

PROPERTIES OF THERMO-MOLDED GLUTEN/GLYCEROL/SILICA COMPOSITES*

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Abstract Environmentally friendly thermosetting composites were successfully prepared by conventional blending wheat gluten as matrix, glycerol as plasticizer and silica as filler followed by thermo-molding of the mixture at 120°C. The strong interfacial interaction between silica particles and gluten proteins led to an increase in storage modulus and a decrease in loss factor as revealed by dynamic mechanical analysis. The moisture absorption and elongation at break decrease while Young's modulus and tensile strength increase with increasing silica content from 0 to 10 wt%. However, the moisture absorption and mechanical properties show discontinuous changes at a silica content of 6 wt%. The glycerol content also has a marked influence on the moisture absorption and mechanical properties of the composites with a constant gluten-to-silica ratio.

Keywords: Wheat gluten; Particle-reinforced composites; Mechanical properties; Scanning electron microscopy (SEM).

INTRODUCTION

Due to the potential limitation of petroleum resources as well as increasingly stringent environmental concerns, biodegradable materials made from renewable agricultural resources such as carbohydrates, starch and proteins have attracted much attention for sustainable development and environmental conservation. Plant proteins from soy^[1, 2], corn^[3, 4], cottonseed^[5] and wheat^[6–10] show the advantage for usage as films and plastics because of their abundant resources, low cost, good biodegradability and suitable properties.

Industrial wheat gluten contains more than 75% proteins with 40%–50% gliadins and 35%–45% glutenins. Gliadins are single-chain polypeptides with a molecular weight of 20–70 kg/mol, whilst glutenins are multiple-chain polymeric proteins interlinked by intermolecular disulphide and hydrogen bonds having molecular weight in a range from 10² kg/mol to well beyond 10⁵ kg/mol^[11, 12]. Wheat gluten can fully biodegrade after 36 days in aerobic fermentation and within 50 days in farmland soil without releasing toxic products, which makes it an ideal candidate for development of biodegradable materials^[13]. Wheat gluten has been studied as a film former due to its cohesive and elastic properties^[14]. Reactive side groups of wheat proteins susceptible to physical, chemical or enzymic modifications^[9, 15–17] make them possible to obtain a three-dimensional network with appropriate strength and functional properties^[18].

Wheat gluten containing plasticizer is able to form network upon thermosetting^[19] so that it can be processed into degradable bioplastics conveniently through thermal molding^[20–22]. Glycerol as a plasticizer can reduce intermolecular forces and the glass transition so as to increase chain mobility of proteins^[23] and allow melt processing^[24]. Strong shearing during mixing at low temperatures facilitates viscous flow of plasticized gluten due to depolymerization of protein macromolecules through disulfide-thiol interchange reactions^[25, 26]. On the other hand, heat treatment of gluten induces an aggregation reaction by covalent crosslinking through

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disulfide bonding that stabilizes the protein network^[27, 28].

The application of bioplastics is severely limited due to their low stiffness and strength properties as well as their strong tendency to absorb moisture. Native fibers or inorganic particles have been used to reinforce plant proteins so as to prepare green biocomposites with improved mechanical properties and water resistance^[29–41]. Unidirectional basalt fibers have been used to reinforce wheat gluten and to prevent the brittle failure^[38]. A low content of natural or organically modified montmorillonite can significantly reduce the water permeability of glycerol-plasticized wheat gluten films with appropriate improvement of mechanical properties^[36].

Silica (SiO₂) is widely used in polymer composites for improving mechanical properties and reducing cost. Amorphous silica in nature is very weak, whereas it makes very strong biocomposites when combined with proteins and self-organized into highly ordered structures^[42]. The surface silanol groups on silica can interact through both electrostatic interactions and hydrogen bonding with the active groups in protein macromolecules^[43]. Silica/protein composites or gels have been prepared *via in situ* polymerization^[44] or sol-gel process^[45, 46]. In the present paper, silica is incorporated with the wheat gluten containing glycerol as plasticizer to form a composite using the conventional mechanical mixing and the thermo-molding methods for the first time. Influences of silica and glycerol contents on the moisture absorption, glass transition and tensile mechanical properties of the composites are discussed.

EXPERIMENTAL

Materials

Commercial wheat gluten with a protein content $\geq 75\%$ and an ash content $\leq 0.95\%$ was supplied by Shanghai Wangwei Food Co. Ltd. Glycerol purchased from the Shanghai Chemical Co., China was of analytical grade. Silica powder (Ultrasil VN3 GR) with pH = 5.4–7.0, average diameter 20 nm and special surface area 155–195 m² g⁻¹ was supplied by Degussa Co.

Composite Preparation

Wheat gluten, glycerol and silica powder were hand-mixed in a mortar and then mixed on a three-rolling mixer at room temperature. The resultant material was cold-pressed into dumbbell shape with a thickness of 1 mm and a width of 6 mm in a multicavity mold at 10 MPa for 5 min, followed by a thermo-molding at 120°C and 10 MPa for 15 min. Two sets of samples were prepared. In the first set, the ratio of gluten to glycerol was 7:3 in weight while the silica content was controlled at 0 wt%, 2 wt%, 4 wt%, 6 wt%, 8 wt%, and 10 wt%, respectively, with respect to the total mass of the composites. In the second set, the ratio of gluten to silica was 9:1 while the glycerol content was controlled at 20 wt%, 30 wt%, and 40 wt%, respectively, with respect to the total mass of the composites. The crosslinking degree of the thermo-molded gluten was determined to be about 1.05×10^4 mol m⁻³ by using the water swelling method.

Moisture Absorption

The specimens were preconditioned in a desiccator containing allochroic silica gel powders for 72 h at room temperature of 20°C. After drying, the specimens were transferred into desiccators and allowed to reach moisture equilibrium with two different saturated salt solutions of sodium bromide and sodium chloride giving a relative humidity of 52% and 75%, respectively, at room temperature for 72 h. The moisture absorption was evaluated on a dry basis and was reported as the average of three replicates at each relative humidity condition.

Mechanical Testing

Tensile test was performed on a universal testing machine (CMT-4204, Shenzhen SANS Test Machine Co. Ltd., China) with an extension rate of 10 mm min⁻¹ at 75% relative humidity at 20°C. Tensile strength, elongation at break and Young's modulus were evaluated from at least three duplicates for each product.

Scanning Electron Microcopy

The morphology of tensile break surface was observed with a field emission scanning electron microscope (SIRION, FEI Co., Netherlands) at 5 kV.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was performed at 1 Hz at a strain amplitude of 30 μm using the single cantilever clamp mode on a Dynamic Mechanical Thermal Analyzer Q800 (TA Instruments, USA) at a heating rate of 5 K min^{-1} . The specimens were rectangular shaped with a size 20 mm $\times$ 5 mm $\times$ 2 mm. Relative humidity in the sample cell varied with increasing temperature, and it was hard to control at a constant value during the testing. The DMA testing was performed at 65% relative humidity of the surroundings at 20°C.

RESULTS AND DISCUSSION

Moisture Absorption

In biopolymer-based plastics, the effect of moisture absorption on the thermal and mechanical properties is of great importance to the ultimate usability of the material. Moisture absorption has a great impact on the glass transition temperature of wheat gluten proteins^[47]. Figure 1 shows the moisture absorption of the gluten composites with a gluten-to-glycerol ratio of 7:3 and containing various percentage of silica. Moisture absorption strongly depends on the relative humidity, the values at a relative humidity of 75% being almost double of those at a relative humidity of 52%. On the other hand, moisture absorption decreases very slightly with increasing filler content. The influence of filler content is therefore negligible in comparison with that of the relative humidity. Specific interactions of water with the gluten matrix and the glycerol plasticizer are responsible for the substantial moisture uptake. There is a discontinuous change at filler content of 6 wt%, which might be caused by a change in the dispersion of silica particles or the morphological change in the composite. At higher silica contents, the aggregation of silica particles causes a reduction in moisture uptake.

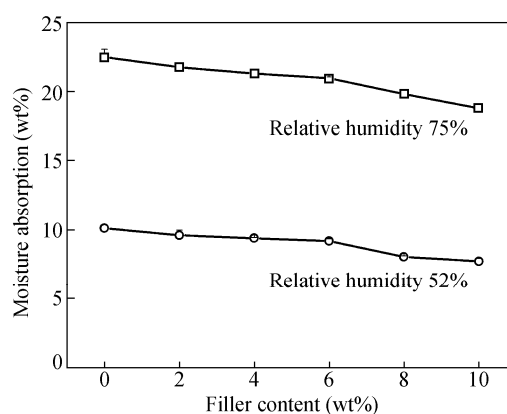


Fig. 1 Influence of silica content on moisture absorption of wheat gluten composite at two different relative humidities

Morphology

Figure 2(a) shows an SEM micrograph with a magnification of 5000 $\times$ taken at the break surface of the 30 wt% glycerol plasticized gluten. The fracture surfaces are rather coarse and fluctuant due to cavitation. Nanoscale pores and microcracks can be observed on the micrograph. Spherulite-like or irregular domains with a size less than 10 μm are present, which might be residual starch granules or might come from poor mixing of gluten proteins with glycerol. Figures 2(b), 2(c) and 2(d) show the SEM micrographs for the composites containing 4 wt%, 6 wt% and 10 wt% silica, respectively. Introduction of the filler particles at 4 wt% and 6 wt% leads to considerable size reduction of the spherulite-like domains. Accordingly, the size and the number of the nanoscale pores are also reduced. At higher filler levels such as 10 wt%, on the other hand, the composites become very inhomogeneous in morphology and there appear large spherulite-like domains with a size of 8–25 μm . Morphological observation is hard to characterize the dispersion of the silica particles with a size much less than the aggregated structure in the gluten phase.

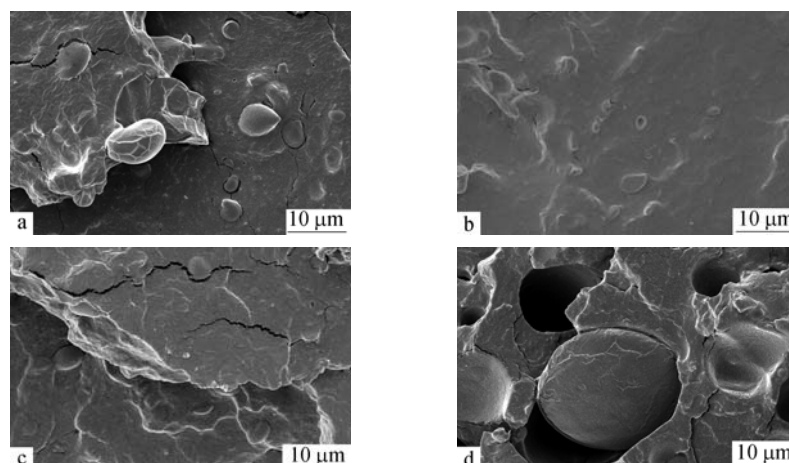


Fig. 2 SEM micrographs taken at the tensile break surface for the 30 wt% glycerol plasticized gluten (a) and for the composites containing silica 4 wt% (b), 6 wt% (c) and 10 wt% (d), respectively

Dynamic Mechanical Analysis

Figures 3(a) and 3(b) show the storage modulus E' and the loss factor $\tan\delta$ as a function of temperature for the 30 wt% glycerol plasticized gluten and for the composites containing different fractions of silica, respectively. With increasing temperature, the samples traverse the glassy region and the transition region ($\tan\delta$ peak and modulus drop) in the temperature range investigated. In the glassy region, E' displays a typical value of 10^9 Pa, and a dramatic decrease in E' is observed at the wide glass-to-rubber transition. The $\tan\delta$ curve of the glycerol plasticized gluten shows a low temperature mechanical loss peaks located at -44.7°C and two high temperature peaks at 53.6°C and 77.3°C , respectively. Gluten proteins exhibit a wide transition region that is commonly observed in heterogeneous biopolymers^[5, 48]. For wheat gluten this may be due to the presence of protein subunits of different molecular weights and in a wide variety of degree of order, as well as a low content of residual nonproteinic molecules. The strong hydrogen bonding intermolecular interactions between gluten proteins and glycerol result in a significant change in molecular motion of proteins. However, the plasticizing effect is different for different wheat proteins so that the system still presents a wide distribution of chain mobility at a scale from the molecular level to 20–30 nm^[49]. The high temperature peaks are associated with the glass transition temperature (T_g) of plasticized gluten proteins, which is much lower than T_g of unplasticized gluten proteins ranging from 124°C to 145°C ^[47]. The low temperature transition is likely associated with T_g of glycerol-rich phase, which is higher than T_g of pure glycerol at -93°C ^[6, 50]. The appearance of the low

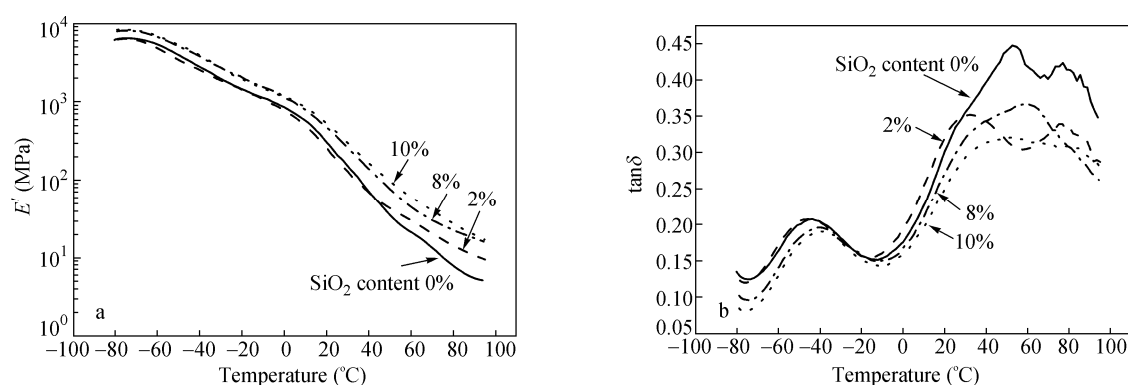


Fig. 3 Temperature dependence of storage modulus E' (a) and loss tangent $\tan\delta$ (b) for the 30 wt% glycerol plasticized gluten and for the gluten composite containing 2 wt%, 8 wt% and 10 wt% silica

temperature peak might indicate the phase separation into a gluten-rich and a glycerol-rich phases, while the two high temperature peaks reveal the different mixing degrees of glycerol with proteins in the gluten-rich phase. The phase separation might occur due to the presence of protein subunits of different molecular weights.

In comparison with the 30 wt% glycerol plasticized gluten, introduction of silica particles to the gluten/silica composite causes a significant increase of E' in the rubbery region. Meanwhile, $\tan\delta$ in this region is lowered considerably. The position of the low temperature transition peak is shifted to high temperatures with increasing silica content. The composite containing 2 wt% silica still exhibits two high temperature $\tan\delta$ peaks at 32°C and 76°C, respectively. However, the composites containing 8 wt% and 10 wt% silica shows only one broad and flat $\tan\delta$ peak with a maximum located at 55°C. In the entire temperature range investigated, E' of the composites containing 8 wt% and 10 wt% silica is higher than that of the plasticized gluten plastics. On the other hand, the $\tan\delta$ curves of the composites containing 8 wt% and 10 wt% silica are lower than that of the plasticized gluten plastics. This might be ascribed to the strong interfacial interaction between the silica particles and the gluten matrix which restricts the molecular motion of protein macromolecules^[34]. The interfacial interaction is facilitated *via* electrostatic attraction and hydrogen bonding of silanol groups on silica surface with the reactive polar amine groups of gluten proteins^[43].

Mechanical Properties

Figure 4 shows stress-strain relationship for the gluten composites with different silica contents. The samples show yielding-like deformation where stress increases rapidly at small strains and much slowly after yielding at strains of *ca.* 15%. This kind of deformation dominates in the temperature region of the glass transition of the amorphous gluten matrix. After yielding, stress increases almost linearly with strain up to break, and the slope of stress against strain representing the strain-hardening behavior increases with increasing silica content.

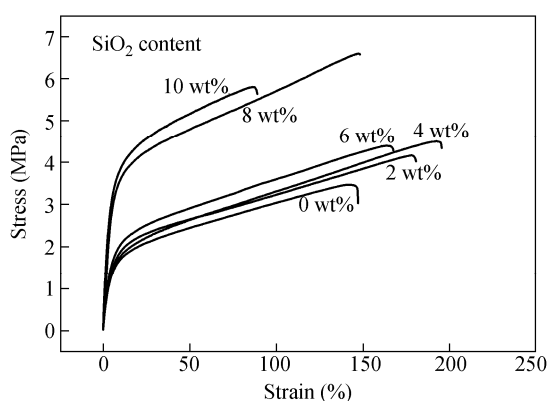


Fig. 4 Stress-strain curves of the gluten composites

Effects of filler content on Young's modulus (E), tensile strength (σ_b), and elongation at break (ϵ_b) are shown in Fig. 5. E and σ_b increase from 21.8 MPa to 55.2 MPa and from 3.5 MPa to 5.9 MPa, respectively, with increasing silica content from 0 wt% to 10 wt%. On the other hand, ϵ_b decreases from 221% to 145%. This indicates that the strong interfacial interaction restricts the deformability of the gluten matrix. There are discontinuous changes of E , σ_b , and ϵ_b at a filler content of 6 wt%, which is much more marked in comparison with the change of moisture uptake behavior in Fig. 1. The discontinuous changes in both mechanical properties and moisture uptake may be related to the morphological changes of the composites, as seen in Fig. 2. E as a function of silica content is fitted to the Guth-Gold model^[51]

$$E = E_0(1 + 2.5\phi + 14.1\phi^2) \quad (1)$$

Here E_0 is the Young's modulus of the plasticized gluten, and ϕ is the volume fraction of silica in the composite.

The theoretical curve of Eq. (1) is plotted in Fig. 5. It is seen that a change in E at silica content below 6 wt% can be well described by Eq. (1) while E deviates from the theoretical prediction at higher silica contents. It is suggested that silica particles with content below 6 wt% are finely dispersed in the matrix, therefore E varies according with the Guth-Gold model. There exists strong hydrogen bonding interaction between silanol groups on silica surface, which causes aggregation of silica particles at content above 6 wt% in the highly inhomogeneous composites. The silica aggregation significantly influences the mechanical behavior and also the moisture uptake. The reinforcing effect at high silica contents might be governed by the percolation mechanism.

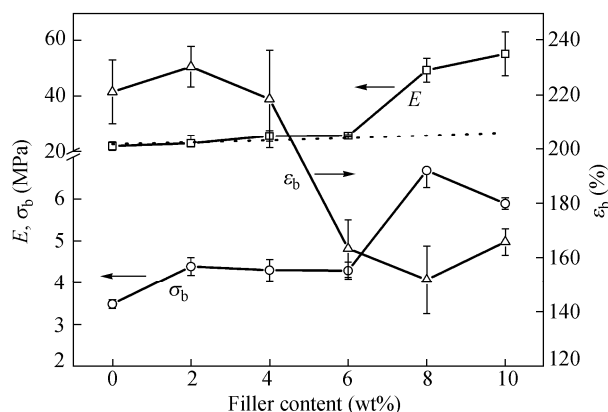


Fig. 5 Effects of silica content on Young's modulus (E), tensile strength (σ_b) and elongation at break (ϵ_b) for the gluten composites

Influence of Glycerol Content

As commonly shown for biopolymers, films obtained from gluten/silica without the addition of any plasticizer are brittle and cannot be handled. In this study a minimum glycerol content of 20 wt% was necessary to overcome the brittleness of the composites. Figures 6 and 7 show the influences of glycerol content on moisture absorption and mechanical properties of the gluten composite with a gluten-to-silica ratio of 9:1. Moisture absorption and ϵ_b increase while E and σ_b decrease as the amount of glycerol increases, which is in agreement with previous findings in plasticized glutes^[9, 10, 52]. Glycerol is very hygroscopic and tends to uptake water molecules into the gluten composites. The variations of mechanical properties against glycerol content agree with the plasticizing effect that causes a decrease in glass transition temperature of gluten^[48, 52] and lowers the cohesiveness of protein chains, resulting in improvements in segmental mobility and the free volume of the network. Consequently, a large amount of plasticizer reduces the strong intra/intermolecular interactions among wheat protein macromolecules and therefore improves the flexibility and the extensibility of the resultant composites^[8, 24, 48, 53–55].

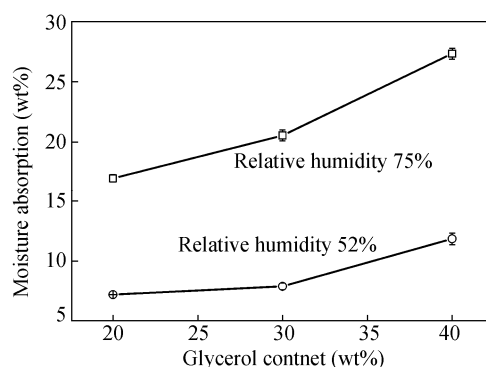


Fig. 6 Influence of glycerol content on moisture absorption of the gluten composite at two different relative humidities

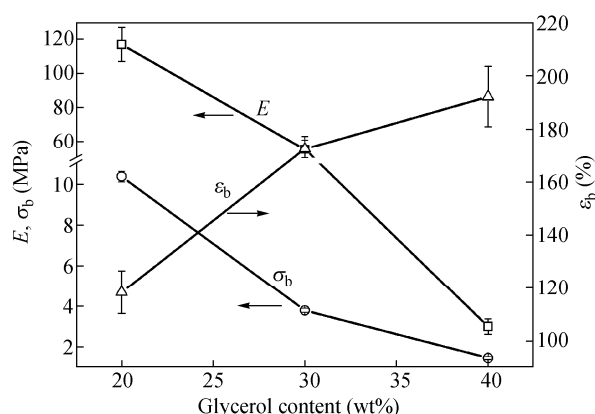


Fig. 7 Influences of glycerol content on Young's modulus (E), tensile strength (σ_b) and elongation at break (ϵ_b) for the gluten composite

CONCLUSIONS

Silica particle reinforced wheat gluten composites containing glycerol plasticizer can be obtained using conventional mixing and thermo-molding methods. The silica filling restrains the molecular motion of gluten protein due to the strong interfacial electrostatic interactions and hydrogen bonding, which increases the storage modulus and lowers the loss tangent in a wide temperature range. The moisture and mechanical properties of the gluten composites can be tailored through adjusting the contents of silica and glycerol.

REFERENCES

- 1 Lodha, P. and Netravali, A.N., *Ind. Crops Prod.*, 2005, 21: 49
- 2 Zhang, J., Mungara, P. and Jane, J., *Polymer*, 2001, 42: 2569
- 3 Gioia, L. and Guilbert, S., *J. Agric. Food Chem.*, 1999, 47: 1254
- 4 Romero-Bastida, C.A., Flores-Huicochea, E., Martin-Polo, M.O., Velazquez, G. and Torres, J.A., *J. Agric. Food Chem.*, 2004, 52: 2230
- 5 Grevellec, J., Marquie, C., Ferry, L., Crespy, A. and Vialettes, V., *Biomacromolecules*, 2001, 2: 1104
- 6 Cherian, G., Gennadios, A., Weller, C. and Chinachoti, P., *Cereal Chem.*, 1995, 72: 1
- 7 Gontard, N., Guilbert, S. and Cuq, J., *J. Food Sci.*, 1992, 57: 190
- 8 Irissin-Mangata, J., Bauduin, G., Boutevin, B. and Gontard, N., *Eur. Polym. J.*, 2001, 37: 1533
- 9 Mangaval, C., Barbot, J., Bervas, E., Linossier, L., Feys, M., Gueguen, J. and Popineau, Y., *J. Cereal Sci.*, 2002, 36: 157
- 10 Sanchez, A.C., Popineau, Y., Mangavel, C., Larre, C. and Gueguen, J., *J. Agric. Food Chem.*, 1998, 46: 4539
- 11 Carceller, J.L. and Aussenac, T., *J. Cereal Sci.*, 2001, 33: 131
- 12 Dobraszczyk, B.J., *J. Non-Newtonian Fluid Mech.*, 2004, 124: 61
- 13 Domenek, S., Feuilloley, P., Gratraud, J., Morel, M.H. and Guilbert, S., *Chemosphere*, 2004, 54: 551
- 14 Payne, P.I. and Corfield, K.G., *Planata*, 1979, 14: 83
- 15 Hernandez-Munoz, P., Kanavouras, A., Ng, P.K.W. and Guavara, R., *J. Agric. Food Chem.*, 2003, 51: 7647
- 16 Hernandez-Munoz, P., Villalobos, R. and Chiralt, A., *Food Hydrocolloids*, 2004, 18: 403
- 17 Rayas, L.M., Hernandez, R.J. and Ng, P.K.W., *J. Food Sci.*, 1997, 62: 160
- 18 Hernandez-Munoz, P., Kanavouras, A., Lagaron, J.M. and Gavara, R., *J. Agric. Food Chem.*, 2005, 53: 8216
- 19 Strecker, T.D., Cavalieri, R.P., Zollars, R.L. and Pomeranz, Y., *J. Food Sci.*, 1995, 60: 532
- 20 Cuq, B., Boutrot, F., Redl, A. and Lullien-Pellerin, V., *J. Agric. Food Chem.*, 2000, 48: 2954
- 21 Mangavel, C., Rossignol, N., Perronnet, A., Barbot, J., Popineau, Y. and Gueguen, J., *Biomacromolecules*, 2004, 5: 1596
- 22 Pommet, M., Redl, A., Guilbert, S. and Morel, M.H., *J. Cereal Sci.*, 2005, 42: 81

- 23 Matveev, Y.I., Grinberg, V.Y. and Tolstoguzov, V.B., *Food Hydrocolloids*, 2000, 14: 425
- 24 Redl, A., Morel, M.H., Bonicel, J., Vergnes, B. and Guilbert, S., *Cereal Chem.*, 1999, 76: 361
- 25 Bloksma, A.H., *Cereal Chem.*, 1975, 52: 170r
- 26 Morel, M.H., Redl, A. and Guilbert, S., *Biomacromolecules*, 2002, 3: 488
- 27 Schofield, J.D., Bottomley, R.C., Timms, M.F. and Booth, M.R., *J. Cereal Sci.*, 1983, 1: 241
- 28 Kokini, J.L., Cocero, A.M., Madeka, H. and de Graaf, E., *Trends Food Sci. Tech.*, 1994, 5: 281
- 29 Lodha, P. and Netravali, A.N., *J. Mater. Sci.*, 2002, 37: 3657
- 30 Huang, J., Zhang, L. and Chen, F., *J. Appl. Polym. Sci.*, 2003, 88: 3284
- 31 Huang, J., Zhang, L. and Chen, F., *J. Appl. Polym. Sci.*, 2003, 88: 3291
- 32 Huang, J., Zhang, L., Wang, X., *J. Appl. Polym. Sci.*, 2003, 89: 1685
- 33 Liu, W., Mohanty, A.K., Askeland, P., Drzal, L.T. and Misra, M., *Polymer*, 2004, 45: 7589
- 34 Lu, Y., Weng, L. and Zhang, L., *Biomacromolecules*, 2004, 5: 1046
- 35 Wu, Q., Sakabe, H. and Isobe, S.P., *Ind. Eng. Chem. Res.*, 2003, 42: 6765
- 36 Olabarrieta, I., Gallstedt, M., Ispizua, I., Sarasua, J.R. and Hedenqvist, M.S., *J. Agric. Food Chem.*, 2006, 54: 1283
- 37 Beg, M.D.H., Pickering, K.L. and Weal, S.J., *Mater. Sci. Eng. A.*, 2005, 412: 7
- 38 Ye, P., Reitz, L., Horan, C. and Parnas, R., *J. Polym. Environ.*, 2006, 14: 1
- 39 Liu, W., Mohanty, A.K., Drzal, L.T. and Misra, M., *Ind. Eng. Chem. Res.*, 2005, 44: 7105
- 40 Otaigbe, J.U. and Adams, D.O., *J. Environ. Polym. Degrad.*, 1997, 5: 199
- 41 Tkaczyk, A.H., Otaigbe, J.U. and Ho, K.L.G., *J. Polym. Environ.*, 2001, 9: 1
- 42 Kuhn-Spearing, L.F., Kessler, H., Chateau, E., Ballarin, R. and Heuer, A.H., *J. Mater. Sci.*, 1996, 31: 6583
- 43 Coradin, T., Durupthy, O. and Livage, J., *Langmuir*, 2002, 18: 2331
- 44 Schuleit, M. and Luisi, P.L., *Biotechn. Bioengin.*, 2001, 72: 249
- 45 Watzke, H.J. and Dieschbourg, C., *Adv. Colloid Interf. Sci.*, 1994, 50: 1
- 46 Coradin, T., Bah, S. and Livage, J., *Colloids Surface B: Biointerfaces*, 2004, 35: 53
- 47 Noel, T.R., Parker, R., Ring, S.R. and Tatham, A.S., *Int. J. Bio. Macromol.*, 1995, 17: 81
- 48 Redl, A., Pouplin, M. and Gontard, N., *J. Agric. Food Chem.*, 1999, 47: 538
- 49 Zhang, X., Burgar, I., Do, M.D. and Loubakos, E., *Biomacromolecules*, 2005, 6: 1661
- 50 Ogale, A.A., Cunningham, P., Dawson, P.L. and Acton, J.C., *J. Food Sci.*, 2000, 65: 672
- 51 Guth, E. and Gold, O., *Phys. Rev.*, 1938, 53: 322
- 52 Gontard, N., Guilbert, S. and Cuq, J., *J. Food Sci.*, 1993, 58: 206
- 53 Pommet, M., Redl, A. and Morel, M.H., *Polymer*, 2003, 44: 115
- 54 Redl, A., Morel, M.H., Bonicel, J., Guilbert, S. and Vergnes, B., *Rheology Acta*, 1999, 38: 311
- 55 Zhang, X., Burgar, I., Loubakos, E. and Beh, H., *Polymer*, 2004, 45: 3305