} = \frac{A_{\text{polymer}}(t)}{A_{\text{coating}}(t) + A_{\text{polymer}}(t)} \frac{A_{\text{coating}}^0 + A_{\text{polymer}}^0}{A_{\text{polymer}}^0} \quad (2)$$

The second term scales  $k_{\text{nano}}$  with respect to the initial peak ratio obtained directly after incubation with the polymer and, hence, offers values for  $k_{\text{nano}}$  that are comparable to  $k_{\text{macro}}$ .

### 3.2.1. Carbohydrate-base polymer desorption

Depending on the surface functionalization, the consideration of  $k_{\text{macro}}$  for HPC-PVP incubated surfaces (Fig. 2 b-f), demonstrates different desorption behaviors. A propyl-functionalization already causes a significant decrease of  $k_{\text{macro}}$  after 1 min of rinsing.  $k_{\text{macro}}$  stabilizes at a diminutive value of  $0.11 \pm 0.18$  after 5 min. In contrast,  $k_{\text{macro}}$  of the amino-, cyano- and PMPI-functionalized systems decreases immediately but stabilizes at significantly higher values after 5 min of rinsing;  $k_{\text{macro}}$  of the amino-functionalization corresponds to  $0.52 \pm 0.44$ , the cyano-functionalization to  $0.93 \pm 0.26$  and the PMPI-functionalization to  $0.39 \pm 0.17$ . Interestingly, a mercapto-functionalization results in a constant decrease of  $k_{\text{macro}}$  over the entire rinsing time to a final value of  $0.10 \pm 0.60$ . The fast and tremendous decrease of  $k_{\text{macro, propyl}}$  evidences a negligible adhesiveness of HPC-PVP to the hydrophobic coating. Since HPC, respectively PVP, are hydrocolloids, their low affinity to a hydrophobic surface is reasonable. The stabilization of  $k_{\text{macro}}$  at higher values proves a higher adhesiveness to other coatings. Based on the equilibrium value of  $k_{\text{macro}}$ , the functionalized surfaces can be ranked with respect to the adhesiveness of HPC-PVP: cyano > amino > PMPI. Note that  $k_{\text{macro}}$  for amino- and cyano-functionalized surfaces is larger than 1 after the 1 min of rinsing (Fig. 2 c & e). According to its definition,  $k_{\text{macro}} > 1$  might correspond to an increase of polymer adsorbed to the surface, which is excluded in our experimental setting. Considering the high water solubility of the hydrocolloids, it is reasonable that excess quantities present after incubation will dissolve in the water droplet during contact angle measurement. As the properties of the probing water droplet are now changed this might force a spreading of the water droplet resulting in lower contact angles and consequently in values of  $k_{\text{macro}} > 1$ . After a first rinsing, the weakly bound fraction of polymer has been desorbed and, thus,  $k_{\text{macro}}$  becomes <1. The persisting decrease of

$k_{\text{macro, mercapto}}$  is rather unexpected. However, the standard derivations indicate a highly inhomogeneous surface and thus, a desorption behavior which cannot be determined unambiguously based on the macroscopic approach.  $k_{\text{nano}}$  essentially confirms the observations of  $k_{\text{macro}}$  (compare Fig. 2 b-f) with Fig. 3 a-e) and also gives rise to a ranking of the polymer adhesiveness: amino > PMPI > propyl. Compared to the macroscopic approach, the detection limit for adsorbates is higher in XPS. Therefore,  $k_{\text{nano, propyl}}$  is higher than  $k_{\text{macro, propyl}}$  during all rinsing steps. The substantial decrease of  $k_{\text{macro, propyl}}$  demonstrates that the small amount of polymer remaining on the coated surface is still detected at the nanoscopic level but has no functional effect on droplet formation at the macroscopic level, at all. The unusual behavior of  $k_{\text{macro, mercapto}}$  is not found for  $k_{\text{nano}}$  which stabilizes around 0.80 after an initial decrease. In the nanoscopic approach, XPS reveals an amount of adsorbed polymer, which is averaged over a large surface area. In contrast, the contact angle is just defined by the edges of a water droplet, which corresponds to only a small local area. Therefore, inhomogeneities in the surface composition are strongly pronounced in  $k_{\text{macro}}$ , resulting in vast standard derivations, as seen for the mercapto-functionalized surface. Despite this inhomogeneity for mercapto-functionalized surfaces,  $k_{\text{nano}}$  proves the adsorption of considerable amounts of polymer even after long rinsing times. Consequently, the adhesiveness of HPC-PVP on a mercapto-functionalized surface can also be evaluated as strong. The cyano-functionalized surface cannot be addressed by XPS as overlapping signals arising from the coating and the polymer are not deconvoluted uniquely. Therefore, we refrained from a calculation of  $k_{\text{nano}}$ . However, the N 1s core level of the cyano groups on the surface is significantly attenuated with respect to the signal intensity before polymer incubation and, thus, indicates that a constant fraction of HPC-PVP remains adsorbed at the surface during all rinsing steps.

### 3.2.2. Protein-based polymer desorption

Analyzing the functionalized surfaces after a gliadin incubation by  $k_{\text{macro}}$  does not lead to meaningful values, e.g.  $k_{\text{macro}} > 3$  for amino-functionalized surfaces (compare Fig. 2 e). In contrast to the defined

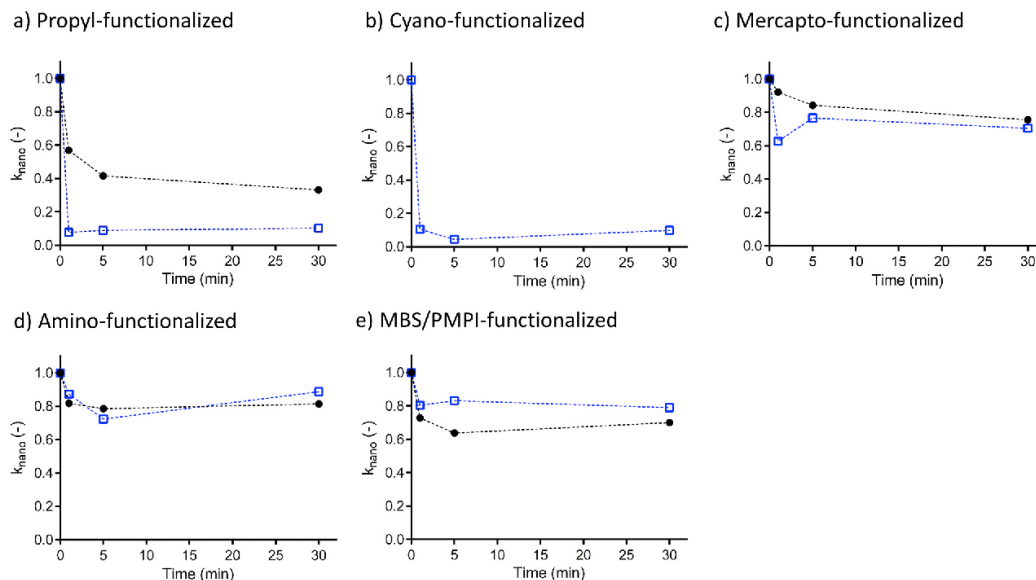


Fig. 3. Evaluation of polymer adhesiveness on functionalized SiO<sub>2</sub> surfaces by XPS measurements. Adhesiveness, expressed by  $k_{\text{nano}}$ , over rinsing time for HPC-PVP ( $\Delta$ ) and gliadin ( $\circ$ ) in a) – e) depending on surface functionalization: Propyl-functionalized surface (a), cyano-functionalized surface (b), mercapto-functionalized surface (c), amino-functionalized surface (d) as well as MBS- (for gliadin) and PMPI (for HPC-PVP)-functionalized surface (e).

structure of the carbohydrate-based polymers, gliadin is a naturally occurring, large protein with a highly complex structure. In general, the high sensitivity of proteins easily leads to modified folding or denaturation. Changes in the protein structure might be induced due to the functional groups present at the coated surface during adsorption and explain the arbitrary results for  $k_{macro}$ . Nonetheless,  $k_{nano}$  provides reliable information about the adhesiveness of gliadin to different surface functionalizations. For propyl- and cyano-functionalized surfaces,  $k_{nano}$  significantly decreases after 1 min of rinsing to a negligible value of 0.03 and 0.10, respectively (see Fig. 3 a & b). In contrast, amino-, mercapto- and MBS-functionalized surfaces lead to a significantly lower decrease within the first minute of rinsing to values of 0.87, 0.62 and 0.85, respectively (see Fig. 3 c, d, e). Even longer rinsing times do not affect  $k_{nano}$  anymore. Consequently, propyl- and cyano-functionalized surfaces offer a low adhesiveness for gliadin, whereas the adhesiveness to amino-, mercapto- and MBS-functionalized surfaces is significantly higher and corresponds to an increasing order of mercapto < amino < MBS. In general, all surface functionalizations show a decrease of  $k_{nano}$  after the first rinsing step, even if the adhesiveness is high. Based on the analyzed peak intensities, a desorption of weakly adsorbed multilayers of polymer can be concluded. After multilayer desorption, a stable monolayer remains at the surface, which appears as a stabilized value for both coefficients.

Depending on the polymer matrix (protein- or carbohydrate-based) and the surface functionalization, systems with different adhesivenesses in relation to each other were identified. Table 2 summarizes the functionalities of the different coatings. In combination with the observed desorption kinetics, possible interaction mechanisms with the polymers can be assumed. Cyano and propyl coatings enable weak and unspecific interactions, such as van der Waals forces, dipole-dipole, or hydrophobic interactions, explaining the fast polymer desorption during rinsing. Amino and mercapto coatings can induce more stable, specific and directed chemical interactions, like hydrogen or disulphide bonds. Mercapto-coated surfaces in combination with heterobifunctional cross-linkers enable strong specific covalent interactions.

3.3. Polymer adsorption controlled by functionalized glass beads

3.3.1. Validation of glass bead surface functionalization

A successful evaluation of the polymer adhesiveness using a flat model system paves the way towards the characterization of the impact of various particle surface functionalities on the network formation. Therefore, glass beads with a size range (2.60 μm–19.27 μm) typical for microscopic particles in foods, are coated with functionalized silanes. The presence of the desired functional groups at the glass bead surface is verified by fluorescence labeling in combination with CLSM imaging and by XPS measurements. In the first method, the binding of specific fluorescence dyes visualizes amino or mercapto groups. Fig. 4 shows a homogeneous dye layer across the z-axis of the glass bead surface proving a successful amino (a) and mercapto (b) coating. In contrast, for uncoated glass particles (Fig. 4 c) just a few undefined spots of

fluorescence dye are visible which probably result from impurities [18] with a high affinity to the dye. Consequently, a successful coating can be concluded in case of amino and mercapto groups. Cyano and propyl coatings have low affinities to interact with dyes. Therefore, fluorescence labeling could not be performed. However, every functional group which was coated onto the glass bead surface could be detected by XPS. The characteristic photoemission lines already presented in chapter 3.1 are found for the glass beads, as well (see supplementary data).

3.3.2. Network formation depending on particle-polymer adhesiveness

To analyze the impact of the modified particle surface on the dynamic formation of protein- (gluten) or carbohydrate-based (HPC-PVP) polymerized matrices, a recording mixer (z-kneading system; Dough Lab) is used. With progressive network formation, the resistance against the induced deformation by the z-kneading geometry increases. This increasing resistance is recorded as mNm by the Dough Lab. Thus, plotting the recorded mNm against kneading time enables the monitoring of network formation (compare Fig. 5). Typical parameters to evaluate the network development are the peak resistance, which indicates the maximum network strength during the mixing process, and the development time to reach this peak. Comparing these two parameters for the different coatings and polymer matrices reveals a remarkable impact of the particle surface on the network development. As shown in Fig. 5, development time as well as peak resistance varies depending on the coating; the weakest network (lowest peak) is developed with the amino coating, followed by the propyl, cyano and mercapto coatings, whereas the systems with cross-linkers (MBS or PMPI) resulted in the strongest networks. Interestingly, this order of increasing peak resistance applies to both network types, protein- and carbohydrate-based. Comparing amino with propyl and cyano coatings, a lower or respectively unspecific adhesiveness towards the polymeric matrices exists in case of the latter ones. Assuming limited or nonspecific adsorption between the particle and the polymer allows unhindered polymerization of the network. This would result in higher peak resistance and thus, higher network strength. In contrast, the higher and more specific adhesiveness (hydrogen bonding) between amino coated particles and polymer might hinder the network formation due to the adsorption of polymers on the particles. However, this explanation does not apply to mercapto coated particles. For gluten proteins, thiol/disulphide exchange reactions are known to be essential regarding network formation. The addition of further thiol groups affects the network formation significantly [20–22]. Therefore, a divergent behavior of mercapto coated particles compared to other particles with similar adhesiveness (amino) is reasonable for gluten. Baudouin et al. (2020) suggested a mechanism of gluten network development depending on thiol interfering chemicals. In general, the thiol/disulphide exchanges are considered as determinant for the required mechanical energy since breaking of disulphide bonds leads to a release of mechanical stress. Blocking this reaction by introducing interfering chemicals like N-ethylmaleimide (NEM), which binds to free SH groups, leads to an increase of mechanical stress. Since energy dissipation by

Table 2 Resulting interactions with the polymer matrix depending on surface functionalization.

Functional group of coating		Supposed mediated interaction with the matrix type:	
<b>Type</b>	<b>Properties</b>	<b>Protein (gliadin)</b>	<b>Carbohydrate (HPC-PVP)</b>
<b>Cyano</b>	Strongly dipolar, hydrophilic, prevents chemical binding of proteins [19]	Weak, unspecific (Van der Waals forces, dipole-dipole)	Strong, unspecific (dipole-dipole)
<b>Propyl</b>	Non-polar, hydrophobic	Weak, unspecific (hydrophobic interactions, Van der Waals forces)	Weak, unspecific (Van der Waals forces)
<b>Amino</b>	Polar, hydrophilic	Intermediate strong, specific (H-bonds)	Strong, specific (H-bonds)
<b>Mercapto</b>	Polar, hydrophilic	Intermediate strong, specific (H-bonds, disulfide bonds)	Strong, specific (H-Bonds)
<b>MBS</b>	Covalent cross-linking	Strong, highly specific (covalent binding with primary amines)	Not used
<b>PMPI</b>	Covalent cross-linking	Not used	Intermediate strong, highly specific (covalent binding with hydroxyl groups)

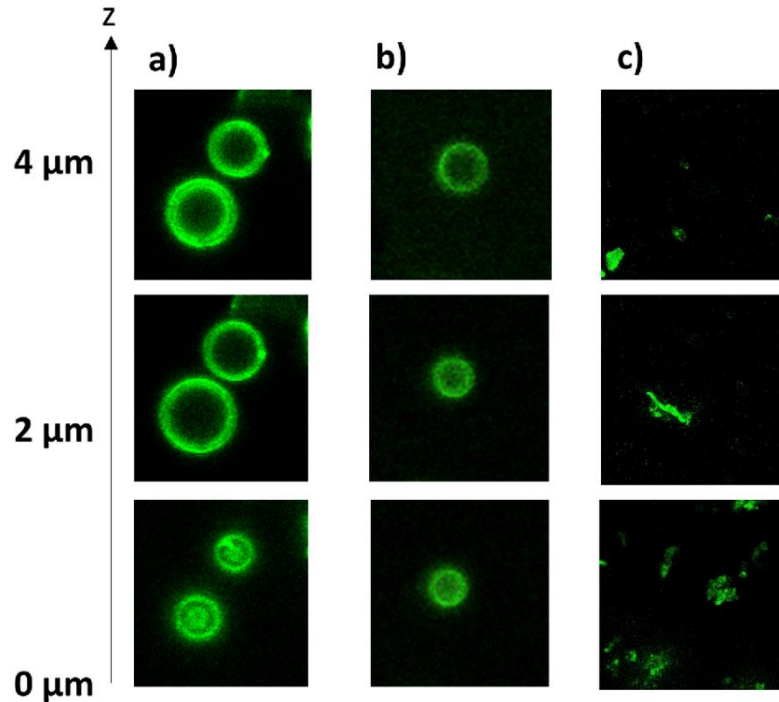


Fig. 4. Validation of glass bead functionalization by CLSM imaging: Glass beads at three different z-axis positions. a) amino-coated glass beads labeled with fluorescein-5-isothiocyanate. b) mercapto-coated glass beads labeled with fluorescein-5-maleimide. c) uncoated glass beads with fluorescein-5-isothiocyanate.

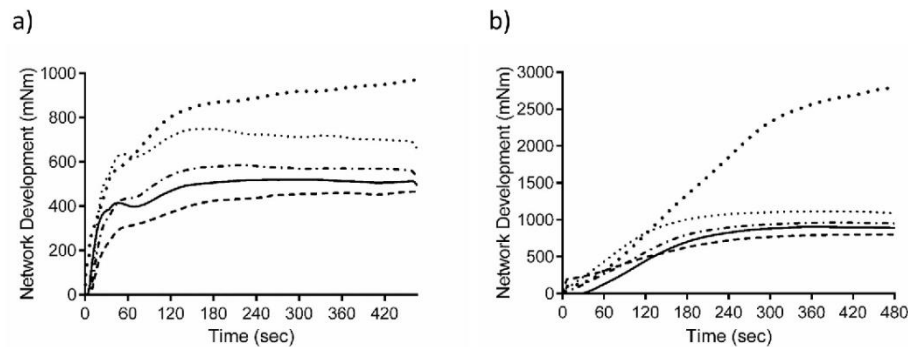


Fig. 5. Network formation monitored by a recording mixer a) for gluten mixtures and b) for HPC-PVP glass bead mixtures with varying coatings: mercapto (· · ·), amino (---), propyl (—), cyano (- - -) as well as MBS for gluten in a) and PMPI for HPC-PVP in b) (· · ·).

breaking disulphide bonds is not possible anymore, a direct stress transfer along the polymer chain is assumed [21]. Adding mercapto coated particles shows effects similar to thiol interfering chemicals. The additional thiol groups on the particle surface can also influence the thiol/disulphide exchanges of gluten by blocking free thiol groups. As described by Baudouin et al. (2020) the resulting direct stress transfer to the polymeric matrix causes the higher mNms and a shortened network development time. However, this approach cannot explain the high peak resistance of mercapto coated particles in carbohydrate-based systems. The molecular mechanisms causing the high peak resistance remain concealed. The addition of particles which are supposed to covalently interact with the polymers (MBS or PMPI coated) causes significant effects. For protein-based systems, the peak resistance is almost twice as

high and the development time two to three times longer than for all other coatings; the peak resistance and development time in the carbohydrate-based system is even outside the detection limit. On the one hand, the strong adhesiveness between particles and polymers provides a very effective stress transfer [23], which results in high mNm for MBS- or PMPI-coated particles. On the other hand, the polymeric linking is hindered/delayed and results in long development times. Regarding the adhesiveness of coatings, the protein-based networks are affected stronger by the different coating types than the carbohydrate-based systems. The development time of gluten-based systems range from 3.2 min for mercapto-coated particles to 6.0 min for amino-coated particles. In contrast, the HPC-PVP-based systems just range from a development time of 6.1 min for propyl to 6.7 min for

mercapto. As already mentioned, the adhesiveness between particle and polymers can hinder the network development by an adsorption, induced by the adhesiveness, and a desorption, induced by the mechanical forces, until a stable equilibrium of adsorbed particles and inter-polymeric junctions exists. Depending on the adhesiveness and the type of particle-polymer interaction, the network development time varies. Since gluten has a vast variety of polymeric junction types (hydrophobic and van der Waals interactions, H-bonds, disulfide-bonds, entanglements), each of the particle coatings will affect a different type of network junction, resulting in very different network development times. In contrast to the gluten polymer, the network structure of HPC-PVP is mainly based on hydrogen-bonds and only to a minor amount on entanglements and polar forces [24]. Consequently, each coating type affects the same network junction type (for hydrogen bonding). The similar adsorption mechanisms of the particles, independent of their coating, could explain the small range of network development times for the HPC-PVP matrix.

#### 4. Conclusion

Within the scope of this study, the impact of particle surface functionality on the network formation in food-based matrices was analyzed. By using a model system, the adhesiveness of protein- and carbohydrate-based polymers was evaluated on defined surfaces, functionalized by different coatings, respectively. The combination of macro- and nanoscopic analytics enables to determine the degree of interaction between polymer and coating. As a result, systems with an adhesiveness ranging from weak unspecific adsorption to strong specific adsorption of polymers were established and can be used to imitate naturally occurring interactions in particle-polymer-based food systems. Based on the findings about polymer adhesiveness with a specific coating, the impact of particle surface functionality on network development could be analyzed in a new way. Independent of food matrix type, particle adhesiveness influences the mixing time for reaching maximum network strength, thus indicating the ability of particle surface functionality in affecting network formation. In particular, the heterogeneity of network junction types seems to enhance the effect of particle surface functionalities on the network development. Polymeric networks, mainly formed by one junction type (HPC-PVP), exhibit a smaller range in network development time as heterogenic networks, consisting of many different junctions (gluten). The observations made in studies, which analyze the impact of network modifying chemicals (e.g. urea or NEM) on network development, are in accordance with the observed modifications of network development by using coated particles. For example, mercapto coated particles lead to a shorter network development time and a more effective stress transfer in a similar way as thiol interfering chemicals cause. At the one hand, this can be considered as a proof of principle for using silane coated particles to control the adhesion/interactions between particles and polymers, since the blocking of polymeric functional groups by particles resulted in the same mechanical trends as adding the pure chemicals. On the other hand, this implies that the presented approach offers a powerful method for analyzing the impact of particle-polymer interfaces in food based systems. The large number of commercial available silanes enables the imitation of nearly every natural occurring surface in a very defined and reproducible way. Combining the presented approach with fundamental rheological tests, contributes to a deeper understanding of particle-polymer interactions on the overall mechanical properties in food and is considered as following step.

#### CRedit authorship contribution statement

**Silvia Brandner:** Conceptualization, Methodology, Writing – original draft. **Tim Kratky:** Investigation, Formal analysis, Writing – review & editing. **Kerstin Holtz:** Investigation, Validation. **Thomas Becker:** Supervision. **Mario Jekle:** Writing – review & editing.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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### 3.5 Impact of the particle-polymer interface on small- and large-scale deformation response in protein- and carbohydrate-based food matrices

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## Impact of the particle-polymer interface on small- and large-scale deformation response in protein- and carbohydrate-based food matrices

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## ABSTRACT

Interfaces are important regarding the mechanical behavior of foods. In particle-polymer-based food systems, the rheological effect of interface characteristics between microscopic particles and viscoelastic polymers is controversial. By using a new approach of presenting defined glass beads surfaces, which imitate functional groups of starch particle surfaces, the adhesiveness and the adsorption mechanism between particle and polymeric food matrix (protein-/carbohydrate-based) can be controlled. The combination of defined particle-polymer interfaces with a comprehensive rheological analysis gives new insights into the effect of particle-polymer interfaces on the mechanical properties of food. Independent of the matrix-type, non-adhesive particles show the strongest network at low stress (protein-based: network strength  $A_f = 2.02 \pm 0.16 \cdot 10^4 \text{ Pas}^{1/2}$ ), but the fastest network breakdown under higher stress (fracture strain protein-based  $4.40 \pm 0.08$ ). Adhesive particles behave inverse ( $A_f = 1.02 \pm 0.24 \cdot 10^4 \text{ Pas}^{1/2}$ ; fracture strain  $5.38 \pm 0.32$ ). Consequently, particle supplemented protein-/carbohydrate-based matrices have properties similar to particle reinforced rubbers and exhibit a more or less pronounced Payne effect depending on the adhesiveness. Besides the adhesiveness, the adsorption mechanism affects the deformation behavior of particle-polymer based system. The highly adhesive but unspecific adsorption of carbohydrate-based polymers at cyano-functionalized surfaces shows a similar relaxation behavior as non-adhesive surface functionalization.

## 1. Introduction

Plenty of foods are dispersed systems with a highly specific interface between the dispersed and the continuous phase. A common type of dispersed food systems are particle-polymer-based systems. Here, different types of particles are dispersed in diverse types of polymeric matrices. In addition to the naturally occurring dispersed food system, like wheat dough, designed particle-polymer based food systems gain more and more attention since they allow the control of many material-related properties like rheology, texture or a target delivery of nutrients in human nutrition [1]. Often, the polymeric matrix is protein- or carbohydrate-based [2], but particles can be of very different character, like micelles, liposomes, nano-emulsions, micro-hydrogels or of varying resources (protein- or carbohydrate-based). This high variety of particle types comes along with many different properties concerning their shape, size, hardness and especially their surface functionality. The character of the particle surface as part of the interface determines the interaction with the surrounding polymeric matrix [3]. Due to the large

area of the particle-polymer interface, mechanical properties of the overall system can be significantly affected by this interface [4]. Consequently, gaining a fundamental knowledge about the impact of the particle surface functionality and the resulting interface with the polymeric matrix on the rheological properties is essential. However, this task remains challenging, particularly when analyzing food systems. The natural character makes food systems poorly reproducible and implies fluctuations regarding the composition and properties of the interface. Furthermore, most food systems are highly sensible with respect to chemical or mechanical modifications. Consequently, the commonly used methods for analyzing the impact of particle-polymer interfaces in food, like reconstitution experiments [5] or chemical/mechanical modifications [6], frequently lead to contradictory statements. Applying techniques known from material/polymer science in the field of food sciences offers a novel and promising approach to shed light on the effect of surface functionalities of microscopic particles on the mechanical properties [57]. In material sciences, coupling agents are used to create defined interactions between filler particles and polymers [3,7,9,57].

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This enables the design of materials with defined mechanical properties. In food sciences, only a few studies replaced particles by inorganic fillers with a defined surface modified by coatings [8,10,11]. In contrast, the effects of adding particles with a defined surface to a plant-based polymeric matrix, like gluten, are intensively studied for non-food systems like packaging materials [12,13,14]. Only the addition of particles lends appropriate mechanical properties to the polymerized matrix (gluten) [15], which makes it suitable as a biodegradable packaging material. These studies already indicate the strong impact of particles and their specific surface functionality on the mechanical properties, same as for the polymer networks used in foods. However, the network forming process and particle surface functionality used for packaging differs from that of food. Consequently, the insights gained from packaging research cannot simply be transferred to food systems. Thus, material science approaches have to be adapted to investigate food systems. This will be achieved by the following experimental approach:

- Selection of particles and modification of their surface: Inert particles of microscopic size and spherical shape (glass beads) were selected and a defined particle surface was created by coating. According to Brandner et al. (2021) the following coatings can imitate the surface composition of food particles (e.g. starch): Propyl-functionalization imitates the hydrophobic and non-polar character of fats (alkyl chains), cyano-functionalization imitates hydrophilic and polar/ionic parts, mercapto- and amino-functionalization imitate sulphur respectively nitrogen containing parts of proteins. Heterobifunctional cross-linkers offer a covalent binding site (MBS/PMPI). A successful surface modification by these coatings could be demonstrated [57].
- Determination of representatives of a protein and carbohydrate based matrix: A common protein-based food matrix, which contains dispersed microscopic particles, is wheat dough. In this system, gluten polymers form a network and starch particles are dispersed within the formed network. With a molecular weight up to 10 million Da [18], gluten polymers are one of the biggest natural occurring polymers. This makes gluten kind of unique and simultaneously predestined for analyzing the effect of the particle-polymer interface on the rheology of high molecular weight polymers. The second common polymer type in food-based particle-polymer systems are carbohydrates, which are often used for gel formation or as thickening/stabilization agents. The specific interactions between particle and surrounding carbohydrate become more and more relevant, for example for the target delivery of therapeutic proteins [19] and for analogues of common food products. In this study, a primarily carbohydrate-based network, containing 0.25 parts of a modified cellulose (hydroxypropylcellulose, HPC) is used. The addition of 0.07 parts of the synthetic polymer polyvinylpyrrolidone (PVP) give the mixtures attributes, which are similar to the rheology of gluten

polymers [20]. This facilitates a comparison of the effects originating from the particle surface functionalities on the rheological properties in two common food-based matrixes (protein and carbohydrate).

- Properties of the particle-polymer interface depending on surface functionalization and polymer: The understanding of interface characteristics regarding adhesiveness and adsorption mechanism between particle surface and polymer on a molecular level is required for understanding the rheological properties and was analyzed in our previous study [27]. Depending on the surface functionality, interfaces are defined by weak/intermediate/strong polymer adhesiveness following unspecific/specific adsorption mechanisms (compare Table 1 and Fig. 1).
- Formation of particle-polymer systems: Classically, food-based matrixes are formed by the addition of water and the input of mechanical energy (mixing; method 1). This way of production will already affect the network formation, depending on the particle properties, as demonstrated in Brandner et al. (2021) [57]. To overcome this impact, a network can also be formed just by hydration (non-developed network, method 2) [21]. This will only affect the particle-particle and particle-polymer interactions but not the polymer-polymer interactions.
- Comprehensive fundamental rheological tests: Based on defined interface characteristics, the impact of particle-polymer interactions on the mechanical properties were evaluated. A rheological test set-up with two different stress levels needs to be applied. Particle-particle and particle-polymer interactions belong to short-range interactions, which were analyzed by using small-scale deformation tests, whereas the long-range interactions (polymer-polymer) were analyzed by large-scale deformations [22].

Using this innovative approach makes it possible to shed light on the effect of interfaces between microscopic particles and polymers on the rheology of food systems on a new level.

## 2. Experimental

### 2.1. Materials

The polymeric network was constructed by using vital gluten (Kröner-Stärke, Ibbenbüren Germany) or a system imitating gluten consisting of hydroxypropylcellulose (HPC, Klucel H, Kremer Pigmente, Aichstetten Germany) and polyvinylpyrrolidone (PVP, K 90, VWR, Darmstadt, Germany). Furthermore, the particle imitating glass beads (GBs), with a size ranging from 2.60 µm to 19.27 µm, were purchased from Microperl Sovitec (Schönborn, Germany). The used silane coupling agents in combination with the heterobifunctional linkers and their mediated adhesiveness/specificity of adsorption to the surrounding polymer matrix are all listed in Table 1. All silanes (purity 97 - 98%),

**Table 1**  
Overview of used coupling agents and their functionality with respect to the polymer matrix.

Silane coupling agent	Functional group	Imitates which part of particle surface	Mediated interactions (according to Brandner et al. (2021) with [57])	
			Gluten	HPC-PVP
2-Cyanoethyltriethoxy-silane	CH	Parts having dipole character	Weak, unspecific (Van der Waals forces, dipole-dipole); prevents protein adsorption [16,17]	Strong, unspecific (dipole-dipole)
n-Propyl-triethoxysilane	CH <sub>3</sub>	Hydrophobic, non-polar parts, like fats	Weak, unspecific (hydrophobic interactions, Van der Waals forces)	Weak, unspecific (Van der Waals forces)
3-Aminopropyltri-ethoxysilane	NH <sub>2</sub>	Proteins containing amino groups (asparagine, lysine, proline)	Intermediate strong, specific (hydrogen-bonds)	Strong, specific (hydrogen-bonds)
3-Mercaptopropyltri-ethoxysilane	SH	Proteins containing mercapto groups (cysteine)	Intermediate strong, specific (hydrogen-bonds, disulphide bonds)	Strong, specific (hydrogen-bonds)
MBS (m-maleimidoben-zoyl-N-hydroxysuccin-imide ester)	NHS ester	covalent particle-polymer interactions	Strong, highly specific (covalent binding with primary amines)	/
PMPI (N-[p-maleimido-phenyl] isocyanate)	Isocyanate	covalent particle-polymer interactions	/	Strong, highly specific (covalent binding with hydroxyl groups)

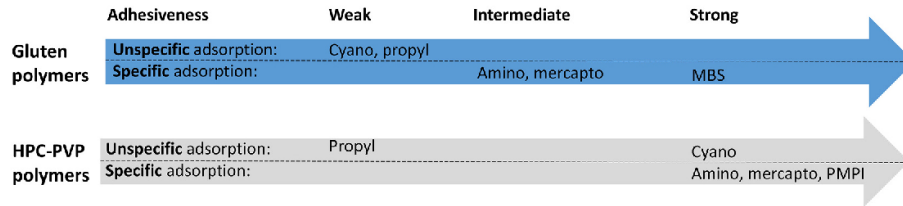


Fig. 1. Characteristics of the interface between cyano-, propyl-, amino-, mercapto- or MBS/PMI- functionalized surfaces and gluten or HPC-PVP polymers. The interface was previously analyzed in Brandner et al. (2021) regarding the adhesiveness and the specificity of polymer adsorption [57].

linkers were purchased from ThermoFisher (Germering, Germany) or Alfa Aesar (Karlsruhe, Germany).

2.2. Preparation of particles

GBs are cleaned in freshly prepared piranha solution and subsequently functionalized with the different silanes mentioned above and if required incubated with the heterobifunctional linker MBS or PMPI following the procedures described in Brandner et al. (2021) [57]. Except for the GBs with linker, which are used directly after the removal of unattached linker, all GBs were dried and stored in dry air until usage (up to 3 days).

2.3. Mechanical formation of particle-polymer systems

Classically, dough is formed by the addition of water and the input of mechanical energy (mixing). For gluten-based polymer matrices, a modified glutomatic (Perten instruments, Hamburg, Germany) is used. Therefore, the sieve insert was replaced by a closed one and water was added manually [23]. A mixing time of 7 min is necessary to create a developed gluten-based particle-polymer system. In contrast, to develop the HPC-PVP-based particle-polymer system, a home-built z-kneading system with a mixing time of 10 min at a speed of 63 rpm is necessary.

2.4. Non-mechanical formation of particle-polymer systems (hydration)

To create non-developed particle-polymer matrices, the method according to Campos et al. (1996) was used [21]. Ice and dry ice were crushed to a particle size ≤250 μm. After the sublimation of dry ice, GBs, polymers and crushed ice were mixed (hand mixer) in corresponding quantities of Table 2 in a walk-in freezer. The mixtures were pressed into cups, weighted and allowed to hydrate for 24 h at room temperature.

2.5. Rheological analyses

Rheological analyses were performed at two stress levels: within and exceeding the linear-viscoelastic region. For small-scale deformation tests, an AR-G2 rheometer (TA instruments, New Castle, USA) with a 40 mm parallel plate system (upper plate cross hatched) was used and for large-scale deformation tests, an MRC 502 rheometer (Anton Paar, Ostfildern-Scharnhausen, Germany) with a 25 mm parallel plate system (cross hatched) was used. All measurements were performed in triplicate with a sample gap of 2 mm and a temperature of 30 °C. To prevent the samples from drying, the edges were coated with paraffin oil. Before each measurement, samples were allowed to rest for 2 min.

Table 2 Food matrix composition and particle proportion. Quantity in parts.

Particle-polymer system	Distilled water (30 °C)	Glass beads	Gluten	HPC	PVP
Gluten-GB	1	1.59	0.68	/	/
HPC/PVP-GB	1	0.74	/	0.25	0.07

2.5.1. Small-scale deformation

To analyze the impact of particle-particle and particle-polymer interactions on the rheological properties, a frequency-sweep and a creep test within the linear viscoelastic limit were performed. For the frequency-sweep, the measurement frequency was varied from 0.1 to 100 Hz at a deformation of 0.1%. The complex modulus G\* was analyzed according to the power law equation (Eq. (1)) [24].

$$G^*(\omega) = A_f \cdot \omega^{1/z} \tag{1}$$

where A<sub>f</sub> (Pa s<sup>1/z</sup>) describes the gel strength and z (-) describes the network elements' connectivity. Directly after the frequency-sweep, the creep test was performed by applying a constant stress of 5 Pa for 120 s. The creep curve was evaluated using the Burgers Model (Eq. (2)):

$$J(t) = J_0 + J_1 \left[ 1 - e^{-t/\lambda} \right] + \frac{t}{\eta_0} \tag{2}$$

where J<sub>0</sub> (Pa<sup>-1</sup>) corresponds to the instantaneous compliance, J<sub>1</sub> to the viscoelastic compliance, λ (s) to the retardation time and η<sub>0</sub> (Pa s) to the zero shear viscosity [25,26].

2.5.2. Large-scale deformation

To analyze the impact of polymer-polymer interactions, three tests beyond the linear viscoelastic limit including creep recovery were performed. Here, a shear stress of 100 Pa was applied for 360 s. Afterwards, the shear stress was removed and the recovery was monitored for 720 s. The creep curve was analyzed according to Eq. (2). In addition, the elastic recovery after stress elimination was analyzed using Eq. (3).

$$Elasticity = \frac{J_{min, recovery}}{J_{max, creep}} \cdot 100 \tag{3}$$

The stress-growth behavior was analyzed by applying a constant shear rate of 0.1 s<sup>-1</sup> for 400 s. The strain was calculated by multiplying the shear rate with time. The stress growth behavior was evaluated by the peak stress (maximum stress arising under strain) and its corresponding strain according to Kim et al. (2008) [27]. Furthermore, flow-relaxation measurements were performed. A deformation of 100% was applied with a shear rate of 0.02 s<sup>-1</sup>. After reaching 100%, the deformation was kept constant and the stress recession was monitored for 90 s. Finally, the relaxation behavior was analyzed by the relaxation half-times, which correspond to the time needed to halve the maximum stress at a deformation of 100% [28].

3. Results and discussion

For analyzing the impact of particle surface functionalities, respectively particle-polymer interfaces, on the rheology of protein- or carbohydrate-based food matrices, four different system types were considered. Systems consisting of protein-based polymers (gluten) were combined with GBs modified with five different functional groups. Particle-polymer systems were produced by mixing (developed matrices, type 1) or by hydration (non-developed matrices, type 2).



Systems consisting of carbohydrate-based polymers (HPC-PVP) were also combined with GBs bearing five different functionalization and produced by mixing (developed matrices, type 3) or by hydration (non-developed matrices, type 4). To distinguish between the effects of particle-particle, particle-polymer and polymer-polymer interactions on the mechanical behavior, small- and large-scale deformation tests were performed. Since our previous study has shown an influence of glass beads surface functionalities on the mechanical network development [57], additional small-scale deformation tests were performed with non-developed matrices to exclude the impact of particle surface functionality on network formation.

As mentioned in the introduction, the understanding of interface characteristics is a prerequisite for understanding the rheological properties. Therefore, the previously assessed adhesiveness and polymer adsorption mechanisms with the functionalized surfaces are shortly summarized [57]. Considering contact angle and X-ray photoelectron spectroscopy (XPS) data of functionalized SiO<sub>2</sub> surfaces before (reference) and after incubation with a polymer solution (gliadin or rather HPC-PVP), the adsorption of the polymers was analyzed. Subsequent rinsing steps of different durations enable polymer desorption and, thus, determine the adhesiveness between polymer and functionalized surface on a macroscopic and nanoscopic level. Fig. 1 summarizes the resulting interface characteristics, which are based on weak/intermediate/strong unspecific/specific adsorptions.

### 3.1. Small-scale deformations

To investigate the effects of particle-particle and particle-polymer interactions, a frequency sweep and a creep test within the linear viscoelastic limit were performed and analyzed using the power law and the Burgers model, respectively (Fig. 2). Raw data of frequency sweeps (complex module G\*), creep tests (compliance J(t)) and remaining

parameters of power law, respectively Burger Model can be found in the supporting information.

#### 3.1.1. Gluten-based matrices

The functionalization of particle surface and thus, the characteristics of particle-polymer interface affects the rheological properties. The network strength  $A_f$  of mechanical developed particle-polymer systems (Fig. 2 a) corresponds to a decreasing order of cyano- ~ mercapto- > propyl- ~ amino- > MBS- functionalized surfaces. The decreasing order of  $A_f$  corresponds to an increasing adhesiveness between particle surface and gluten polymers, with the exception of mercapto. At low deformations, stiff particle-particle networks increase the complex modulus  $G^*$ , whereas particles with a high adhesiveness towards polymers lower  $G^*$  [3]. Based on the high  $A_f$  the formation of a particle network or particle aggregates during the mechanical network development is estimated for the cyano-functionalized particle-polymer system, whereas the higher adhesiveness of gluten polymers with amino- and MBS-functionalized surfaces inhibits a particle-based network formation and thus, lowers  $A_f$ . The instantaneous compliance  $J_0$  of developed particle-polymers systems (Fig. 2 b) shows an appropriate trend according to the adhesiveness with an increasing order of cyano (< mercapto) < propyl < amino < MBS. Consequently, increasing adhesiveness (except mercapto groups) between particles and polymer causes a higher elasticity. The binding of particles to polymers induces a modification of the local segmental dynamics. This reduction of polymer mobility contributes to the elastic behavior at low stress levels [29]. The reduced mobility of the polymer chains also becomes visible by the increased zero shear viscosity  $\eta_0$  (Fig. 2c) for amino- and MBS-functionalized particles compared to cyano- and propyl-functionalized particles. Despite the comparable adhesiveness of gluten polymers to mercapto- and amino-functionalized particles, mercapto-functionalized particles results in deviating values for  $A_f$ ,  $J_0$  (higher) and  $\eta_0$  (lower). A

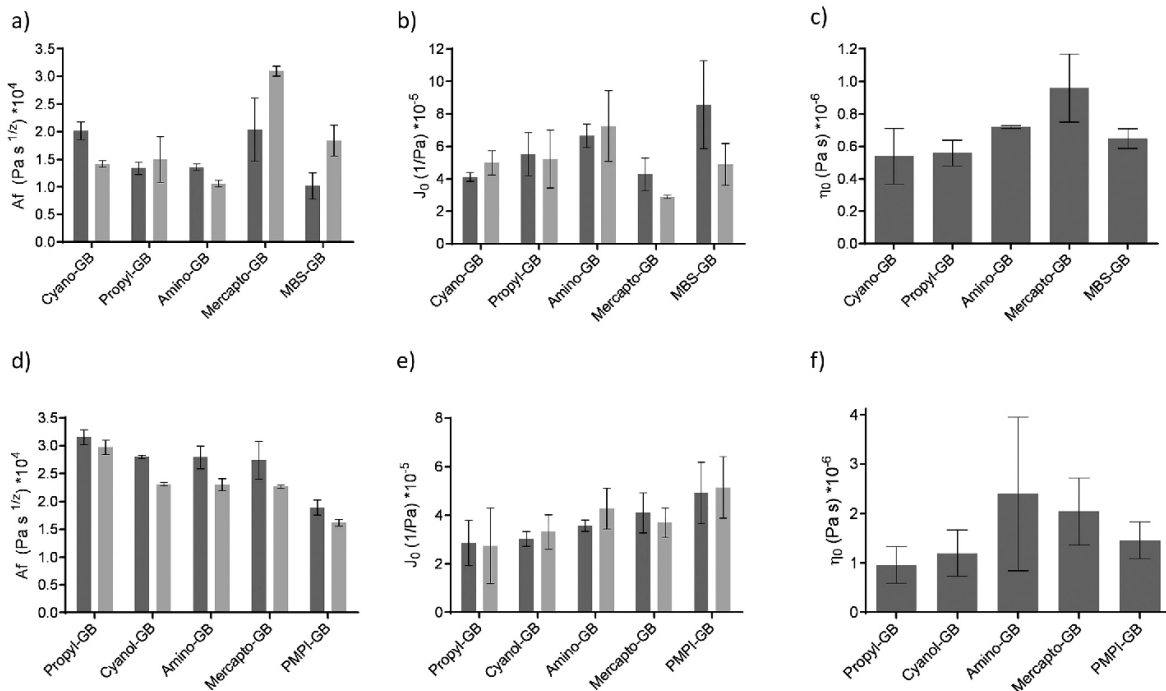


Fig. 2. Results of small-scale deformation tests for gluten- and for HPC-PVP-based matrices in a-c) and d-f), respectively, with differently functionalized glass beads, produced by mixing (■; developed) or hydration (□; non-developed). The frequency sweep reveals the network strength  $A_f$  (a and d), the creep test (5 Pa) the instantaneous compliance  $J_0$  (b and e) and the zero-shear viscosity  $\eta_0$  (c and f). Error bars are based on standard derivations.

possible explanation is based on the different adsorption mechanisms of gluten polymers. Mercaptans are able to form covalent interactions with cysteines of the gluten polymer [30] which are mainly present at the ends of glutenin chains [31], whereas amino groups appear along the whole polymer. Consequently, much more amino-functionalized GBs can interact specifically with gluten compared to mercapto-functionalized GBs. Therefore, a surplus of mercapto-functionalized particles compared to the available cysteine groups is assumed. Consequently, particle-particle interactions of mercapto-functionalized GBs might arise, which explain a rheological behavior comparable to particle surface functionalization with a low polymeric adhesiveness (cyano).

Since our previous study has shown a modified dough development depending on the GB surface functionalization [57], a comparison of the rheological behavior of developed and non-developed particle-polymer systems becomes meaningful.  $A_f$  as well as  $J_0$  are affected in the non-developed systems due to particle surface functionalization (Fig. 2 a, b).  $\eta_0$  depends on the molecular mass of unlinked polymers only [32]. Due to the missing mechanical energy input, most of the polymer is expected to be unlinked independent of the surface functionalization. Therefore,  $\eta_0$  is not meaningful for non-developed matrices. Network strength  $A_f$  and instantaneous compliance  $J_0$  of cyano- and propyl-functionalized particles show similar values for the non-developed systems, but divergent values for the developed systems. For the structuring of gluten proteins, hydrophobic interactions are important [58]. However, accessibility seems to be dependent on the mechanical energy input, since an increase of gluten surface hydrophobicity occurs after mixing [48]. If no mechanical energy input is applied, an adsorption of gluten polymers by hydrophobic interactions at the hydrophobic surface of propyl-functionalized GBs could be lowered as the accessibility of the hydrophobic parts of the proteins will be low due to the orientation of hydrophobic parts in an aqueous environment.

The divergent behavior of mercapto-functionalized GBs (highest  $A_f$  and lowest  $J_0$ ) becomes clearer for the non-developed system. During the mechanical network formation, thiol/disulphide exchange reactions occur and enable an adsorption of gluten polymers at the mercapto-functionalized particle surface by disulphide bond formation [57]. If no mechanical network formation takes place, the opportunities for polymer adsorption by disulphide bond formation will be reduced and thus, more particle-particle interactions seem reasonable, which cause a high  $A_f$  and low  $J_0$ . The non-developed particle-polymer system with a MBS surface functionalization shows an unexpected behavior. Instead of the lowest  $A_f$  and highest  $J_0$ , due to the strong adhesiveness between particle and polymer, an increase of  $A_f$  and a decrease of  $J_0$  occurs. Due to the way of network development (freezing of MBS coupled mercapto GBs), a loss of functionality (adhesiveness) of the MBS-linker is likely, resulting in an inactive GB surface. This is confirmed by the rheological behavior similar to the non-developed cyano system, which has a low adhesive surface.

### 3.1.2. HPC-PVP-based matrices

For the interpretation of the rheological results of the HPC-PVP-based matrices, some deviations of particle-polymer adhesiveness in comparison to the gluten-based matrix have to be considered (compare Fig. 1). HPC-PVP polymers showed the lowest adhesiveness to a propyl surface functionalization. HPC as well as PVP are hydrocolloids with no/few hydrophobic parts. Consequently, with the non-polar propyl group, no notable interactions are possible, whereas the dipolar cyano surface functionalization enables a strong adhesiveness based on unspecific adsorption mechanisms. In addition, amino- and mercapto-functionalized surfaces demonstrated a strong adhesiveness with HPC-PVP, but here, based on a specific adsorption mechanism (hydrogen-bond formation) [57].

Regarding the network strength  $A_f$  (Fig. 2 d), the instantaneous elasticity  $J_0$  (Fig. 2 e) and the zero shear viscosity  $\eta_0$  (Fig. 2 f), corresponding correlations to the gluten-based matrices become visible considering the of particle-polymer adhesiveness. Particle surface

functionalizations with low adhesiveness to the polymers (cyano) show the highest  $A_f$  and  $J_0$  as well as the lowest  $\eta_0$  values and thus, indicating the presence of a particle-based network also in the HPC-PVP matrix. In contrast, surface functionalizations, which cause a strong adhesiveness of HPC-PVP (cyano, amino, mercapto, PMPI), decrease  $A_f$  and increase  $J_0$  as well as  $\eta_0$ . Depending on the surface functionalization of GBs, the non-developed HPC-PVP systems show the same behavior for  $A_f$  and  $J_0$  as the mechanical developed ones. Therefore, in contrast to the gluten-based matrices, a mechanical energy input seems to be dispensable for a total accessibility of polymer and functionalized particle surface.

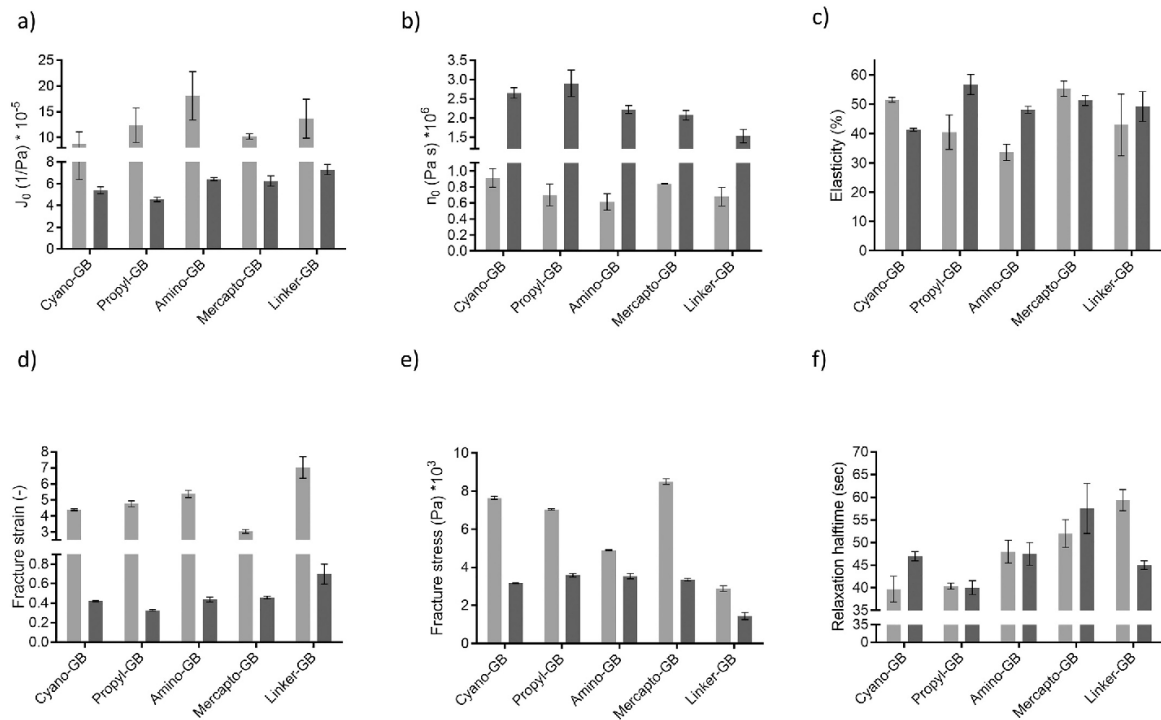
The results of the small-scale deformation tests demonstrate that the adhesiveness as well as the specificity of polymer adsorption at the functionalized particle surface define the rheological effects. In general, a low adhesiveness between particles and polymers promotes the formation of a particle network with a higher network strength and lower elasticity and zero shear viscosity, whereas the adsorption of polymers causes a decrease of network strength and an increase of elasticity as well as zero shear viscosity at small-scale deformations.

### 3.2. Large-scale deformations

Based on the interface characteristics of particle and polymer, the impact on large-scale deformation rheology will be discussed. In total, three different tests were used: A creep-recovery test, whose creep phase was analyzed by the Burgers Model (Fig. 3 a and b) and creep-recovery phase by calculating the elasticity (Fig. 3 c), a stress-growth curve assessed by the strain (Fig. 3 d) and stress (Fig. 3 e) at peak (fracture) and a flowrelaxation test assessed by the relaxation halftime (Fig. 3 e). Raw data of creep curve, stress-growth curve, flowrelaxation test and remaining parameter of the Burger Model can be found in the supporting information. Since network formation based on hydration (non-developed) affects only the particle-particle and particle-polymer interactions, non-developed polymer matrices were not further considered for large-scale deformations. The interpretation of the rheological results is based on the previously assessed interface characteristics of functionalized particle surface and polymer regarding the adhesiveness and the adsorption mechanism (compare section 3, Fig. 1).

#### 3.2.1. Gluten-based matrices

All rheological figures of merit are affected by functionalized particle surfaces at the large-scale deformation level. The creep experiments (100 Pa) of the gluten-based matrices show an increase of the instantaneous elasticity  $J_0$  (Fig. 3 a), respectively a slight decrease of zero shear viscosity  $\eta_0$  (Fig. 3 b) in the order cyano, mercapto, propyl ~ MBS, amino. The elasticity (Fig. 3 c) shows a similar order of decrease as  $\eta_0$ . Only the elasticity of mercapto is higher than the one of cyano. Referring to the particle-polymer adhesiveness, surface functionalizations with a low adhesiveness for gluten polymers show a lower  $J_0$ , as well as a higher  $\eta_0$  and elasticity as surfaces with a higher adhesiveness. By using coupling agents (equal to surface functionalization with high adhesiveness) in filled rubber systems, a decrease of particle agglomeration (particle-particle interactions) and an increase of bound rubber (adsorbed polymer at the particle surface due to particle-polymer interactions) is often monitored [33,34]. This structural modification could create a polymer network with less polymer-polymer but more particle-polymer cross-links, due to the adsorption of polymers on the particle surface (bound rubber). A reduced amount of polymer-polymer interactions is expected to raise the proportion of elastic deformation ( $J_0$ ) and lowers the resistance against flow ( $\eta_0$ ) under stress, while reducing the elasticity after the removal of stress. Studies on gluten network modifying denaturants, like urea, for reducing interchain hydrogen bonds, show corresponding rheological changes for wheat dough (reduced  $\eta_0$  and elasticity, increased  $J_0$ ) [35,36] and thus, support the assumption of reduced polymer-polymer interactions in combination with a particle surface functionalization having a high adhesiveness. Analyzing the response of the particle-polymer systems during a continuously



**Fig. 3.** Results of large-scale deformation tests for gluten- (■) and HPC-PVP-based (■) matrices with differently functionalized glass beads. Particle surfaces were functionalized by cyano, propyl, amino, mercapto groups and a linker (MBS for gluten, PMPI for HPC-PVP). The creep test (100 Pa) is evaluated using the instantaneous compliance  $J_0$  (a) and the zero-shear viscosity  $\eta_0$  (b), the creep-recovery test by using the elasticity (c), the stress-growth curve by using the fracture strain (d) and fracture stress (e) and the flow-relaxation test by using the relaxation half-time (f). Error bars are based on standard deviations.

increasing deformation by the fracture strain (Fig. 3 d) and stress (Fig. 3 e) shows an increasing and decreasing order, respectively, of mercapto, cyano, propyl, amino, MBS. Except for mercapto, this order corresponds to an increasing adhesiveness between particle surface and polymer. A low adhesiveness between particle and polymer raises the capacity of stress reduction by dissipation of energy [37,38]. This affects the deformation behavior under stress by preventing the polymeric structure from a premature fracture, as well as the relaxation process after stress removal. In contrast, particles with an adhesive surface cause an effective stress transfer to the polymeric matrix, which lowers the deformability. The relaxation half-time (Fig. 3 f) increases in the order cyano  $\sim$  propyl  $<$  amino  $\sim$  mercapto  $<$  MBS. This fully complies with the order of increasing adhesiveness of gluten polymers with particle surface functionalization and confirms the effect of energy dissipation by weakly adsorbed polymers regarding the relaxation of the polymeric matrix [45].

Comparable to the small-scale deformation behavior, the mercapto surface functionalization results in divergent rheological properties as a surface functionalization of comparable adhesiveness (amino). Particle-polymer systems with a mercapto surface functionalization show a lower  $J_0$  and fracture strain and a higher  $\eta_0$ , elasticity and fracture stress than systems with amino-functionalized GBs. The consideration of adsorption mechanisms of gluten polymers at mercapto-functionalized GBs in combination with the impact on the network formation, which was analyzed in our previous study [57], shed light on the divergent rheological behavior. During the network formation of gluten polymers, the thiol groups of the cysteine residues of glutenins act as chain extenders by linking gluten polymers via interchain disulphide interactions [31,39]. If these gluten polymers adsorb at the mercapto-

functionalized particle surface by disulphide bond formation, no further chain elongation is possible during the process of network formation. Consequently, a gluten network with shorter polymer chains and fewer intermolecular disulphide bonds is created. In addition, the formation of a strong particle-particle network (compare 3.1) is expected [59]. Based on these structural modifications and the Loop and Train Model of Belton [40], which explains the elasticity of gluten networks by the formation of non-covalent interchain interactions (train regions) and interactions between gluten and solvent (loop regions), the rheological properties can be explained as follows: A surface functionalization with mercaptans affects the chain lengths of gluten polymers, but not the ratio of train to loop regions along these polymers, due to the highly specific adsorption mechanism based on the cysteine residues at the glutenins. According to Belton, the ratio of loops to trains is responsible for the elastic part of network deformation [40]. In combination with the presence of a strong particle network, a high instantaneous elastic response ( $J_0$ ), comparable to that of cyano, becomes comprehensible. Regarding deformations beyond that of loops (post fracture), the deformation behavior will be determined by the polymeric chain length. Structural relaxation depends mostly on the polymeric chain length and is proportional to the square of the chain length [41]. Based on the chain terminating effect of mercapto-functionalized GBs, the shorter gluten polymers enable a faster recovery after the removal of stress, which is synonymous to a higher elasticity (Fig. 3 c). In addition, a lower polymeric chain length (lower molecular mass) reduce the ability to form entanglements [42]. During network deformation, entanglements allow a slippage of polymer chains and prevent the premature breakdown of network structure [43,44]. Therefore, a low fracture strain in combination with a high fracture stress becomes

transparent. Regarding the relaxation half-time (Fig. 3 f) each surface functionalization shows a consistent trend with the particle-polymer adhesiveness. Relaxation time increases with adhesiveness. This indicates that the adhesiveness between the particles and the polymer is of primary importance for the relaxation behavior under constant tension. Highly adhesive particles are effective in transferring stress to the polymeric matrix, whereas particles with a low adhesiveness to the polymer contribute to energy dissipation by debonding [37,38] and facilitate the relaxation of the polymeric matrix [45].

### 3.2.2. HPC-PVP-based matrices

In general, the results of the HPC-PVP-based matrices confirm the impact of particle-polymer interface characteristics, which was previously discussed for the gluten-based matrix. Depending on the adhesiveness of polymer with the functionalized particle surface, the deformation behavior is affected as follows: Surface functionalizations of low adhesiveness to the polymers (propyl) show the lowest instantaneous elasticity  $J_0$ , fracture strain and relaxation half-time in combination with the highest elasticity,  $\eta_0$  and fracture stress. Surface functionalization of higher adhesiveness with the polymers (cyano, amino, mercapto, PMPI) show an inverse behavior. Therefore, the effect of particle-polymer adhesiveness on the mechanical properties seems to be general applicable as long as the adsorption mechanism does not lead to a strong structural modification of the polymer network (impact of mercapto-functionalized GB in combination with gluten network). By a closer consideration of particle surface functionalization and the effect on the deformation behavior, the impact of adsorption mechanism becomes also visible for the HPC-PV- based matrices. Despite the highest adhesiveness of cyano-functionalized surfaces with HPC-PVP polymers [57], rheological values, which reflect the deformation behavior ( $J_0$  and  $\eta_0$ ), are closest to that of propyl-functionalized surfaces. In contrast, rheological test, which evaluate the relaxation behavior (elasticity, relaxation half-time) comply with the values of other adhesive surface functionalization. This means, the lowest elasticity (Fig. 3 c) for the cyano-functionalized GBs and a relaxation half-time (Fig. 3 f) corresponding to amino-functionalized GBs. With a cyano surface functionalization (strong but unspecific) Van der Waals forces are mediated by the polarity of the nitrile group. Based on these unspecific forces, polymer adsorption can occur globally. In contrast, adsorptions, which are based on specific interactions, like hydrogen bonds, can only occur locally at the appropriate parts of the polymer (like hydroxyl groups). Assuming a global ability for adsorption of the carbohydrate-based network, the detachment between particle and polymer is impeded compared to a low adhesive surface functionalization. However, a sliding along the polymers without a detachment will be simplified, since the adsorption is not limited to a local embedding. In consequence, deformation dependent behavior ( $J_0$  and  $\eta_0$ ) will be similar to that of particle surface functionalization with low adhesiveness until deformation will result in a complete structural break down (stress-growth curve, Fig. 3 d, e). In contrast, structural relaxation is controlled by the adhesiveness and thus, cyano-functionalized GBs show a decelerated relaxation behavior.

Compared to the protein-based network, the rheological impact of surface functionalization is lower for the carbohydrate-based matrix. A possible reason could be the higher heterogeneity of gluten polymers according to the functional groups/elements, which are involved in network formation. Here, hydrophobic and polar interactions, hydrogen bonds, covalent interactions, and entanglements are involved. In contrast, the network formation of HPC-PVP is mainly based on hydrogen bonds [46] and to a lower extent on chain entanglements and polar forces. This high homogeneity of polymer-polymer cross-links makes the network formation, depending on the particle surface functionality, less variable. Independent of the particle surface functionality, the interactions with the polymeric matrix can occur mainly at just one cross-link type (hydrogen bond). Consequently, the effect of particle adhesiveness on the network will be similarly independent of the surface

functionalization type, which could explain the lower rheological differences. In conclusion, the observations made above indicate, that the particle surface affects not only the adhesiveness with the polymer, but also the polymeric network structure based on the adsorption mechanism of polymers at the functionalized surface. Here, gluten seems to be particularly sensitive regarding these modifications and simultaneously, in some modifications, special.

## 4. Conclusion

The above shown examples of protein- and carbohydrate-based polymer matrices with particles bearing different surface functionalizations illustrate the major impact of the particle surface on the rheological properties of particle-polymer-based food systems. The small- and large-scale deformation behavior are significantly affected. Interestingly, the achieved results of both matrix types are in accordance (except for mercapto-functionalized GBs in gluten matrices) with the strain depending behavior of filled rubber systems. Regardless of the exact character of the polymeric matrix, the following observations of filled rubber systems can be transferred to food-based particle-polymer systems:

Particles with poor polymer adhesiveness show a higher complex modulus due to the strong particle network at low strain, but a more pronounced and earlier decrease of modulus at higher strain. Whereas, particles with a high adhesiveness to polymers show a lower complex modulus at low strain due to the inhibition of particle network formation [3], but a higher modulus under strain [34,49,50]. This behavior is confirmed for the gluten as well as for the HPC-PVP matrices by the high  $A_f$  and the fast transition in the stress-growth curve from pre- to yield region for surface functionalization with low adhesiveness. For these rheological properties, mainly three mechanisms are responsible [51].

1. Payne effect based on particle-particle interactions. In general, breakdown and rearrangement of particle agglomerates cause non-linear behavior. A high degree of particle network (surface functionalization with low adhesiveness) causes a high modulus at low strain. However, the dissipation of energy by breaking the particle network results in a pronounced decrease of modulus under high strain. For the achieved results, this effect becomes visible in the highest network strength  $A_f$  and the lowest shear stress under high strain for a low adhesive surface functionalization for gluten (cyano) and HPC-PVP (propyl).
2. Payne effect based on particle-polymer interactions ("trapped entanglements"). The adsorption of polymers on the particle surface can lead to trapped entanglements with dangling tails. Under high strain, debonding of trapped entanglements occurs and results in non-linear behavior. Here, the dissipation is based on the disentanglement, which results in a decrease of modulus and lower stiffness [45,52]. In this study, surface functionalization with a high adhesiveness to the polymer matrix show the lowest shear stress under high strain due to the dissipation of energy by disentanglement.
3. Modified polymer network (polymer-polymer interactions in the matrix phase). The adhesiveness between particle and polymer can lead to the formation of so-called "bound rubber" [53] which affects the local polymeric structure [29,51]. Due to the adsorption of polymers at the particle surface, a shift from polymer-polymer interactions to a higher number of interface interactions between particle-polymer occurs, resulting in the formation of a rigid interface around the particle for the surfaces with a high polymer adhesiveness [23]. This effect becomes visible in the long relaxation half-time for surfaces with a specific and strong adsorption of the polymer. The protein-based matrix is chosen and visualized in Fig. 4 to sum up the effect of particle surface functionality on the network structure. For surface functionalization of low adhesiveness (cyano) with polymers (a), two separate networks are formed: A particle- and a polymer-based one. The intermediate strong hydrophobic



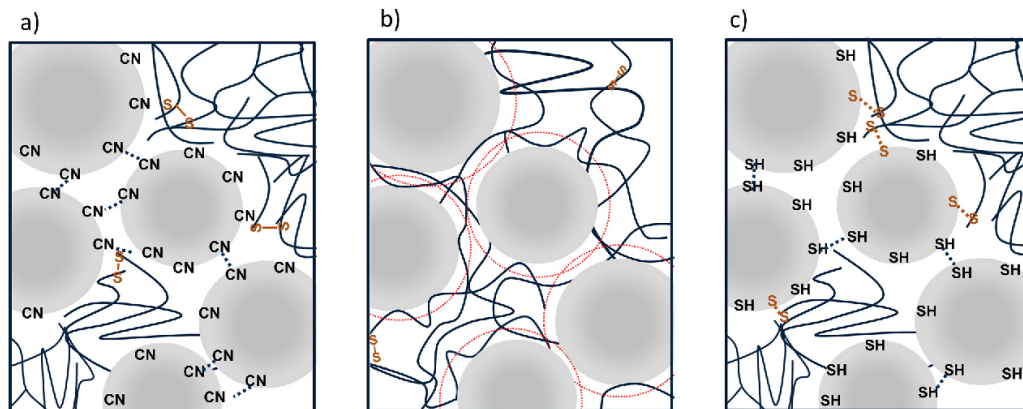


Fig. 4. Schematic illustrations of the network properties for gluten proteins, depending on particle surface functionality. For a surface functionalization of low adhesiveness (cyano) in a); a surface functionalization of adhesive character (propyl, amino or MBS) in b) and a polymer chain terminating surface functionalization (mercapto) in c).

character [17] and the dipole moment of nitrile groups [54] promote the formation of a weak particle network. However, the protein adsorption is inhibited by particle surface functionalization [16], resulting in the formation of a separate polymeric network. In contrast, surface functionalization of adhesiveness character (propyl, amino, MBS) with polymers cause a polymer adsorption at the particle surface and the formation of a combined particle-polymer network (b). The adsorption of polymers results in the formation of trapped entanglements and a lower number of particle-particle interactions [45,55]. Consequently, the polymer mobility is restricted at low strain [3], whereas a debonding mechanism takes place under high strain [45]. Regarding network types a) and b), gluten proteins behave like a typical filled rubber system. In contrast, gluten proteins in combination with mercapto-functionalized GBs (c) demonstrate the influence of the adsorption mechanism on network formation and rheological behavior. Regarding the rheological results in combination with the molecular structure of the protein, the function of mercapto-functionalized GBs as polymeric chain terminator appears plausible. Consequently, a network with shorter polymer chains and a high number of particle interactions is created.

In summary, the presented results illustrate the ability of particle surface functionality or rather the particle-polymer interface to alter the rheology of particle-polymer-based food systems for two common food matrixes (protein- and carbohydrate-based). The combination of defined particle-polymer interfaces with well-analyzed characteristics and comprehensive rheological analysis enabled an assessment of the impact of particle surface functionality on the mechanical properties of food-based matrixes for the first time. Especially for designed food systems, which aim at a target supply of certain components or a defined texture/rheology, the control of surface functionality is essential to reach these specific requirements.

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#### Appendix A. Supplementary data

Raw data frequency sweep (complex module  $G^*$ ), raw data creep-step ( $J(t)$ ) for 5 and 100 Pa, Stress-growth curves. Supplementary data to this article can be found online at doi:<https://doi.org/10.1016/j.ijbimac.2021.09.048>.

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## 3.6 Gluten-starch interface characteristics and wheat dough rheology – insights from hybrid artificial systems



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# Gluten–starch interface characteristics and wheat dough rheology—Insights from hybrid artificial systems

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### Abstract

Referring to the total surface existing in wheat dough, gluten–starch interfaces are a major component. However, their impact on dough rheology is largely unclear. Common viewpoints, based on starch surface modifications or reconstitution experiments, failed to show unambiguous relations of interface characteristics and dough rheology. Observing hybrid artificial dough systems with defined particle surface functionalization gives a new perspective. Since surface functionalization standardizes particle–polymer interfaces, the impact on rheology becomes clearly transferable and thus, contributes to a better understanding of gluten–starch interfaces. Based on this perspective, the effect of particle/starch surface functionality is discussed in relation to the rheological properties of natural wheat dough and modified gluten–starch systems. A competitive relation of starch and gluten for intermolecular interactions with the network-forming polymer becomes apparent during network development by adsorption phenomena. This gluten–starch adhesiveness delays the beginning of non-linearity under large deformations, thus contributing to a high deformability of dough. Consequently, starch surface functionality affects the mechanical properties, starting from network formation and ending with the thermal fixation of structure.

### KEYWORDS

artificial dough, network formation, particle–polymer interface, small-/large-scale deformation

## 1 | INTRODUCTION

Much research has been devoted to the networks of wheat dough, the mechanisms of network building, and their resulting functional properties (Brandner et al., 2019). Regarding the viscoelastic dough characteristics, the assumption that starch is a ‘network active’ particle is gaining more attention. Beside starch particles, wheat dough contains several other types of ‘network active’ particles. They originate mainly from cell wall components

(Autio, 2006) and are not considered any further, due to the immense water absorbency (Tufail et al., 2019) which significantly alters their rheological properties (Miš et al., 2020). Taking a closer look at the composition of starch surface, an active participation in the network formation and, consequently, the rheological properties, becomes obvious. Starch particles offer several functional groups at their surface. Mainly, they originate from surface-located lipids (Finnie et al., 2010) or proteins (Baldwin, 2001). This ‘active’ starch surface offers several opportunities

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for interacting with surrounding gluten polymers: Hydrogen bond formation can occur between amino groups of gluten (especially glutamine) and the OH-group of glucose molecules of starch (especially 2. or 3. OH-group) (Bertolini, 2010) or with polar surface lipids like glycolipids (McCann et al., 2009). Based on the observations of Dahle et al. (1975) who observed a diminishing of gluten–starch interactions by the reduction of disulfide bonds, but not by sulfhydryl blocking agents, Wang et al. (2017) concluded that disulfide bonds are involved in the protein–starch interaction. In addition to these chemical interactions, weak physical forces, like non-ionic ones, cause an unspecific adsorption of proteins (Eliasson & Tjerneld, 1990). For example, starch surface-located non-polar lipids can interact via hydrophobic interactions with gluten polymers (McCann et al., 2009). Despite this precise understanding of the molecular interactions at gluten–starch interfaces, the effect of individual interaction types on the rheological behavior of wheat dough remains largely unclear. Regarding the current state of knowledge, only some general effects of gluten–starch interfaces on mechanical dough properties can be summarized. For example, the way in which gluten and starch interacts affects the height of moduli (Petrofsky & Hosene, 1995) and, at higher deformations, the yield strain at which moduli are reduced (Watanabe et al., 2002). These observations make an effect of gluten–starch interface on the network formation during kneading obvious. Yang et al. (2011) also assumed such a relation between gluten–starch interactions and network formation, without giving any further explanations. In addition, Li et al. (2019) observed an influence of starch on network formation and resultant modified mechanical properties due to altered protein–starch interactions. However, their observations cannot be associated unambiguously. They could be due to modified hydrogen bonding, hydrophobic interactions, or disulfide bridges (Li et al., 2019). Analyzing particle–polymer interfaces in natural food systems is challenging due to their high sensitivity, where a modification causes several changes and leads to ambiguous results. In contrast to cereal science, the rheological impact of particle–polymer interface is well understood in polymer/material sciences (Ramier et al., 2007). Using the approach of particle surface functionalization from polymer sciences (like silanization) in combination with a hybrid artificial dough system, offers opportunities for understanding gluten–starch interfaces and their effect on dough rheology. Brandner, Becker, et al. (2021) and Brandner, Kratky, et al. (2021) used different functionalized glass particles to imitate wheat starch and surface functionality. Due to the inert character of glass beads, starch imitation is limited to native starch. Effects occurring from a modified water absorbency, as is the case with damaged starch, for example, cannot be covered by

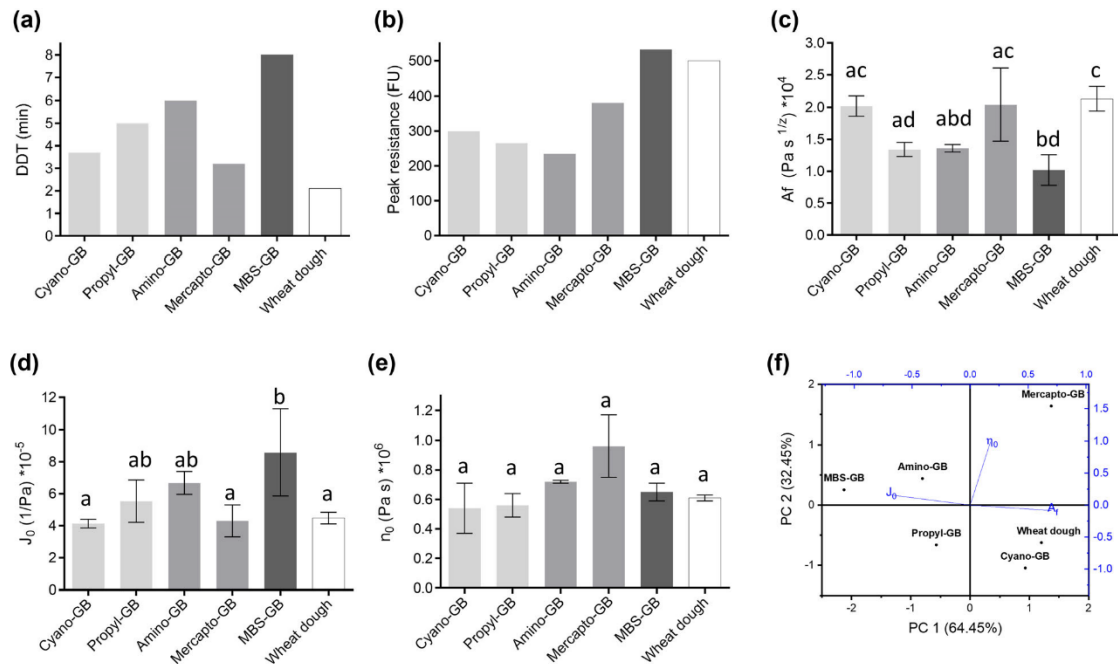
this approach. Surface functionalizations were chosen to imitate naturally occurring chemical groups on particle surfaces, like hydrophobic parts of lipids (alkyl chains) or amino groups (NH<sub>2</sub>) of proteins. The defined particle surface functionalities resulted in gluten adsorption of different nature and strength (Brandner, Kratky, et al., 2021). Based on defined particle–polymer interface characteristics (strength and mechanism of adsorption, compare Table 1), the impact on gluten network formation and resulting mechanical properties could be considered for the first time with regard to a specific particle surface functionality. The adhesiveness, as well as the mechanism of adsorption (functional group of polymer involved in adsorption), showed a considerable impact on network formation, in addition to notable changes to small and large shear deformation rheology (Brandner, Becker, et al., 2021). A comparison of rheological characteristics of wheat dough with those of hybrid artificial systems would be useful for transferring the insights from hybrid artificial systems to natural dough systems and for evaluating the significance of gluten–starch interfaces on mechanical dough properties.

## 2 | WHEAT DOUGH NETWORK FORMATION DEPENDING ON PARTICLE–POLYMER INTERFACES—INSIGHTS FROM HYBRID ARTIFICIAL SYSTEMS

Wheat dough formation depends on the quality and quantity of flour components, especially gluten and starch. For evaluating starch quality, particle size/-distribution, or starch damage are often considered with respect to their water-binding capacity. However, the understanding of gluten–starch interactions and their effect on network formation is very limited. The interface between starch particles and gluten polymers is defined by the affinity of functional groups presented at the particle surface to the gluten polymer. Therefore, surface functionalization by coating with defined chemical groups (cyano, propyl, amino, mercapto, and linker) is predestined for analyzing the impact of gluten–starch interface on network formation. The surface functionalizations can be grouped regarding their adhesiveness for gluten (compare Table 1). Weak unspecific adsorptions by ionic or non-ionic forces occur for cyano- or rather propyl-functionalizations. Stronger specific chemical interactions (hydrogen bonds or rather disulfide bonds) occur for amino- or rather mercapto-functionalized surfaces (Brandner, Kratky, et al., 2021). For evaluating network formation of natural/hybrid artificial dough systems, the plot of torque/Farino Units (FU) against mixing time (Farinograph curve) reveals useful

**TABLE 1** Overview of glass beads surface functionalization, the adsorption characteristics of gluten polymers, and the resulting mechanical properties based on particle induction network modifications. Changing of mechanical properties is evaluated by ↑/↓ for a strong impact and ↑/↓ for a weaker impact

Surface functionalization	Adsorption characteristics (Brandner, Kratky, et al., 2021)	Resulting mechanical properties depending on deformation level (Brandner, Becker, et al., 2021)		
		Small-scale	Large-scale	
Cyano-GB	Weak, unspecific (Van der Waals forces, dipole-dipole)	Rigid particle network	$A_f$ ↑; $J_0$ ↓; $\eta_0$ ↓	Unhindered polymer-polymer cross-linking Elasticity ↑; Fracture stress ↑ and strain ↓, relax. Halftime ↓↓
Propyl-GB	Weak, unspecific (hydrophobic interactions, Van der Waals forces)	Particle network	$A_f$ ↑; $J_0$ ↓; $\eta_0$ ↓	Almost unhindered polymer-polymer cross-linking Elasticity ↓; Fracture stress ↑ and strain ↑, relax. Halftime ↓↓
Amino-GB	Intermediate strong, specific (H-bonds)	Non/weak particle network	$A_f$ ↑; $J_0$ ↑; $\eta_0$ ↑	Hindered polymer-polymer cross-linking by particle adsorption Elasticity ↓↓; Fracture stress ↓ and strain ↑, relax. Halftime ↑
Mercapto-GB	Intermediate strong, specific (H-bonds, disulfide bonds)	Rigid particle network	$A_f$ ↑↑; $J_0$ ↓↓; $\eta_0$ ↑↑	Polymer chain terminating effect by particle adsorption Elasticity ↑↑; Fracture stress ↑↑ and strain ↓↓, relax. Halftime ↑
MBS-GB	Strong, highly specific (covalent binding with primary amines)	Non/weak particle network	$A_f$ ↓↓; $J_0$ ↑↑; $\eta_0$ ↑	Hindered polymer-polymer cross-linking by particle adsorption Elasticity ↓; Fracture stress ↓↓ and strain ↑↑, relax. Halftime ↑↑



**FIGURE 1** Comparison of network formation by dough development time (DDT) in (a) and peak resistance in (b) according to Brandner, Becker, et al. (2021), small-scale deformations behavior by network strength  $A_f$  in (c), instantaneous compliance  $J_0$  in (d) and zero shear viscosity  $\eta_0$  in (e) between hybrid artificial systems with different particle surface functionalizations (gluten and functionalized glass beads, ratio 1:2.33) according to Brandner, Becker, et al. (2021) and wheat dough\*; principal component analysis in (f) showing bi-plot (score plot of surface functionalization and loading plot of variables for small-scale deformation behavior). Particle surface functionalizations were grouped regarding their adhesiveness with the gluten polymers into low adhesive surfaces (■), intermediate adhesive surfaces (■) and strong adhesive surfaces (■). \*Wheat dough (□) is produced according to AACC method 54-21.02 using commercial flour type 550 and analyzed according to Brandner, Becker, et al. (2021) and Brandner, Kratky, et al. (2021). Different letters indicate significant differences between means (ANOVA,  $p < 0.05$ ).

information. The progressive network formation becomes visible with increasing torque/FU, until the development of a peak indicates the maximum of cross-linking/network strength. The time, which is necessary to reach this peak (dough development time (DDT)) and the torque/FU value at this point (peak resistance), enable an evaluation of network formation. As can be seen in Figure 1, just the variation of chemical groups at the particle surface induces varying DDT and also shows different peak resistances. For all, except mercapto-functionalization, a low adhesiveness between particle and polymer results in shorter DDT with a higher peak resistance compared to strong adhesive particles. Actually, it would be expected that a low adhesiveness between particles supports the dissipation of energy due to a lower friction between the sliding polymer chains at the particle surface, and consequently, a lower peak resistance should be expected. However, this effect does not seem to be decisive regarding the final peak resistance, since low adhesive surface functionalizations show higher peak resistance than strong adhesive surface functionalizations (Brandner, Kratky, et al., 2021). A further influ-

encing factor of peak resistance could be the water retention capacity (WRC, according to AACC method 56-11 with water as solvent). Among the differently coated particles, amino-functionalized particles exhibit the highest WRC (non-published results) but the lowest peak resistance. Thus, WRC also fails to explain a higher peak resistance for low adhesive particles. Therefore, a competing relation of particle surface and gluten polymer for intermolecular interactions with the gluten polymer seems to be probable regarding DDT and peak resistance in the hybrid artificial systems. In consequence, an unhindered polymer network formation can take place in combination with low adhesive particles, which increase the peak resistance (Brandner, Kratky, et al., 2021). This assumption is confirmed by the equivalent effect of particle surface functionalizations in hybrid artificial systems and network-interfering chemicals on network formation in natural wheat dough. As reported by Baudouin et al. (2020), SH-interfering chemicals cause a reduction of DDT in wheat dough. Here, this effect also becomes visible for mercapto-functionalized surfaces in the hybrid artificial system. Consequently, the



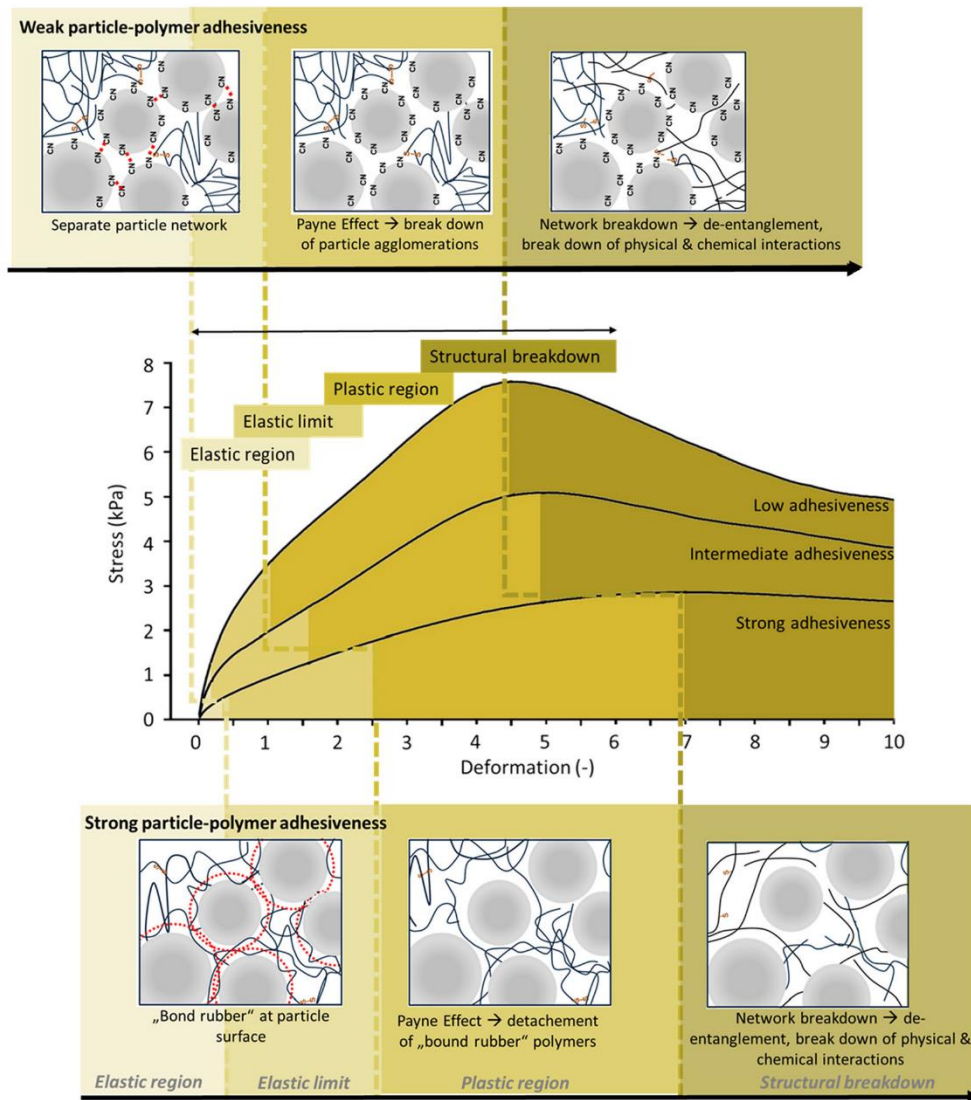
previously made assumption that solely (starch) particle surface functionality affects gluten network formation can be confirmed. The relation of intermolecular interactions between starch–surface to gluten and gluten to gluten is competitive. If the starch surface is highly adhesive for the gluten polymer, it will result in lower FU due to a less cross-linked gluten–gluten network. Thus, the composition of starch surface offers a possibility for controlling the final network strength through the adhesiveness of starch surface, which therefore should be considered for understanding dough development. Based on these modified network developments, the rheological properties of final dough have to be affected too.

### 3 | DOUGH RHEOLOGY AFFECTED BY PARTICLE–POLYMER INTERFACES

#### 3.1 | Small-scale deformation of wheat dough depending on gluten–starch interface

Since different deformation levels affect various structural elements of dough, a differentiation between small- and large-scale deformation behavior is necessary. Applying small deformations affects particle–particle and particle–polymer interactions (Amemiya & Menjivar, 1992). After the breakdown of these particle-based interactions (Payne effect) at larger deformations, polymer network properties become assessable (Amemiya & Menjivar, 1992). For assessing the particle-based effects, a frequency sweep and a creep test were performed within the linear viscoelastic limit and analyzed by the power law and the Burgers model, respectively. The power law fit of  $G^*$  enables the evaluation of network strength ( $A_f$ ), whereas the Burger model evaluates the instantaneous elasticity ( $J_0$ ) and the zero shear viscosity ( $\eta_0$ ). Considering the rheological variables and the results of the PCA (compare Figure 1), some agreements between natural wheat dough and hybrid artificial systems become visible. PC 1 and PC 2 explain 64.45% and 32.45%, respectively, of the total variance. Based on the loading plot, PC 1 contains information from  $J_0$  and  $A_f$ , whereas PC 2 is determined by  $\eta_0$ . Regarding the score plot, wheat dough and hybrid artificial systems with mercapto- and cyano-functionalized particles are situated on the positive side of PC 1 axis. The clustering of wheat dough and cyano-functionalized particles could implement the highest similarity between these two systems. Cyano-functionalized surfaces exhibit a low adhesiveness for gluten (Brandner, Kratky, et al., 2021). The strong polarity of the nitrile group leads to a high affinity for the water phase, as well as for other CN particles. Consequently, cyano-functionalized particles have a high tendency to

form particle networks (Brandner, Becker, et al., 2021). Compared to strong adhesive surface functionalizations (amino and MBS),  $A_f$  of cyano-functionalized particles is higher, whereas  $J_0$  is lower. This indicates the presence of a rigid particle network, which determines the rheological properties at low deformation levels (Brandner, Becker, et al., 2021) (compare Table 1). Since  $A_f$  and  $J_0$  of cyano-functionalized hybrid artificial systems are in good agreement with the rheological variables of natural wheat dough, the presence of a particle network, which determines the mechanical properties at small-scale deformations, is likely. This assumption is in accordance to Meerts et al. (2017), who suggest a gluten-dominating effect of particle interactions at small deformations for wheat dough. Taking into account the  $\eta_0$  of the hybrid artificial systems, the hypothesis of gluten-dominating particle interactions becomes more concrete.  $\eta_0$  corresponds to the deformability of the sample under the applied stress at the steady state flow: The higher  $\eta_0$  the lower the deformability (Van Bockstaele et al., 2011). Low adhesive surface functionalizations (cyano, propyl) show low  $\eta_0$ , whereas strong adhesive surface functionalizations result in high  $\eta_0$  (Brandner, Becker, et al., 2021). The strong adsorption of polymers onto particle surfaces can result in a rigid polymer layer with modified segmental dynamics (reduced mobility) of the polymeric chains. This becomes visible by the increase of  $\eta_0$  (Brandner, Becker, et al., 2021; Jouault et al., 2012). Since  $\eta_0$  of wheat dough corresponds to  $\eta_0$  of strong adhesive surface functionalizations in hybrid artificial systems, there is evidence that starch granules interact with the gluten polymers. Consequently, the comparison of rheological variables between hybrid artificial systems and wheat dough at small-scale deformations demonstrate the following: Stiffness and elasticity of dough are determined by starch–starch interactions, whereas deformability ( $\eta_0$ ) is determined by the adhesiveness towards the gluten matrix. Further interesting effects on dough rheology can be determined by comparing the effects of starch or flour modification, e.g., defatting, to the impact of the corresponding surface functionalization in the hybrid artificial system. Both fatty acids of flour and starch surface lipids consist of alkyl chains. Therefore, a surface functionalization with propyl groups is suitable to imitate starch surface lipids (Brandner, Kratky, et al., 2021). As stated by Melis and Delcour (2020), the mediation of interactions between starch and gluten by lipids is still under debate. Several mechanisms like the linkage through a lecithin layer (Hess & Mahl, 1954) or by starch surface-associated galactolipids (Pomeranz, 1973) are proposed. In general, the addition of non-polar fats to wheat dough causes a decrease of storage modulus  $G'$  (Watanabe et al., 2002), whereas the removal of free flour lipids (mainly nonpolar) results in an increase of  $G'$  (Katyál et al., 2020). For propyl-functionalized



**FIGURE 2** Stress response of particle filled gluten matrices with different particle surface functionalities at increasing deformation levels (elastic region, elastic limit, plastic region, and structural breakdown). Depending on the adhesiveness between particle surface and gluten matrix, stress increases with varying magnitude and thus deformation levels are achieved at different degrees of deformation (middle part). The divergent stress increase is based on the particle–polymer adhesiveness as illustrated for weak (upper part) and strong (lower part) particle–polymer adsorptions.

particles, the fat-imitating groups are presented at the particle surface. Despite this difference in localization, comparable rheological effects become apparent between hybrid artificial systems with propyl functionalization and wheat dough. Similar to wheat dough, a lower  $G'$  (not shown) as well as a lower network strength  $A_f$  (compare Figure 1) result from the surface functionalization with propyl groups in the hybrid artificial system. Based on corresponding rheological effects between propyl-

functionalized particles and free lipids (non-polar), a comparable effect between starch surface-bound lipids and free lipids would, at least for nonpolar ones, be expected. However, most starch surface-bound lipids are polar (Finnie et al., 2009). Therefore, a further distinction between the rheological effect of polar and non-polar particle coatings, by using surface functionalization that present alkyl chains of polar or rather nonpolar character, would be informative.



### 3.2 | Large-scale deformation of wheat dough depending on particle–polymer interface

Large-scale deformations should correspond to the polymer–polymer interactions. As assumed by Yang et al. (2011) and confirmed by the presented results (compare chapter 2), the particle surface functionality affects the network development. Therefore, at least indirect effects of particle surface functionality on the polymer network should be detectable at large-scale deformations. The assessment of large-scale deformation is based on three different measurements. Each of them applies deformations beyond the linear-viscoelastic limit. The deformability and resistance until structural breakdown evaluates the fracture strain and shear stress in a stress–growth curve test (constant shear rate of  $0.1 \text{ s}^{-1}$  for 400 s.). The structural relaxation during stress load is assessed by flow relaxation halftime (time to halve the maximum stress at maximum deformation) in a two-step flow relaxation test (1. sample deformation to 100% with  $0.02 \text{ s}^{-1}$ , 2. constant deformation for 90 s), whereas the structural relaxation after stress removal is assessed by the elasticity (ratio of minimum compliance during recovery phase to maximum compliance during creep phase) in a creep-recovery test (Brandner, Becker, et al., 2021). Depending on surface functionalization in the hybrid artificial systems, the difference between rheological variables becomes apparent in Figure 3. Thus, also on large-scale deformations, a rheological impact of particle surface functionality can be hypothesized. To characterize the similarity between wheat dough and hybrid artificial systems under large-scale deformation, a PCA was performed. PC 1 and PC 2 explain 63.38% and 27.44%, respectively, of the total variance. Based on the loading plot, PC 1 contains information from fracture strain, fracture stress, and elasticity, whereas PC 2 is determined by flow relaxation halftime. Regarding the score plot, wheat dough and hybrid artificial systems with MBS- and amino-functionalized particles are situated on the negative side of PC 1 axis. Similar rheological properties can only be detected for MBS- and amino-functionalized particles, and respectively, for cyano- and propyl-functionalized particles. Nonetheless, some interesting observations regarding wheat dough can be discussed. Watanabe et al. (2002) analyzed gluten–starch systems with varying starch contents and suggested that the beginning of non-linearity is based on a loss of adhesion between starch particles and gluten polymers. Mohammed et al. (2012) confirm this loss of adhesion between gluten and starch under mechanical stress by cryo-scanning electron microscopy. From material/polymer science, this effect is well known

as Payne Effect (Chen et al., 2014; Ramier et al., 2007). The breakdown of particle–particle interactions or the detachment of particles from polymers causes a reduction of moduli through the dissipation of energy by the facilitated sliding of polymer chains/particles. Based on the adhesiveness of the functionalized particle surface in the hybrid artificial systems, the yield point of gluten matrix significantly shifts. For particle surface functionalization with low adhesiveness (propyl and cyano) for gluten, fracture strain occurs at lower deformations and at higher fracture stress compared to surface functionalizations with stronger adhesion for gluten (Brandner, Becker, et al., 2021). This indicates a kind of control mechanism for structural breakdown under stress through the particle adhesion strength. The fracture stress and strain of natural wheat dough corresponds most to that of strong adhesive surface functionalizations (MBS and amino) in hybrid artificial systems. These surface functionalizations imitate the functionality of proteins by presenting  $\text{NH}_2$  groups or NHS esters, which imitate the functionality of primary amines by forming amide bonds (Brandner, Kratky, et al., 2021). Therefore, an active role of starch surface-located proteins in controlling the debonding from gluten polymer under mechanical stress is suggested. Beside this adhesiveness-controlled debonding mechanism, the homogeneity of particle distribution could also affect the fracture stress by a phenomena called shear banding. Peighambardoust et al. (2006) showed that wheat dough with a heterogeneous structure (starch clusters) exhibits higher fracture stress than dough with a homogenous structure. Since particle surface functionalizations with a low adhesiveness, also have a high tendency for cluster formation, an increase of fracture stress by shear banding is likely. In general, the extensibility of dough, before a structural breakdown occurs, is very important with regard to the processing steps fermentation and baking. If the starch surface would be less adhesive for the gluten polymers, the induced mechanical stress would quickly cause a breakdown of particle agglomerates or a debonding of loosely adsorbed particles. Subsequently, a direct stress transfer to the polymeric matrix would occur faster. In consequence, the entire breakdown of structure would be reached at lower deformation levels. In relation to the processing of wheat dough, a lower gas holding capacity would result. Concerning gas holding, so far, the surface-located lipids and proteins of starch granules were mainly considered as functional parts of the liquid dough phase (Dubreil et al., 2002; Sloan & MacRitchie, 2009). Undoubtable, a stabilizing effect corresponds to the detached amount of starch surface-active components (proteins and lipids) in the liquid lamella surrounding gas bubbles. However, as described by Sloan et al. (2009)

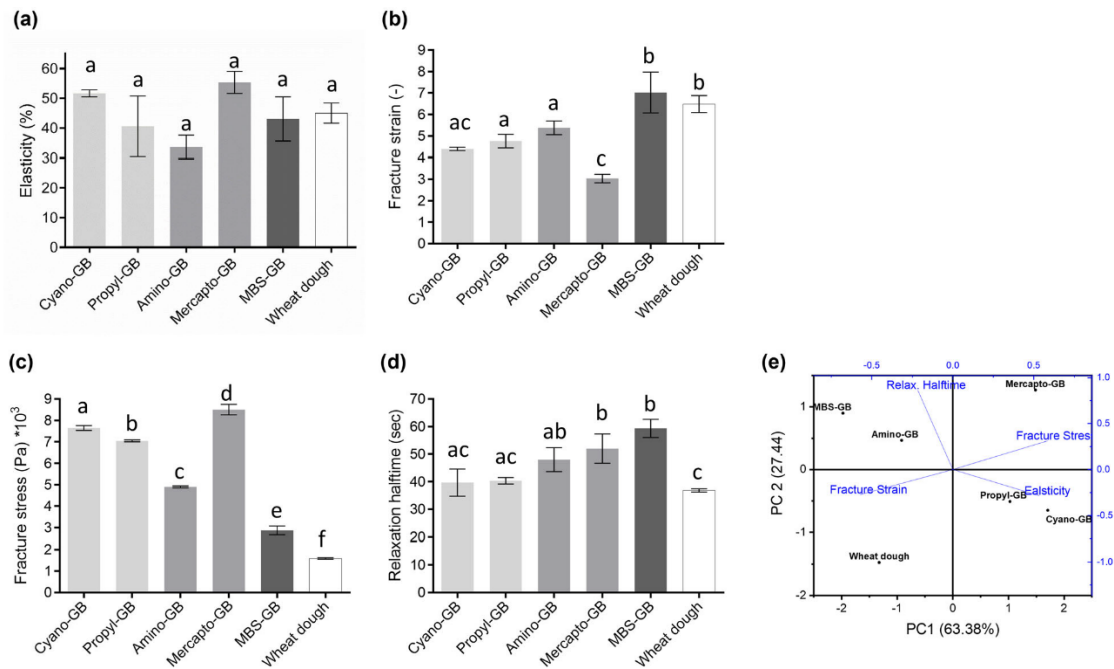
and Sroan and MacRitchie (2009), the stabilizing effect of liquid lamella became active after first failures in gluten–starch matrix occurred. Therefore, they stated the integrity of gluten–starch matrix as the primary stabilizing factor. Based on an entanglement network theory, the ability of dough matrix to maintain its integrity is explained (Sroan et al., 2009): After the breakdown of particle clusters/particle–polymer interactions, a sliding of particles within the entangled polymeric network enables an energy dissipation (compare Figure 2, upper/lower side) and thus, a lower stress transfer to the polymeric matrix. Since the mobility of the particles is limited within the entangled network system, stress will be transferred completely to the polymeric matrix after a certain deformation is exceeded. As already mentioned, the stress level for structural breakdown depends on the particle surface adhesiveness for the gluten polymer (compare Figure 2, middle part). Therefore, the adhesion strength between starch and gluten determines the stress level at which stress will be transferred to the polymeric matrix. Consequently, the proteins and lipids attached to the starch granule surface contribute to the primary stabilization mechanism, since they define the adhesion strength to the gluten polymers and thus the deformation level for transferring stress to the polymeric matrix. Monitoring the structural relaxation indicates an irreversible detachment of starch granules from the gluten polymer during load, at least for the limited time scale of the flow-relaxation measurement. The structural relaxation during a constantly applied stress depends on the adhesion strength of the particle surface to the gluten matrix. For the hybrid artificial systems, low adhesive surface functionalizations show a faster relaxation behavior compared to strong adhesive surface functionalization (see Figure 3). This can be explained by the higher effectiveness of strong adhesive particles in transferring stress to the polymeric matrix. In contrast, low adhesive particles dissipate the induced energy by debonding (Edwards, 1990) and thus, facilitate the structural relaxation (Sternstein & Zhu, 2002). Since the relaxation halftime of wheat dough containing gluten–starch interactions (Wang et al., 2017) corresponds to that of low adhesive surface functionalizations in hybrid artificial systems, an irreversible detachment of starch granules during stress load is concluded for wheat dough. In comparison to the covalent attached and short-chained surface functionalizations of glass beads, the proteins and lipids at a natural granule surface are quite large and absorbed in an undefined manner. This makes a modification of starch surface functionality due to the applied stress by desorption, elongation or breaking of surface-located molecules more likely. Consequently, a modified surface functionality and thus an altered relaxation behavior would occur. The fast structural relaxation of wheat dough

could contribute to higher gas-holding capacity of dough matrix. If the induced stress of expanding gas bubbles can be compensated quickly, the integrity of the matrix at the lamella, where large deformations occur, would be supported. In contrast, slower relaxation processes would contribute to a faster increase of stress level during the continuous expanding process of the bubbles. Surprisingly, the proportion of structural relaxation of wheat dough after the removal of stress (elasticity expressing the degree of back deformability) corresponds to strong adhesive surface functionalizations in the hybrid artificial systems. In contrast, the structural relaxation of wheat dough during stress load (relaxation halftime) corresponds to low adhesive surface functionalizations in the hybrid artificial systems. This ambivalent behavior of wheat dough regarding the relaxation remains questionable. As already explained in the introduction, disulfide interactions could take place at the gluten–starch interface (Dahle et al., 1975). The presence of thiol groups at the particle surface in hybrid artificial systems causes a divergent behavior from wheat dough for the analyzed rheological variables, except  $A_f$  and  $J_0$  under small-scale deformations. In consequence, gluten–starch interactions mediated by disulfide bonds are unlikely or occur at such a small level that no rheological impact becomes apparent. For the divergent behavior of mercapto-functionalized particles an impact on the thiol/disulfide exchange reactions during dough formation is expected. For a closer consideration of this effect, the reader is referred to Brandner, Becker, et al. (2021). In summary, the above made considerations clearly indicate the sensitivity of mechanical dough properties depending on the gluten–starch interface characteristics. The new perspective, given by defined particle surface functionalities, demonstrated, that in particular, the adhesiveness between starch and gluten determines the beginning of non-linearity and the extensibility until structural breakdown (compare Table 1).

#### 4 | CONCLUSION

Combining hybrid artificial systems and well-defined methods for particle surface functionalization from polymer science provides a new perspective on the effect of gluten–starch interface on the rheology of wheat dough. An active role of starch in determining rheological properties of wheat dough has been accepted for quite some time. However, most mechanisms of gluten–starch interfaces affecting dough rheology are still questionable. Based on the new perspective on particle–polymer interactions in dough systems, some of the proposed effects of starch on dough network and functionality could be supported or complemented. The high similarity of wheat dough and





**FIGURE 3** Comparison of large-scale deformations behavior between hybrid artificial systems (gluten and functionalized glass beads, ratio 1:2.33) with different particle surface functionalizations according to Brandner, Becker, et al. (2021) and wheat dough by elasticity (a), fracture strain (b), fracture stress, (c) and relaxation half-time (d), principal component analysis in (e) showing bi-plot (score plot of surface functionalization and loading plot of variables). Particle surface functionalities were grouped regarding their adhesiveness with the gluten polymers into low adhesive surfaces (■), intermediate adhesive surfaces (■) and strong adhesive surfaces (■). \*Wheat dough is produced according to AACC method 54-21.02 using commercial flour type 550 and analyzed according to Brandner, Becker, et al. (2021). Different letters indicate significant differences between means (ANOVA,  $p < 0.05$ ).

cyano-functionalized hybrid artificial systems confirms the importance of rigid particle networks in wheat dough regarding the small-scale deformation response. However, at large-scale deformations, similarity between wheat dough and hybrid artificial systems decreases. Depending on the surface functionalization, only individual measurement values correspond to those of wheat dough. This might indicate that under large-scale deformations a surface functionalization with solely one type of functional group is no longer capable to imitate wheat dough. The ambivalent character of starch surface functionality, based on different functional groups, seems to induce a more complex deformation behavior. Despite this deviation, the importance of starch surface functionality on the mechanical behavior of reinforced gluten matrices becomes visible by a significant shift of fracture strain/stress. For further research, a heterogeneous surface functionalization of glass beads with different functional groups could compensate this divergence and thus, could help to gain further insights on the impact of gluten–starch interfaces even on large-scale deformation behavior.

## AUTHOR CONTRIBUTIONS

**Silvia Brandner:** conceptualization; formal analysis; investigation; methodology; visualization; writing – original draft. **Mario Jekle:** conceptualization; supervision; validation; writing – review & editing. **Thomas Becker:** supervision, validation, writing – review & editing; supervision, validation, writing – review & editing.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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## 4 Discussion, conclusion and outlook

The inclusion of particles significantly affects the rheological properties of viscoelastic matrices. In particular, the particle-polymer interface affects delocalization mechanisms of network structure under mechanical strain. The sensitivity and the limited standardizability of particle reinforced food systems make the analysis of their particle-polymer interfaces still challenging and results in an undefined contribution of this interface on the overall mechanical properties. The usage of hybrid artificial systems with inert particles and defined surface functionalities avoids the issues of sensitivity and limited standardizability and represents a new approach for analyzing the impact of starch surface functionality on the mechanical properties of (starch) particle reinforced food systems, like wheat dough. The commercial availability of silane coupling agents with an enormous variety of functional groups allows the modification of surfaces (glass) for specific applications. For providing a defined particle surface functionality, which complies with constituents and functionality of natural wheat starch, a critical review of starch surface and polymer composition was necessary.

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1. *A literature review supported by a critical examination of wheat dough* ✓  
*should reveal suitable coatings, which imitate wheat starch surface*  
*functionality, as well as suitable polymers, which imitate gluten* (⚡)
- 

According to the first hypothesis, the literature review should reveal suitable coatings for imitating wheat starch surface functionality and the resulting interfaces with the polymeric gluten phase. Starch surface is mainly composed of lipids and proteins (Finnie et al., 2010); (Baldwin, 2001). Their characteristics regarding polarity (polar vs. non-polar) and functional groups (amino, thiol groups) can be imitated with different silanes. The non-polar character of alkyl chains of lipids can be imitated by propyl-functionalized silanes, whereas the polar character of lipids or proteins can be imitated by cyano-functionalized silanes. Amino and sulphur containing parts of proteins can be imitated by amino-functionalized and mercapto-functionalized silanes. To enhance the effects arising from a covalent interactions between functionalized surface and polymer, two different heterobifunctional cross-linkers (MBS and PMPI) were used additionally. Thus, commercial silanes/coatings are available that can represent the surface constituents of wheat starch. Therefore, coating of glass particles with a

particle size distribution comparable to that of wheat starch with these silanes, imitates the functionality, in particular surface functionality, of the starch. The comprehensive review of gluten polymers/wheat doughs regarding their rheological/mechanical behavior, their network architecture, as well as their molecular and thermodynamic properties demonstrated the high complexity of the polymers and those ambivalent character regarding a viscoelastic liquid- or solid-like behavior (Brandner et al., 2019). Therefore, an imitation of gluten matrix by polymers with a higher degree of standardization was aspired. A blend of a modified cellulose (HPC) and a synthetic polymer (PVP) demonstrated comparable rheological properties to wheat dough (Brandner et al., 2018). Beside the higher degree of standardization, the utilization of the hydrocolloid-based gluten imitating matrix enables a general consideration of particle-polymer interfaces in food systems. The chosen hydrocolloids are carbohydrate-based and thus, together with the protein-based gluten polymers, the two most common types of food matrices are represented.

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**2. *Coated glass beads bearing a specific functional group can imitate wheat starch and whose surface functionality in a defined way*** ✓

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For analyzing the impact of particle-polymer interfaces on the mechanical properties of particle reinforced viscoelastic food matrices, the evaluation of defined surface functionalization has to precede. A successful surface functionalization is demonstrated in Brandner et al. (2021a) (c.f. section 3.4) by XPS measurements and a combination of fluorescence-labeling and CLSM-imaging (Brandner et al., 2021a). Specific core levels of the functional groups of the coatings (CH<sub>3</sub>, CH, NH, SH), or rather fluorescent dye layers, which results from interactions between the functional groups of coating and the dye, indicated the successful coating process. Consequently, the hypothesis of imitating wheat starch surface functionality by specific coatings can be confirmed. The analysis of surface modification by silane coating is of qualitative character. Therefore, statements relating to the surface coverage or mono-/multilayer formation are not possible. Nonetheless, presenting functionalized glass particles instead of starch particles cause a tremendous increase of surface standardization, even if some irregularities of coatings may occur, since each silane molecule have exactly the same structure and thus functionality. This enables a fundamental understanding between particle surface functionality and the resulting mechanical properties of the particle-polymer system. A quantitative analysis of



surface coverage by coating and a subsequent polymer adsorption would increase this understanding, since a correlation between mechanical properties and the amount of particle polymer interaction would be possible. However, a comprehensive consideration of surface coverage by polymer adsorption would also imply the assessment of effects arising from steric hindrance in polymer adsorption. In general, a limitation in polymer adsorption based on steric hindrance (due to the large size of polymers) appears more likely compared to a limitation based on the presented functional groups of the coating.

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3. *Particle-polymer interfaces are based on different adsorption mechanisms of varying adhesiveness, depending on particle surface functionality* ✓  
*Adsorption mechanism and adhesiveness is specific for each polymer* +
- 

Specific adsorption/desorption mechanisms of polymers on the functionalized surfaces were demonstrated at the nano- and macroscopic level by XPS or rather contact angle measurements in a model system by using flat SiO<sub>2</sub> surfaces instead of spherical glass beads. Comparing the received surface characteristics of functionalized surface before and after polymer incubation enabled the assessment of adsorption mechanism, whereas the comparison of surface characteristics after rinsing steps gives insights into the desorption mechanism. It could be demonstrated, that polymer adsorptions based on weak unspecific forces (Van der Waals forces, dipole-dipole, and hydrophobic interactions), strong unspecific forces (dipole-dipole), or strong specific forces (hydrogen or disulphide bonds) occur. Thus, the supposed dependency of particle-polymer interface on the particle surface functionality is confirmed. However, an extension of this hypothesis is necessary. Regarding one coating type, different adsorption mechanisms and varying adhesiveness can occur. For example, a cyano-functionalized surface cause a weak unspecific adsorption of gluten polymers, but a strong unspecific adsorption of HPC-PVP (Brandner et al., 2021a). Based on the different molecular structures of gluten and HPC-PVP polymers, different functional groups are involved in the adsorption mechanism on the functionalized surfaces and hence divergent interface characteristics results. Based on these logical and inevitable correlations, the hypothesis was expanded to include the causal connection regarding the influence of polymer characteristics on the particle-polymer interactions. In addition, the dependency on polymer functionality leads to a restriction of hypothesis one. As assumed in hypothesis one and previously confirmed, gluten polymers can be



imitated by other polymers. However, the deviating adsorption mechanism between gluten and gluten imitating polymers, results in a limitation of this approach for analyzing the impact of particle-polymer interfaces on the mechanical properties of wheat dough in a complete artificial system (HPC-PVP matrix and glass beads). Indeed, the imitating polymeric matrix (HPC-PVP) enables a general consideration of particle-polymer interfaces and their impact on the mechanical properties of viscoelastic food matrices.

For evaluating polymer adsorption and adhesiveness, dissolving the polymer in an appropriate solvent is necessary. Regarding the protein-based matrix, the gluten polymer offers a limited solubility. Therefore, only a constituent of the gluten polymer (gliadin), which is soluble in a mild organic solvent (EtOH/H<sub>2</sub>O 60/40 v/v), was used for evaluation. An utilization of the second gluten fraction (glutenin) would require a stronger solvent (dilute sodium dodecyl sulfate) (Wrigley, 2006). To exclude an impact of solvent on the coating and the functionality of the polymer, the experiments were limited to gliadin. The differences in the molecular structure of gliadins (intramolecular disulphide bonds) and glutenins (intermolecular disulphide bonds) (Lindsay & Skerritt, 1999) may result in divergent adsorption mechanisms and adhesiveness for glutenins. In consequence, the incorporation of functionalized glass beads into the gluten-matrix during network formation could imply particle-polymer interfaces, which are not considered within the experimental approach of the model systems (SiO<sub>2</sub> surfaces). Even gliadins correspond to the larger portion of gluten polymers (Schmid et al., 2017); (Koenig et al., 2015), glutenins are important for network formation and mechanical properties (Wrigley et al., 2006). Based on the higher molecular weight and their branched structure, glutenins increase the elastic proportion of the gluten network (Veraverbeke & Delcour, 2002). In relation to the interface activity, the main difference between gliadins and glutenins may be related to the ability of intermolecular disulfide bond formation in combination with mercapto-functionalized surfaces. Only glutenins can form intermolecular disulfide bonds (Wieser, 2007). In consequence, an additional adsorption mechanism of glutenins by disulfide bond formation appears possible, whereas gliadins adsorption would be limited to hydrogen bonds/hydrophobic/ionic interactions. Even if the entire interface activity of gluten proteins cannot be represented by the model system, Brandner et al. (2021a) clearly demonstrated the formation of defined interfaces of different characteristics. For the carbohydrate-based

matrix the issue of limited solubility became less importance, since HPC as well as PVP are hydrocolloids and thus, are highly soluble in water.

In general, regarding the transferability of adsorption mechanism and adhesiveness into the particle-polymer systems, different ratios of functionalized surface to polymer amount and to water amount has to be considered. An inevitable contact of functionalized particle surface and polymeric matrix will occur, due to the higher density of the particle-polymer systems compared to the model system. In addition, the limited amount of water (and the input of mechanical energy) will affect the structuring of polymers. Due to this differences, an effect on the accessibility of particle surface and appropriate binding sites of the polymer is expected and therefore, an impact on the amount of particle-polymer interactions. However, the mechanism of adsorption and the resulting adhesiveness between particle and polymer should not be affected, since the nature of surface and polymer is comparable, and thus the approach can be considered as suitable for assessing the general effect of the particle-polymer interactions on the mechanical behavior.

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4. *The characteristics of particle-polymer interface affects network structure* ✓  
*and thus network properties of food-based matrices*
- Heterogeneity of polymer network junction types enhances the effects of* +  
*particle surface functionality*
- 

The understanding of interface characteristics, enables a comprehensive analysis of the impact of particle-polymer interfaces on network formation, as well as resulting network properties. Assessed on the basis of currently available information (literature), the combination of presenting defined and well characterized particle-polymer interfaces and performing comprehensive rheological analysis of these particle-polymer systems, was carried out for the first time. The monitoring of network formation in Brandner et al. (2021a) and the subsequent rheological analysis of the particle-polymer systems in Brandner et al. (2021b) indicated a significant impact of particle surface functionality on the overall network properties. Therefore, hypothesis four can be confirmed. By comparing the effect of particle surface functionality on network formation (development time and network strength) and behavior (variables gained from rheological analyses), a lower variability of the analyzed parameters becomes visible for the carbohydrate-based matrix than for the protein-based matrix. Network formation of HPC-PVP is mainly based on hydrogen bond formation

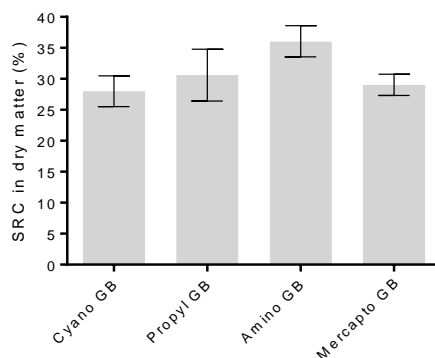
(Kutsenko et al., 2007), whereas the polymerization of gluten polymers implies hydrophobic and polar interactions, hydrogen bonds, covalent interactions, and entanglements (Brandner et al., 2021a). This difference in network junction homogeneity between carbohydrate/protein-based matrix and the lower/higher variability of the analyzed parameters of both matrix types, depending on particle surface functionality, leads to the hypothesis, that network structure and thus, mechanical network properties are more effected by particle surface functionality for heterogeneous network types than homogeneous network types. Therefore, an enhancing effect of a high junction heterogeneity of polymer matrix is assumed. For validating this hypothesis, an analysis of the molecular structure regarding defined network junctions based on vibrational spectroscopies might be beneficial. Assuming this hypothesis, mechanical properties of heterogeneous network could be easy adapted regarding requirements of specific applications, whereas homogenous network types would offer more standardized behavior.

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5. *The impact of particle-polymer interface on the mechanical properties of food matrices becomes transparent, if adhesiveness between particle and polymer as well as adsorption mechanism is understood* ✓
- Particle distribution within the matrix may affect mechanical network properties* +
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The combination of defined particle-polymer interfaces of well characterized properties and a comprehensive rheological analysis gives new insights into the structure function relationship of particle reinforced food systems (publication 4 (Brandner et al., 2021b)), like wheat dough (publication 5 (Brandner et al., 2022)). Depending on particle polymer adhesiveness and the adsorption mechanism different mechanical behaviors were demonstrated. Independent of polymeric matrix, functionalized particles of low adhesives character increased network strength and reduced elasticity at low stress/strain, whereas an increase of stress/strain resulted in a fast decrease of network strength. In contrast, network strength of particle-polymer systems with a higher adhesiveness only decreases at higher stress/strain levels. Based on these observations, the understanding of particle-polymer adhesiveness can be confirmed as an important parameter for analyzing mechanical network properties of reinforced food matrices (first part hypothesis five). Comparing the mechanical effects of coatings of comparable adhesiveness but deviating adsorption mechanisms, like amino- vs

mercapto-functionalized particles in combination with the gluten matrix, or cyano- vs amino-functionalized particles in combination with the HPC-PVP matrix, demonstrated the effect of adsorption mechanism: For example, the highly specific adsorption mechanism of gluten polymers on mercapto-functionalized particles (via disulphide bond formation) resulted in corresponding rheological properties to wheat dough, whose thiol/disulphide exchange reaction were inhibited by chemicals (e.g. N-ethylmaleimide). Moreover, the unspecific strong adsorption of HPC-PVP at cyano-functionalized particles resulted in a corresponding relaxation behavior to less adhesive coatings. These examples demonstrate the impact of adsorption mechanism on the mechanical network properties and thus, verify the second part of hypothesis five.

In general, rheological properties of polymeric networks strongly depend on the amount of water. Since the used coatings, demonstrated significant differences in their hydrophobic/hydrophilic properties (compare results of contact angle measurements in 3.4) an impact on hydration and thus, network properties appears reasonable. Therefore, the hydration capacity of functionalized particles was analyzed by measuring the solvent retention capacity (SRC, according to AACC method 56-11). Figure 7 shows the hydration capacity of particles depending on their surface functionalization.

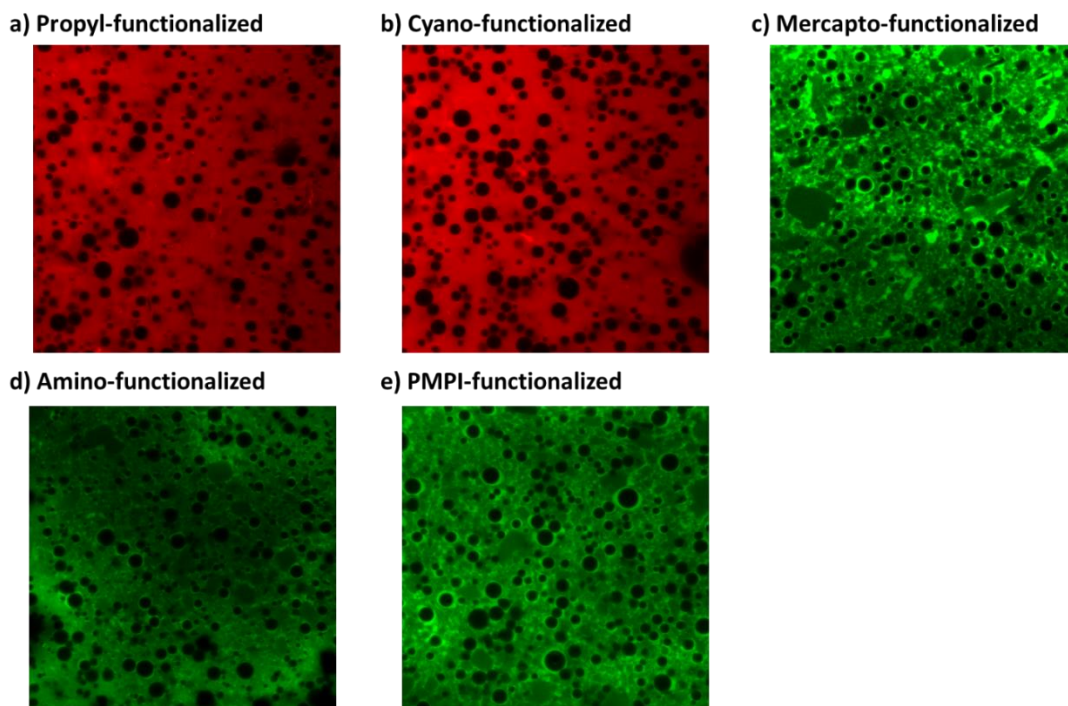


**Figure 7: Impact of surface functionalization of the hydration capacity of glass beads analyzed by the solvent retention capacity (SRC, according to AACC method 56-11).**

Referred to dry matter, the values of SRC are between 28.0 – 36.1 %. The amino-functionalized particles demonstrated the highest hydration. If hydration capacity has a considerable impact, particle-polymer systems with amino-functionalized particles should demonstrate a stiff/strong network. However, network strength during network formation (compare peak resistance in 3.4) and final network strength at low strain

(compare  $A_f$  in 3.5) was lowest, respectively lower as for example, cyano-functionalized particle-polymer systems (with a lower SRC). Therefore, a considerable impact of a varying hydration capacity of differently functionalized particles was excluded.

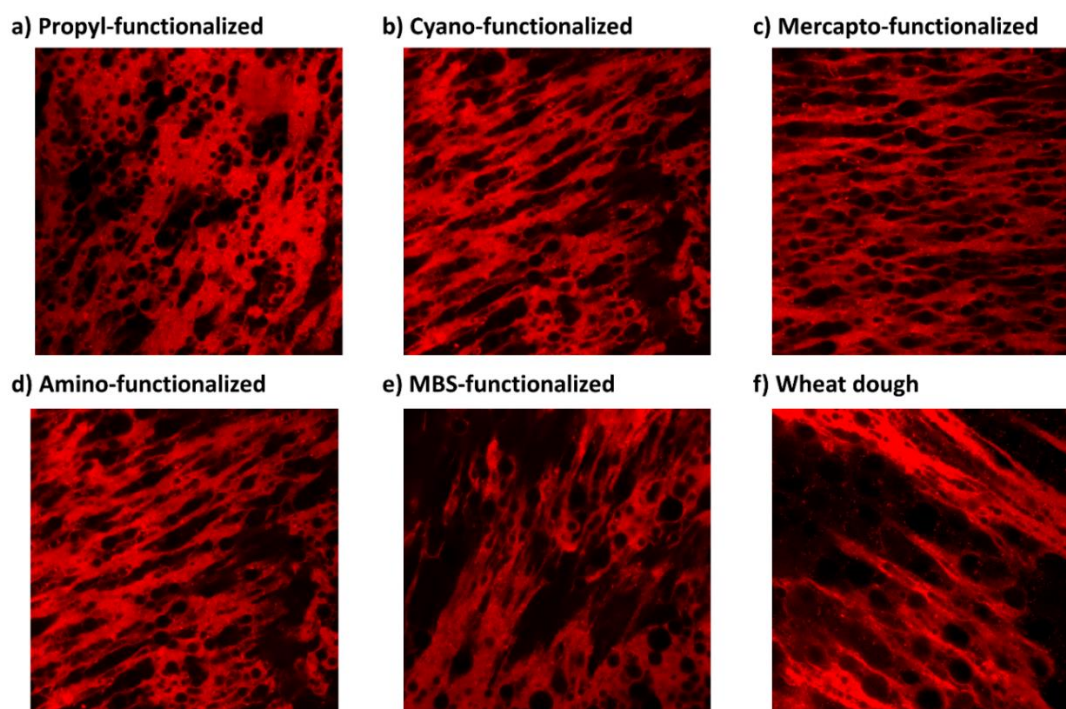
Furthermore, the affinity between particle and polymer may influence the distribution of particles within the polymeric matrix. In general, if a low affinity between two components exists, a separation can occur. In case of reinforced particle-polymer systems, particles with low matrix affinity have a strong tendency for the formation of clusters/aggregations (Fröhlich et al., 2005). For visualizing the particle distribution depending on the surface functionalization within the polymeric matrices (gluten-/HPC-PVP-based), CLSM imaging was used. The matrices or rather the particles were dye-labelled. For all gluten-based particle-polymer systems rhodamine B was used, whereas the HPC-PVP-based systems were labelled according to the particle surface functionalization (mercapto with N-(5-Flouresceinyl)maleimide, amino with flourescein-5-lisothiocyant, propyl/cyano with rhodamine B).



**Figure 8: Embedding of particles within the HPC-PVP matrix depending on the particle surface functionalization.** Particle surfaces were functionalized by propyl-groups (a), cyano-groups (b), mercapto-groups (c), amino-groups (d) or a PMPI-linker (e). For visualization confocal laser scanning microscopy and fluorescent dye-labeling was used.

Figure 8 shows the embedding of particles within the HPC-PVP matrix depending on the surface functionalization. For particle surfaces of low adhesiveness (propyl), as well as surfaces of high adhesiveness with the polymer, no particle clusters/agglomerates are visible. The visual impression of particle embedding is comparable for all surface functionalities. Consequently, the impact of particle distribution appears as negligible for the HPC-PVP-based matrix.

Figure 9 shows the particle embedding of the gluten-based matrix depending on the particle surface functionalization in comparison to wheat dough. Particles with a surface functionalization of intermediate (amino & mercapto) and high (MBS) adhesiveness with the gluten matrix are homogeneously distributed within the matrix (fig. 9 c, d, e), which is comparable to that of wheat dough (fig. 9 f). In contrast, particle surfaces of low adhesiveness with the gluten matrix indicate a cluster/aggregate formation. In particular, the particle-polymer system with propyl-functionalized surfaces (fig. 9 a), shows large areas of protein (red) and particles (black). Interestingly, the embedding of cyano-functionalized particles (fig. 9 b), whose adhesiveness is comparable to propyl-functionalized particles, appears more homogenous.



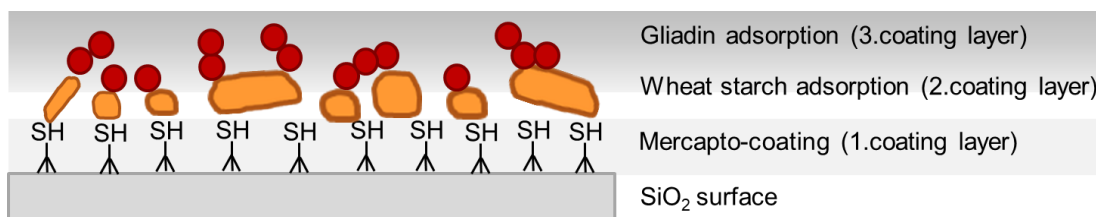
**Figure 9: Embedding of particles within the gluten matrix depending on the particle surface functionalization.** Particle surfaces were functionalized by propyl-groups (a), cyano-groups (b), mercapto-groups (c), amino-groups (d) or a MBS-linker (e) in comparison to wheat dough (f). For visualization confocal laser scanning microscopy and fluorescent dye-labeling was used.



Network formation of polymeric matrix needs water (and mechanical energy). Therefore, the polymer-based environment of particles can be regarded as aqueous. Particle surfaces with a propyl-functionalization are hydrophobic, whereas particles with a cyano-functionalization are hydrophilic. Based on this difference in hydrophobicity, the stronger tendency for cluster/aggregate formation of propyl-functionalized particles seems to be comprehensible. However, the homogenous distribution of propyl-functionalized particles in the hydrophilic, and also aqueous, HPC-PVP matrix makes the previous assumption questionable. In contrast to the hydrophilic HPC-PVP-based matrix, gluten polymers consist to approximately 28 % of hydrophobic side chains, which are not accommodated in a hydrophobic protein core (Delcour & Hosney, 2010). This hydrophobic parts of the gluten protein could promote an accumulation of the propyl-functionalized particles (via hydrophobic interactions) and thus, contribute to the formation of particle-particle and particle-polymer clusters/agglomerates at these hydrophobic parts. In addition, the hydration of the HPC-PVP matrix is strong compared to a gluten-based matrix (Brandner et al., 2018). The lower amount of freely available water could shield the repulsive forces between the hydrophobic particle surface and the hydrophilic matrix and thus, contributes to a homogenous particle distribution. The formation of particle cluster/agglomerates might enhance some mechanical effects, like the Payne effect, by the breakdown of agglomerates. However, since both matrix types (HPC-PVP- and gluten-based) show corresponding rheological properties with respect to the adhesiveness (and adsorption mechanism) between particle and polymer, the cluster/aggregate formation should be less important. In general, the observations made by CLSM-imaging are of qualitative character. For a profound evaluation of particle embedding in dependency of surface functionalization, an objective analysis of particle distribution is necessary. Therefore, a more detailed discussion of particle distribution depending on surface functionalization is not carried out.

The hybrid artificial systems, consisting of glass beads with varying surface functionalization and carbohydrate- (HPC-PVP) or protein-based (gluten) food matrices, demonstrated the tremendous impact of the particle-polymer interface on the overall mechanical properties of particle-polymer based food systems. Understanding particle-polymer interface characteristics (adhesiveness and adsorption mechanism) is of significant importance in the hybrid artificial systems to shed light on rheological properties. Therefore, an interface characterization of natural particle-polymer

systems, like wheat dough, appears as absolutely necessary. The experimental approach of Brandner et al. (2021a) offers direct access to address the interface between starch particles and gluten polymers. Preliminary results prove the applicability and validity of the experimental outline. Figure 10 visualizes the stepwise surface functionalization. Flat SiO<sub>2</sub> surfaces were functionalized with mercapto groups, which were used as binding sites for starch particles (Brandner et al., 2021a). Incubation of the mercapto-functionalized SiO<sub>2</sub> surface in a starch solution and subsequent removal of excess starch in water lead to a closed starch layer on the surface, which was shown to be stable against water and ethanol (*vide infra*). The so formed flat starch surface mimics the surface of a single starch particle and, hence, allows for adsorption experiments with gliadin. After incubation of the starch surface in a gliadin solution, the resulting surface was extensively rinsed with EtOH/H<sub>2</sub>O (60/40 v/v %) to evaluate the starch-gluten adhesiveness.



**Figure 10: Illustration of the stepwise surface functionalization for analyzing starch-gluten adsorption.**

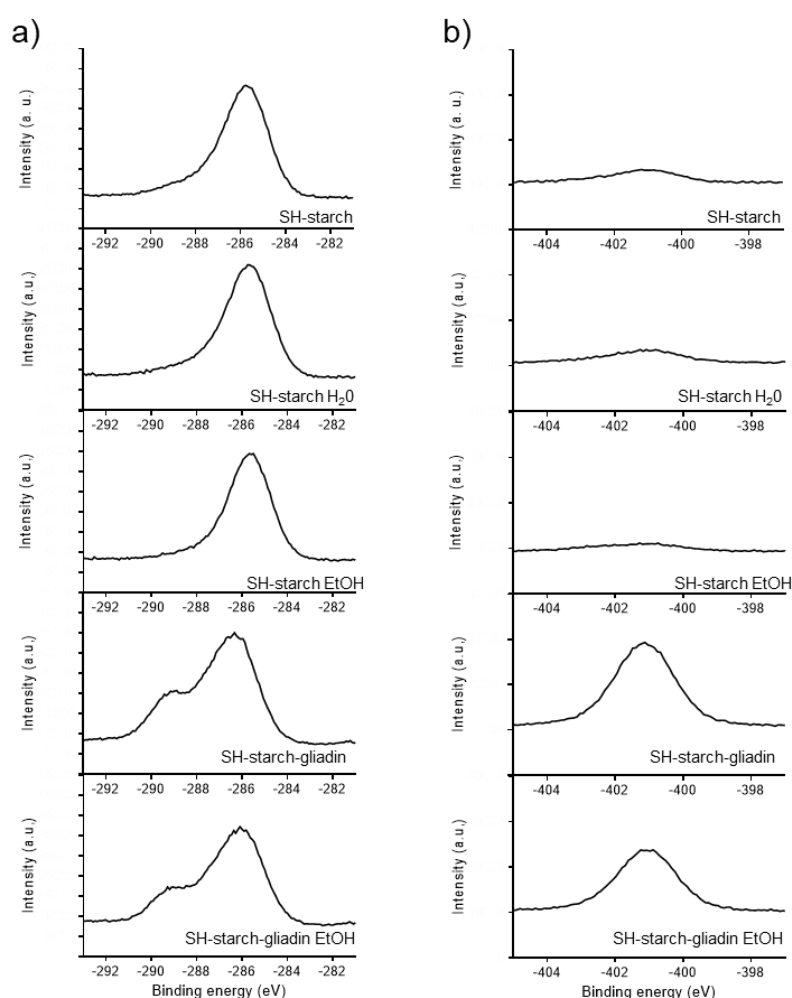
The surface was characterized by contact angle and XPS measurements after formation of the starch layer, after rinsing in water and EtOH/H<sub>2</sub>O (60/40 v/v %), as well as after adsorption of gliadin and subsequent rinsing in EtOH/H<sub>2</sub>O (60/40 v/v %). Table 1 shows the results of the macroscopic evaluation by contact angle measurements.

**Table 1: Macroscopic evaluation of the gliadin adsorption on a starch-functionalized surface based on contact angle measurements.** The error is given as one standard deviation of a single measurement.

	SH-starch	SH-starch rinsed with H <sub>2</sub> O	SH-starch rinsed with EtOH	SH-starch-gliadin incubation	SH-starch-gliadin rinsed with EtOH
Contact angle (°)	67.65 ± 5.42	55.50 ± 1.28	65.92 ± 1.62	55.63 ± 15.73	60.23 ± 1.23

Rinsing of the mercapto-starch functionalized SiO<sub>2</sub> surface causes a decrease of the contact angle and its standard derivation from 67.65 ± 5.42 ° to 55.50 ± 1.28 °. The low standard derivation after rinsing indicates the formation of a homogenous surface

due to the desorption of weakly adsorbed multilayers of starch during rinsing. The incubation of the mercapto-starch SiO<sub>2</sub> surface in gliadin results in a constant contact angle of ~55°. However, a significant increase of the standard deviation (15.73°) occurs. The subsequent rinsing step increases the contact angle (60.23°) and decreases the standard deviation (1.23°). The information given by the contact angles indicate the formation of an inhomogeneous surface after adsorption of gliadin and a homogenization of surface after rinsing. Due to similar contact angles after rinsing the gliadin incubated surface compared to the initial starch surface, deducing the adhesiveness between gliadin and starch is speculative without data revealing the molecular surface composition.



**Figure 11: Nanoscopic evaluation of gliadin adsorption at a SiO<sub>2</sub>-mercapto-starch functionalized surface.** C 1s core level spectra of the mercapto-starch SiO<sub>2</sub> surface in a), after 2x5 min rinsing in H<sub>2</sub>O or rather EtOH/H<sub>2</sub>O, after incubation with gliadin as well as after 2x5 min of rinsing in EtOH/H<sub>2</sub>O. N 1s core level spectra of the mercapto-starch SiO<sub>2</sub> surface in b), after 2x5 min rinsing in H<sub>2</sub>O or rather EtOH/H<sub>2</sub>O, after incubation with gliadin as well as after 2x5 min of rinsing in EtOH/H<sub>2</sub>O.

Therefore, the nanoscopic surface composition was analyzed by XPS. The C 1s (fig. 11 a) and N 1s (fig. 11 b) core level spectra provide useful information regarding the surface modifications. Mercapto-starch functionalized SiO<sub>2</sub> surfaces as are and after rinsing show C 1s peaks of identical binding energies, shapes and intensities. Thus, an irreversible adsorption of starch at the mercapto-functionalized SiO<sub>2</sub> surface is concluded. After gliadin incubation, the C 1s peak position shifts and a shoulder at higher binding energy appears. Also, an N 1s peak becomes detectable which can be attributed to nitrogen-containing amide groups in proteins. Thus, an adsorption of gliadin at the mercapto-starch functionalized SiO<sub>2</sub> surface is confirmed. The subsequent rinsing step did not lead to any relevant changes in the C 1s and N 1s spectra and thus, indicates a stable adsorption of gliadin at the starch surface. Both, contact angle and XPS measurements, indicate a high adhesiveness between gliadin and starch. The experimental approach of Brandner et al. (2021a) has proven to be suitable for an interface characterization in a wider range as exemplarily shown for native starch particles and gluten polymers. This paves the way towards further analyses including also the impact of process conditions, like temperature or pH value, on natural occurring and technically relevant interfaces such as starch-gluten. This leads directly to a deeper understanding of wheat dough behavior.

In conclusion, the presented thesis provides new insights into the effect of particle-polymer interfaces on the mechanical properties of food-based viscoelastic matrices. By using an innovative approach of presenting defined glass bead surfaces for imitating functional groups of natural (starch) particle surfaces, an interface control of particle and polymeric food matrix (protein-/carbohydrate-based) becomes possible without changing size, shape or volume fraction. Based on the displayed adsorption mechanisms of polymers, a new point of view is available for analyzing and understanding the impact of particle surface functionality on network formation and behavior of food matrices.

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## 6 Appendix

### 6.1 Reviewed paper

Brandner, S., Becker, T., Jekle, M.: Gluten-starch interface characteristics and wheat dough rheology – insights from hybrid artificial systems. 87 (2022), 1375-1385.

Brandner, S., Becker, T., Jekle, M.: Instantaneous wheat dough relaxation by alternating current electric fields. Journal of Food Engineering 315 (2021), 110818.

Brandner, S., Becker, T., Jekle, M.: Impact of the particle-polymer interface on small- and large-scale deformation response in protein- and carbohydrate-based food matrices. International Journal of Biological Macromolecules 191 (2021), 51-59.

Brandner, S., Kratky, T., Holtz, K., Becker, T., Jekle, M.: Controlling glass bead surface functionality - Impact on network formation in natural edible polymer systems. Composites Science and Technology 211 (2021), 108864

Brandner, S., Becker, T., Jekle, M.: Classification of starch-gluten networks into a viscoelastic liquid or solid, based on rheological aspects – A review. International Journal of Biological Macromolecules 136 (2019), 1018-1025.

Brandner, S., Becker, T., Jekle, M.: Wheat dough imitating artificial dough system based on hydrocolloids and glass beads. Journal of Food Engineering 223 (2018), 144–151.

### 6.2 Non-reviewed paper

Brandner, S.: Projekt – intelligente Gärsteuerung. Backtechnik – europe 4 (2016)

### 6.3 Oral presentations

Brandner, S., Becker, T., Jekle, M., Ozcelik, M., Först, P.: Simplification and standardization of wheat flour/dough processing by using electric fields. 7<sup>th</sup> Cereals & Europe Spring Meeting, Thessaloniki, Greece, 2022-04-07.

Brandner, S., Jekle, M., Becker, T.: Partikel-Polymer Grenzflächen – Einfluss der Partikeloberfläche auf Netzwerkbildung und –verhalten. Jahrestreffen der ProcessNet-Fachgruppen Grenzflächenbestimmte Systeme und Prozesse, online, 2021-03-11

Brandner, S., Jekle, M., Becker, T.: Teigentspannung in Sekunden – A novel process for immediate dough relaxation. 34. Detmolder Studientage, Arnstein, Germany, 2020-02-17.

Brandner, S., Jekle, M., Becker, T.: Artificial Wheat Dough – Opportunities for a Better Understanding of Structure-Function Relationships of Gluten and Starch Surface Interactions. Cereals & Grains, Denver, USA, 2019-11-04.

Brandner, S., Jekle, M., Becker, T.: Forcierte Teigentspannung – Steuerungs- und Verkürzungspotential im Herstellungsprozess. 8. Frühjahrstagung WIG, Freising, Germany, 2019-03-26.

Brandner, S., Jekle, M., Becker, T.: Interaktion Stärke-Gluten – Einfluss der Oberflächen-Funktionalität auf das Teigverhalten. 8. Frühjahrstagung WIG, Freising, Germany, 2019-03-27.

Brandner, S., Jekle, M., Becker, T.: Optimization of dough resting time by mechanical/electrical stimulation. 32nd EFFoST International Conference, Nantes, France, 2018-11-07.

Jekle, M., Brandner, S., Becker, T.: Alles eine Frage der Spannung – Optimierung von Teigruhezeiten mittels mechanisch-elektrischer Stimulation. 7. Frühjahrstagung WIG, Freising, Germany, 2018-04-17.

Brandner, S., Jekle, M., Becker, T.: Imitation of wheat dough by a synthetic polymer-based medium to investigate gas forming and holding capacity. 15th European Young Cereal Scientists and Technologists Workshop, Bergamo, Italy, 2016-04-29

Brandner, S., Jekle, M., Becker, T.: Lässt sich Weizenteig durch Polymerteigsysteme imitieren? – Möglichkeiten, Grenzen und Vorteile. 5. Frühjahrstagung WIG, Freising, Germany, 2016-04-06.

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