

PREPARATION AND CHARACTERIZATION OF SOY PROTEIN ISOLATE (SPI)/ MONTMORILLONITE (MMT) BIONANOCOMPOSITES*

Li-xue Xiang, Chang-yu Tang, Jing Cao, Chao-yu Wang, Ke Wang, Qin Zhang and Qiang Fu**

*Department of Polymer Science and Materials, Sichuan University, State Key Laboratory of Polymer
Materials Engineering, Chengdu 610065, China*

Shu-gao Zhao

*Key Laboratory of Rubber-Plastics (Qingdao University of Science and Technology), Ministry of Education,
Qingdao 266042, China*

Abstract The bionanocomposites of soy protein isolate (SPI)/montmorillonite (MMT) have been prepared successfully *via* simple melt mixing, in which MMT was used as nanofiller and glycerol was used as plasticizer. Their structures and properties were characterized with X-ray diffraction (XRD), differential scanning calorimetry (DSC), scanning electron microscopy (SEM), thermogravimetric analysis and tensile testing. XRD, TEM and SEM results indicated that the MMT layers could be easily intercalated by the SPI matrix even by simple melt processing. The exfoliated MMT layers were randomly dispersed in the protein matrix as MMT content was low (less than 5 wt%), an incomplete exfoliation was evident from SEM results, and some primary particles were observed as the MMT content was high (from 5 wt% to 9 wt%). A significant improvement of the mechanical strength and thermal stability of SPI/MMT nanocomposites has been achieved. Our work suggests that simple melt processing is an efficient way to prepare SPI/MMT nanocomposites with exfoliated structure.

Keywords: Soy protein isolate; Biodegradable; Nanocomposites; Exfoliation.

INTRODUCTION

Nowadays, the plastics based on biopolymers have attracted more attention and interest due to the imminent petroleum crisis, increase in environmental pollution from consumed petroleum materials and their environmentally friendly nature^[1]. Biopolymers from various natural botanical resources, such as starch, protein and cellulose have been regarded as alternative materials to petroleum plastics because they are abundant, renewable, inexpensive, ecofriendly and biodegradable^[2].

In all of the protein resources, soy protein has been regarded as a readily renewable biopolymer and potential source not only can be used as biodegradable plastics^[3], textile fibers^[4], biodegradable membranes^[5] and adhesives^[6, 7], but also can be acetylated^[8], transglutaminase-treated^[9] and blended with organic or inorganic nanoparticles. There is one kind of soy protein named soy protein isolate (SPI) with more than 90% protein and 18 diverse amino acids. The ultracentrifugal pattern of SPI generally shows a wide range of molecular weights (8–600 kDa), with four major fractions identified as 2S (20%–22%), 7S (37%), 11S (31%–40%), and 15S (10%–11%)^[10, 11]. It is noticeable that plastics made from soy protein isolate possess good biodegradability but have poor flexibility^[12]. Dry SPI is a rigid material so plasticizers are usually used to overcome the brittleness of soy protein plastics, but which unavoidably leads to a significant decrease in mechanical properties^[13].

SPI is usually blended with organic or inorganic fillers by solution mixing and melting-compression due to

* This work was financially supported by the National Natural Science Foundation of China (Nos. 50533050 and 20574081).

** Corresponding author: Qiang Fu (傅强), E-mail: qiangfu@scu.edu.cn

Received September 17, 2008; Revised December 1, 2008; Accepted February 2, 2009

its poor processability^[14]. SPI was blended with cellulose in NaOH/thiourea aqueous solution^[15], and good membranes have been obtained. Huang and co-workers used nano-clay to reinforce the Phytigel-modified soy protein concentrate, and some improved mechanical properties and thermal stability were observed^[16]. They also prepared the so called SPI green composites by using both flax fiber and modified nano-clay particles^[17].

Solution mixing is a easy way to prepare polymer nanocomposites, but it will cost lots of water, heat energy and time, and can not be used in industry for a large scale production of nanocomposites. While thermomechanical processing technique is simple, low-cost, and effective ways of making thermoplastics^[18]. The purpose of this work is to explore the possibility of preparing SPI/clay nanocomposites *via* melt intercalation. SPI was melting-mixed with montmorillonite (MMT) by two-rollers, in which glycerol was used as plasticizer. The prepared SPI/MMT bionanocomposites were characterized, and the relationship between the structure and mechanical properties was analyzed. Moreover, the thermal stability was also investigated.

EXPERIMENTAL

Materials

Commercial SPI with 88% protein was purchased from Harbin High-Tech (Group) Limited Company. Glycerol of analytical grade was used as the plasticizer for SPI and was obtained from Chengdu Kelong Chemical Reagent Factory. Sodium montmorillonite with a cation exchange capacity (CEC) of 92.6 mmol/100 g was purchased from Southern Clay Company.

Sample Preparation

First, soy protein isolate (SPI) and Na⁺-montmorillonite (MMT) were pre-dried in a vacuum oven at 60°C for about 3 h. SPI was pre-mixed with the MMT in a beaker by manpower, and the MMT contents were 0 wt%, 3 wt%, 5 wt%, 7 wt%, 9 wt%. Then the powders were mixed with glycerol at a weight ratio of 70:30. These mixtures were fed to a two-roller at 120°C. The mixing time was 5 min. Subsequently, the mixtures were compression-molded into dumbbell like pieces at 140°C and 15 MPa for 10 min. The test pieces were coded as S_x, where $x = 0, 3, 5, 7, 9$. They were kept in a desiccator with silica gel as the desiccant before characterization.

Mechanical Property Measurements

The tensile properties of the specimen were measured on a universal testing machine (CMT4104, Shenzhen SANS Test Machine Co. Ltd, Shenzhen, China) with a tensile rate of 5 mm/min according to ISO527-3:1995(E). In all mechanical property measurements, five specimens were measured for each sample, and the results were averaged.

Scanning Electron Microscopy

The sheets were frozen in liquid nitrogen and snapped immediately, and then the fracture surface was sputtered with gold and investigated with an SEM instrument, JSM-5900LV using an acceleration voltage of 20 kV.

X-ray Diffraction

X-ray diffraction (XRD) was performed on a D8 Advance Diffractometer (Bruker, U.S.A.) equipped with a Cu K α radiation source ($\lambda = 0.154$ nm). The diffraction data were collected from $2\theta = 1^\circ$ – 10° in a fixed time mode with a step interval of 0.02° .

Transmission Electron Microscopy (TEM)

The SPI/MMT sample was cut into ultrathin films with the thickness of *ca.* 60 nm by using a microtome at normal temperature, and the ultrathin films were directly placed on the copper grids for TEM observation. The structure and morphology of the nanocomposite were visualized by a transmission electron microscope (TEM) at an accelerating voltage of 200 kV.

Dynamic Mechanical Analysis

Dynamic mechanical properties of the as-prepared SPI/MMT nanocomposites were measured using a dynamic mechanical thermal analyzer (DMTA V, Rheometric Scientific Ltd. UK) in the tensile mode with a strain of

0.02%. The temperature range was between 50°C and 160°C with a heating rate of 5 K/min. The frequency of 1.0 Hz was used. The size (length × width × thickness) of the test samples was 35 mm × 10 mm × 4 mm.

Thermogravimetric Analysis

Thermogravimetric analysis was carried out on a Perkin Elmer thermogravimetric analyzer (TGA-7). The test samples (about 2 mg) were heated under a nitrogen atmosphere from 50°C up to 800°C at a heating rate of 20 K/min.

RESULTS AND DISCUSSION

Dispersion of MMT in SPI Matrix

Figure 1 shows the XRD patterns of SPI/MMT nanocomposites with the MMT contents of 0 wt%, 3 wt%, 5 wt%, 7 wt%, 9 wt% and pure MMT. The basal spacing (d_{001}) of pure clay has been calculated to be 1.2 nm from a diffraction peak at $2\theta = 7.2^\circ$ using Bragg function. The characteristic peak of the clay disappears in the X-ray diffraction patterns of SPI/MMT nanocomposites, which means the formation of exfoliated structure of clay. It confirms that the MMT could be easily intercalated and exfoliated with soy protein isolate by simple melt intercalation.

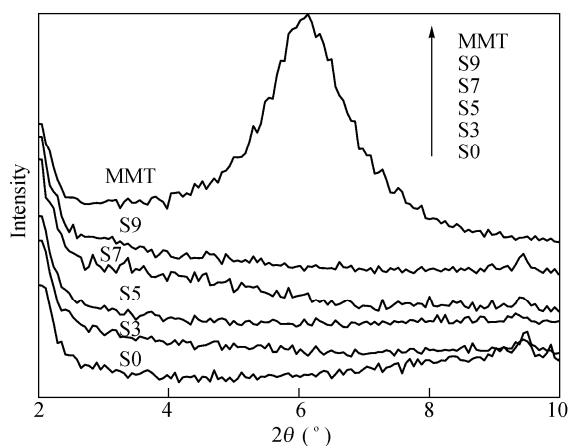


Fig. 1 XRD patterns of SPI/MMT sheets with various MMT contents

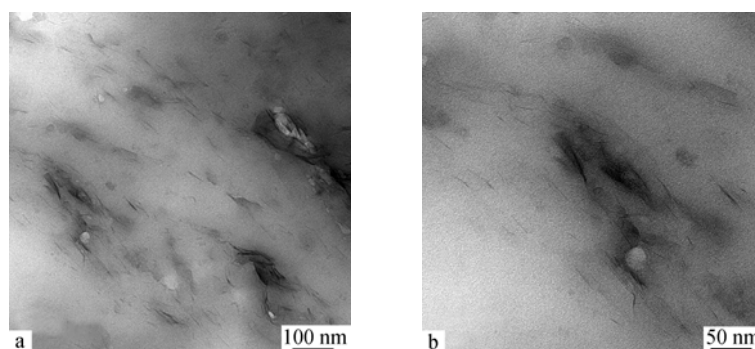


Fig. 2 TEM images of SPI/MMT plastics with 5 wt% MMT with different magnifications

Figure 2 presents the TEM images of SPI/clay nanocomposites with 5 wt% MMT. Seen from the TEM image, the MMT layers are well dispersed in the SPI matrix. The MMT are highly exfoliated into some thin lamellas with a dimension of about 1–2 nm in thickness, indicating an exfoliated structure (Fig. 2a). While some

aggregates with a dimension of about 20–50 nm are also observed (Fig. 2b), indicating an intercalated structure. TEM observation is in good agreement with the results of the XRD patterns. According to the evidence of XRD and TEM, the SPI/MMT nanocomposites with exfoliated or intercalated structure have been successfully prepared *via* a melt-intercalation process. Moreover, the results obviously suggest a strong interfacial interaction between SPI and MMT, including electrostatic interaction and/or hydrogen bonding^[1].

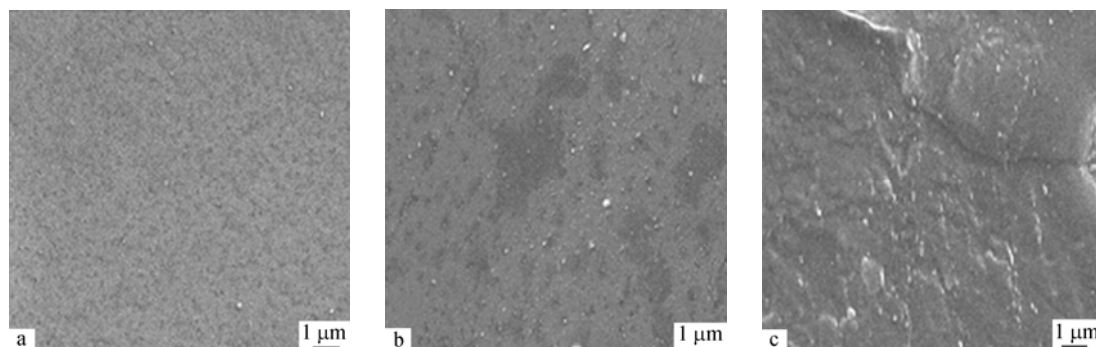


Fig. 3 SEM images of SPI/MMT plastics
a) S0, pure SPI; b) S5, 5 wt% MMT; c) S9, 9 wt% MMT

The SEM images of fractured surfaces of the nanocomposite sheets are shown in Fig. 3. It clearly visualized the sizes and distributions of MMT layers with the MMT content 5 wt% and 9 wt%. Some primary particles of MMT are observed, indicating an aggregation of MMT in SPI matrix at higher contents. Based on the XRD, TEM and SEM results, it can be concluded that the SPI/MMT nanocomposites with an exfoliated structure of clay and well dispersed MMT layers have been successfully prepared through simple melt intercalation method. At higher content of MMT, an incomplete exfoliation is evident from SEM results, and some primary particles are also seen under SEM.

Mechanical Properties and Thermal Stability

Figure 4 shows the effects of MMT contents on the mechanical properties of the nanocomposite sheets. The tensile strength is improved from 24 MPa to 32 MPa, the maximum tensile strength occurs when the MMT content is 5 wt%, and then the value decreases with the increase of MMT content. The tensile modulus changes similarly with the tensile strength while the tensile modulus increases from 874 MPa to 1345 MPa with the MMT content increases from 0 wt% to 5 wt%, and then the value decreases with the increase of MMT content, while the elongation at break gradually decreases with increasing MMT content.

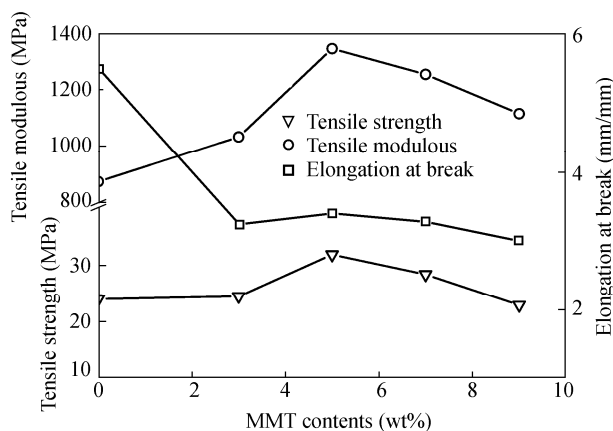


Fig. 4 Effects of MMT contents on tensile strength, tensile modulus and elongation at break

The changes of mechanical properties can be ascribed to the intercalated and exfoliated MMT layers, the well dispersion of MMT in the SPI matrix and the strong interfacial interaction between SPI matrix and MMT. Thus the tensile strength and tensile modulus increase with the increase of MMT content. However at higher content of clay, MMT layers tend to aggregate as clusters which results in a decreased enhancement of tensile properties.

On the other hand, adding MMT also affects the impact strength of the samples. According to Fig. 5, the impact strength of SPI is decreased in the presence of MMT, then it keeps constant with further increase of MMT content. This result also suggests a restrict movement of SPI molecular chains due to the existence of exfoliated and/or intercalated structure.

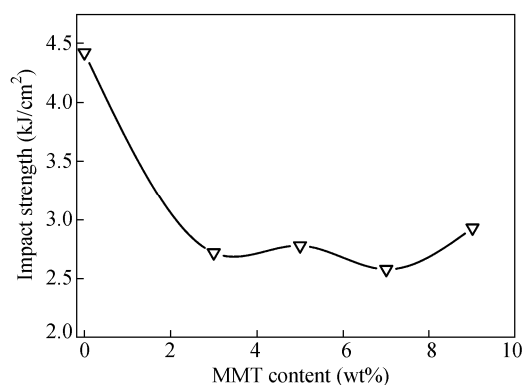


Fig. 5 Impact strength with various contents of MMT

The thermal stability was investigated by TGA, and the weight loss curves and their differential curves are shown in Fig. 6. In the weight loss curves, the water loss temperature range is about 30–120°C. The weight loss in temperature range between 120°C and 250°C is attributed to the glycerol degradation^[3, 9] and from 250°C to 800°C can be explained by protein degradation. From the weight-loss rate curves for the SPI/MMT composites, the peak of the pure SPI is sharper than its composites, so the adding of MMT can slower the degradation rate of SPI matrix obviously. Thus it can be concluded that MMT/SPI composites have a better thermostability than pure SPI.

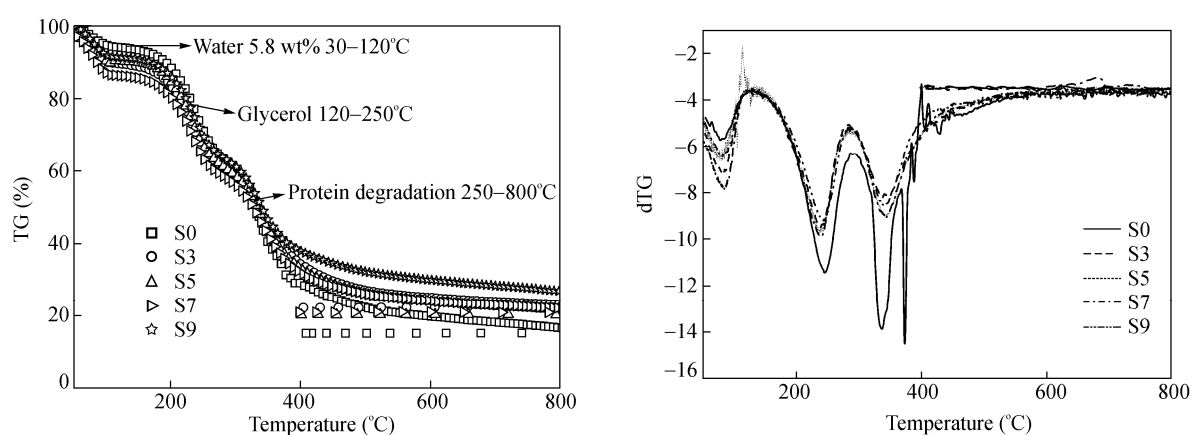


Fig. 6 TGA traces and dTGA curves with various contents of MMT

Figure 7(a) is the storage modulus value of SPI/MMT composites with diversified MMT contents. As seen from the storage modulus curves, the value of the storage modulus increases with the increase of MMT content. The storage modulus decreases with temperature for all of the samples. When the temperature reaches above 100°C, the specimens lose most of their mechanical properties. This can be due to the specimens being just above their glass transition. As seen in Fig. 7(b), the trend of the loss modulus is similar with the storage modulus.

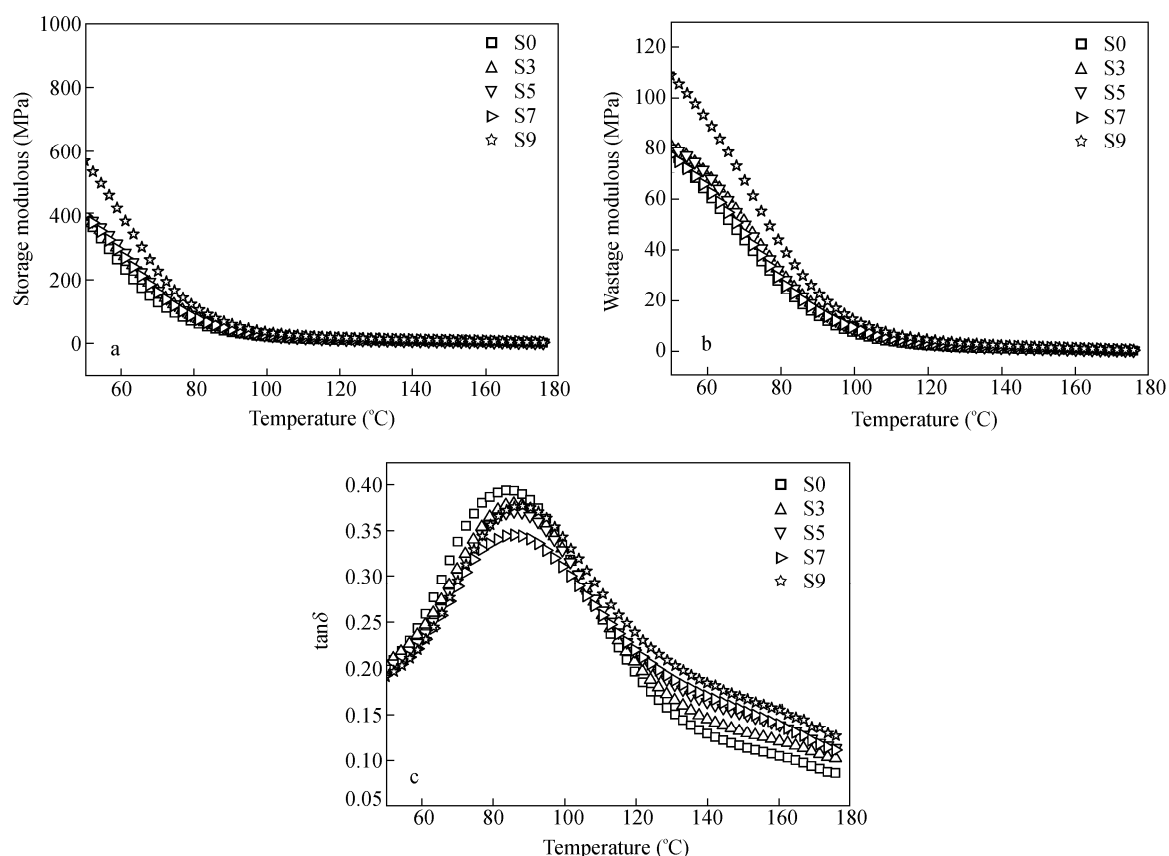


Fig. 7 Dynamic mechanical analysis (DMA) curves of various contents of MMT

a) Storage modulus-temperature curves; b) Loss modulus-temperature curves; c) $\tan\delta$ -temperature curves

As seen in Fig. 7(c) and Table 1, the plots of $\tan\delta$ of SPI/MMT composites with different contents of MMT show the change of glass transition temperature (T_g). T_g is increased from 84.8°C to 88.4°C as the MMT content increased from 0 wt% to 9 wt%. The effect of clay on glass transition temperature of a polymer is some what complicated. Both increased and decreased T_g have been reported^[19, 20].

Table 1. The glass transition temperature (T_g) of SPI/MMT nanocomposite as a function of MMT content

T_g (°C)	Content (%)	$\tan\delta$
84.8	0	0.3958
86.4	3	0.3792
86.5	5	0.3717
87.5	7	0.3445
88.4	9	0.3767

CONCLUSIONS

MMT was blended with SPI to produce reinforced and biodegradable nanocomposites with the simple processing method. When the MMT content was lower than 9 wt%, the MMT was intercalated and exfoliated to some degree seen from the XRD and TEM results. The mechanical properties were enhanced gradually when the MMT content was lower than 5 wt%. The improved mechanical properties were mainly attributed to the well dispersion, restrict movement of SPI molecular chains and the interaction between the MMT and the SPI matrix. In addition, the incorporation of MMT also enhanced the thermal stability.

REFERENCES

- 1 Chen, P. and Zhang, L.N., *Macromol. Biosci.*, 2005, 5: 237
- 2 Mohanty, A.K., Tummala, P., Liu, W., Misra, M., Mulukutla, P. and Drzal, L.T., *J. Polym. Environ.*, 2005, 13: 279
- 3 Zhang, J., Mungara, P. and Jane, J., *Polymer*, 2001, 42: 2569
- 4 Huang, H.C., Hammond, E.G., Reitmeier, C.A. and Myers, D.J., *J. Am. Oil Chem. Soc.*, 1995, 72: 1453
- 5 Brandenburg, A.H., Weller, C.L. and Testin, R.F., *J. Food Sci.*, 1993, 58: 1086
- 6 Lu, Y., Weng, L. and Zhang, L., *Biomacromolecules*, 2004, 5: 1046
- 7 Liu, Y. and Li, K.C., *Macromol. Rapid Commun.*, 2004, 25: 1835
- 8 Foulk, J.A. and Bunn, J.M., *Industrial Crops and Products*, 2001, 14: 11
- 9 Jiang, Y., Tang, C.H., Wen, Q.B., Li, L. and Yang, X.Q., *Innovative Food Science and Emerging Technologies*, 2007, 8(2): 218
- 10 Lodha, P. and Netravali, A.N., *Industrial Crops and Products*, 2005, 21: 49
- 11 Schmidt, V., Giacomelli, C., Soldi, M.S. and Soldi, V., *Macromol. Symp.*, 2005, 229: 127
- 12 Wang, H., Jiang, L. and Fu, L.J., *J. Appl. Polym. Sci.*, 2007, 106: 3716
- 13 Wang, S., Sue, H.J. and Jane, J., *Pure Appl. Chem.*, 1996, 33: 557
- 14 Ai, F.J., Zheng, H., Wei, M. and Huang, J., *J. Appl. Polym. Sci.*, 2007, 105: 1597
- 15 Chen, Y. and Zhang, L.N., *J. Appl. Polym. Sci.*, 2004, 94: 748
- 16 Huang, X.S. and Anil, N.N., *Biomacromolecules*, 2006, 7: 2783
- 17 Huang, X.S. and Anil, N.N., *Compos. Sci. Technol.*, 2007, 67: 2005
- 18 Wu, Q.X. and Zhang, L.N., *J. Appl. Polym. Sci.*, 2001, 82(13): 3373
- 19 Grossiord, N., Miltner, H.E., Loos, J., Meuldijk, J., Mele, B.V. and Koning, C.E., *Chem. Mater.*, 2007, 19: 3787
- 20 Tang, X.Z., Alavi, S. and Herald, T.J., *Carbohydr. Polym.*, 2008, 74: 552