

Solvent-Assisted Extrusion of Polypropylene/Clay Nanocomposites

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Received 15 March 2010; accepted 12 October 2010

DOI 10.1002/app.33605

Published online 18 February 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Polypropylene (PP) nanocomposites were prepared by a melting-compounding process with a montmorillonite (MMT) suspension. In this process, an organically modified MMT was swollen in a polar solvent and blended with molten PP in an extruder; this was followed by solvent removal. The effect of a coswelling agent was also evaluated. The nanocomposites were characterized with X-ray diffraction, transmission electron microscopy, differential scanning calorimetry, and scanning electron microscopy. In addition, the mechanical properties of the

materials were studied. The nanocomposites prepared with the clay suspension presented a remarkable increase in the impact strength with the maintenance of their flexural modulus. The mechanical properties of the nanocomposites were found to be related to the interaction between PP and the clay. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 121: 389–394, 2011

Key words: mechanical properties; nanocomposites; processing; thermoplastics; toughness

INTRODUCTION

Polypropylene (PP) has a large range of applications in the polymer market because of its good mechanical properties and low cost. The use of layered silicates, especially montmorillonite (MMT), to improve the mechanical properties, thermal stability, and barrier properties of PP has attracted academic and industrial interest.^{1–7} The degree of enhancement of the PP/MMT nanocomposite properties is related to the dispersion level and interaction between MMT platelets and the polymer matrix.^{8–10} Melt compounding is the method most commonly used to obtain PP/MMT nanocomposites because of its ease in processing the base resin. However, the achievement of well-dispersed platelets of polar MMT in a low-polar matrix such as PP is a challenge. Several parameters affect nanocomposite formation in a melt-compounding process, such as the clay surface treatment, use of compatibilizing agents, characteristics of the base resin, and compounding conditions.

The hydrophilic clay surface can be modified by an ion-exchange reaction with quaternary alkylammonium salts. This reduces its polarity and produces an orga-

nophilic clay that improves the compatibility between the clay and the nonpolar polymers. Additionally, compatibilizing agents can be used to increase the compatibility between the organically modified montmorillonite (OMMT) and the polymer matrix. PP grafted with a wide variety of polar monomers, such as maleic anhydride, acrylic acid, methyl methacrylate, and diethyl maleate, has been used for this purpose.^{11–14}

The characteristic properties of the base resin, mainly the molecular weight and molecular weight distribution, play an important role in melt compounding because they affect the intercalation of PP chains into clay galleries and the melt viscosity. PP/MMT nanocomposites obtained by twin-screw extrusion have been shown to have the highest degree of dispersion and exfoliation of the clay. However, the processing conditions, including the screw profile and temperature, melt temperature, and addition method of the materials in the extruder, are important aspects in the clay dispersion.^{4,6,15}

Recently, we developed a compounding process wherein an OMMT is swollen in a polar solvent and blended with melting PP in an extruder; this is followed by solvent removal.¹⁶ A remarkable enhancement in the mechanical properties of the nanocomposite was observed with a coswelling agent, mainly in the Izod impact strength. In contrast to what is found most works in the literature, no macromolecular compatibilizer was used in this method. Thus, the aim of this study was to examine

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Contract grant sponsors: Braskem S. A., Capes, Fapergs/Pronex, Finep, Cnpq.

the role of this solvent-assisted process on the mechanical properties of PP/MMT nanocomposites.

EXPERIMENTAL

Materials

The PP homopolymer, with a melt flow index of 3.5 g/10 min (230°C/2.16 kg) and a density of 0.905 g/cm³ (23°C), was supplied by Braskem Triunfo, Brazil S.A. A commercial OMMT, that is, a ditallow dimethyl ammonium ion modified natural MMT (Cloisite 15A), with a cation-exchange capacity of 125 mequiv/100 g and a 44 wt % organic content, was supplied by Southern Clay Products Gonzales, TX. The swelling agent, methyl ethyl ketone (MEK), with a purity of 99%, and the coswelling agent, polypropylene glycol (PPG), with a molecular weight of 1000 g/mol, were supplied by Dow Chemical Co. São Paulo, Brazil.

Clay swelling

The clay was swelled by the dispersion of 50 g of organoclay into 500 mL of MEK and mechanical stirring for 10 min. In samples prepared with the coswelling agent, 10 g of PPG was added to the clay suspension described previously, with 5 min of additional stirring.

Preparation of the nanocomposites

The PP nanocomposites were prepared with a corotating, twin-screw, intermeshing extruder (Haake Rheomex, Waltham, MA PTW 16/25), set up with an optimized screw profile, operating at 170–195°C, 80 rpm, and a feed rate of 10 g/min. Nanocomposites containing 5 wt % organoclay (corresponding to 2.8 wt % inorganic content) were prepared by three different processes. In process 1 (P1), PP pellets were premixed with the organoclay in a tumbling mixer, and this mixture was melt-blended in the extruder at 10 g/min. In process 2 (P2), PP pellets were put into the extruder by the main feeder, and the organoclay, previously swollen in MEK, was pumped into the extruder in the melting zone. The swelling agent, MEK, was removed from the vent port by vacuum. Figure 1 shows a schematic sketch of the solvent-assisted extrusion process. The material obtained was pelletized and dried *in vacuo* at 50°C for 5 h. Process 3 (P3) was performed under the same conditions as P2, but a clay suspension with a coswelling agent was used. The composition of the nanocomposite obtained by P3 was 5.0 wt % organoclay, 1.0 wt % PPG, and 94 wt % PP.

Characterization

The interlayer distance of the organoclay was determined by means of X-ray diffraction (XRD)

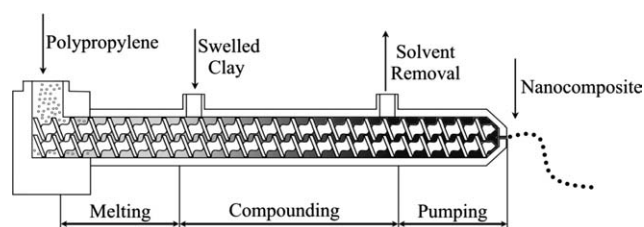


Figure 1 Schematic sketch of the solvent-assisted extrusion process.

with a Siemens Munich, Germany D500 apparatus in the reflection mode and an incident X-ray of Cu K α at a wavelength of 1.54 Å. The morphology of the samples was examined by transmission electron microscopy (TEM). For TEM measurements, ultrathin sections were prepared at –80°C with a Leica Wetzlar, Germany EM UC6 ultramicrotome with a diamond knife. The measurements were carried out on a JEOL Tokyo, Japan JEM-1200 Ex II (80 kV). The crystallization behavior was studied by differential scanning calorimetry with a TA Instrument New Castle, DE DSC 2100, where linear heating and cooling experiments were performed at 10°C/min under a nitrogen atmosphere. The crystallinity (X_c) of the PP matrix in the materials was determined as follows:

$$X_c = \frac{\Delta H_m}{f_p \Delta H_m^0} \times 100 \quad (1)$$

where ΔH_m (J/g) is the enthalpy of melting of the polymer matrix, f_p is the polymer weight fraction in the sample, and ΔH_m^0 is the enthalpy of melting of pure crystalline PP (207.1 J/g).¹⁷ Specimens for mechanical testing were prepared in a Battenfeld Plus 350/75 injection-molding machine according to ASTM Kottlingbrunn, Germany D 4101. Flexural modulus tests were determined in an Instron Norwood, MA 4466 universal testing machine according to ASTM D 790. The Izod impact strength was determined at 23°C according to ASTM D 256 in a Resil Impactor Ceast Pianezza, Italy pendulum-type impact tester. The fracture surfaces of the Izod impact tested specimens were studied with scanning electron microscopy (SEM) in a JEOL JSM 6060 microscope operating at 10 kV.

RESULTS AND DISCUSSION

The XRD patterns of the nanocomposites are compared to that of the pure organoclay in Figure 2. The high-intensity peaks corresponded to the (001) plane reflections of the clay. The interlayer spacing (d_{001}) of OMMT and the PP nanocomposites were determined from the 2 θ position peak with Bragg's law. Pure OMMT had a d_{001} of 3.27 nm before compounding. The P1 nanocomposite exhibited no

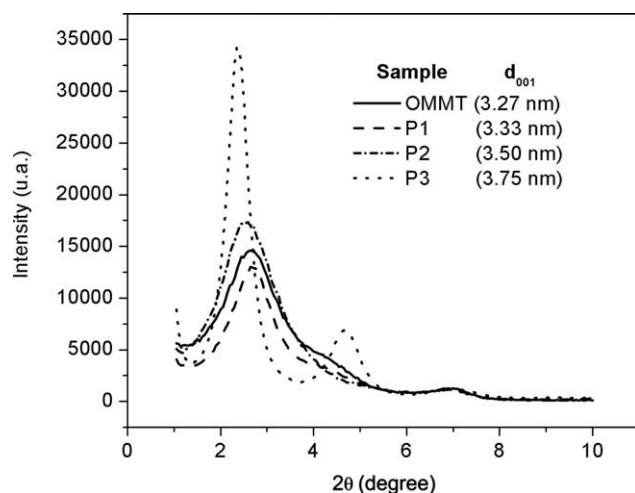


Figure 2 XRD patterns and d_{001} of OMMT and the PP nanocomposites.

significant increase in d_{001} , which varied from 3.27 to 3.33 nm after mixing; this indicated that just a few PP macromolecules were able to intercalate into the clay. The P2 nanocomposite showed a slight shift in the peak toward lower angles; this resulted in a d_{001} of 3.50 nm. It was apparent that the MEK molecules became intercalated into the clay interlayers by the interactions between MEK and the clay surface. Even with a vacuum applied to the vent port, a small amount of residual MEK, around 0.7%, was found in the P2 and P3 nanocomposites.

The use of PPG in sample P3 increased the interlayer distance by 0.48 nm; that indicated that the PPG molecules intercalated into the clay interlayers just as well as the MEK molecules. However, the PPG molecules occupied a higher volume between the clay platelets, probably because of their higher molecular weight compared to MEK. PPG was able to intercalate into the clay galleries because of its high level of polar groups. However, the increase in the interlayer distance of clay was limited by the low molecular weight of PPG. Because only the PPG and MEK molecules intercalated into the clay galleries, the

interlayer distance distribution was low; this resulted in an XRD peak with a high intensity. Perrin-Sarazin et al.¹⁸ found similar results in PP/MMT nanocomposites using low-molecular-weight PP-g-MA maleic anhydride grafted polypropylene.

TEM micrographs of the PP nanocomposites obtained by the different extrusion processes are presented in Figure 3. These micrographs are representative of several images and show a slight difference in the clay dispersion level of the materials. Although tactoids were the dominant morphology in all of the samples, the materials prepared by solvent-assisted extrusion presented some exfoliated layers (see arrows). These materials also presented tactoids that were smaller than did the material obtained by the traditional process, mainly when the coswelling agent was used. This behavior could be related to the swelling capacity of the clay in the solvent. Given that the clay was swollen before it was added to the extrusion and that there were no agglomerates, as shown by Burgentzlé et al.,¹⁹ it was possible to achieve higher dispersion levels. When the coswelling agent was used, this effect was increased, as shown in the TEM images.

Figure 4 presents the mechanical properties of the PP and PP nanocomposites. The increases in the flexural moduli of the P1, P2, and P3 nanocomposites were 32, 16, and 6%, respectively, compared to the that of the pristine PP. The increase in the modulus in the PP/MMT nanocomposites is due to the high modulus and high aspect ratio of the clay.¹⁰ However, the intensity of the increase is influenced by the dispersion level of the clay, the interaction between the clay and the polymer, and the alignment of the silicate layers.⁹ Although the materials prepared by the solvent-assisted extrusion process presented higher clay dispersion levels, they presented a lower modulus increase. This demonstrated that the PP/clay interface was the aspect that seemed to determine the increase in both the impact and flexural properties of the nanocomposites. According to XRD analysis, PPG and MEK

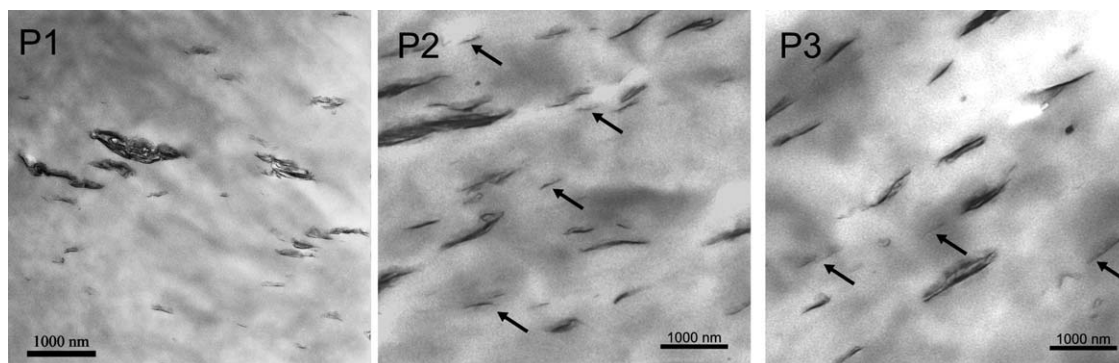


Figure 3 TEM micrographs of the PP nanocomposites obtained by different processes.

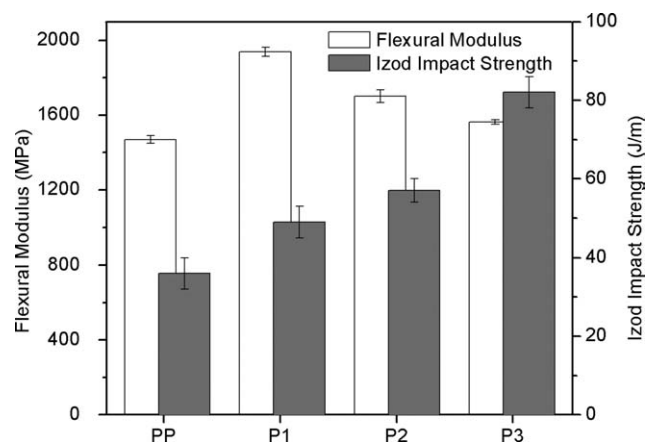


Figure 4 Mechanical properties of PP and the PP nanocomposites.

intercalated into the clay interlayers because of polar interactions of these molecules with the clay surface. In the same manner, these polar molecules probably adhered to the external clay surface, forming a thin film that reduced the interaction between the PP chains and the clay. This decreased the load-transfer efficiency from the matrix to the clay and, consequently, decreased the material modulus. This effect was higher in P3 (d_{001} of 3.75 nm) than in P2 (d_{001} of 3.50 nm).

Although the use of MEK and PPG resulted in a low increase in the flexural modulus, their use resulted in a remarkable increase in the impact strength, mainly when PPG was used. As shown in Figure 4, the increases in the impact strengths of the P1, P2, and P3 nanocomposites were 36, 58, and

127%, respectively, compared to that of the pristine PP. The impact strength is related to the energy-dissipation process during fracture. The most effective dissipative processes in PP are multiple crazing and shear yielding, with a major contribution from the latter.²⁰ However, additional processes take place when a rigid particle is added to the polymeric matrix. According to microvoiding theory,²¹ when the stress applied exceeds the interfacial adhesion strength between the clay and the polymer matrix, debonding at the interface will occur first; this leads to the formation of microvoids. In this case, the deformation restraint of the matrix around the filler is released; this produces extensive elastic deformation and absorbs strain energy. Moreover, the tip of the crack is blunted, and the stress concentration is alleviated. This effect is more apparent with poor interfacial adhesion between the matrix and the reinforcement.

The use of SEM to examine the fractured surface may help in understanding the reinforcement mechanism of the nanocomposites.²² SEM micrographs of the PP and PP nanocomposites, presented in Figure 5, showed that sample P1 presented a small number of cavities, from where the clay agglomerates were removed. In this sample, practically all of the clay agglomerates were covered by the matrix; this indicated that crack propagation occurred preferentially through the matrix and, to a small extent, through the interface. This resulted in a slight increase in the impact strength. In contrast, the samples prepared with swelling agents (P2 and P3) presented more exposed clay agglomerates and cavities,

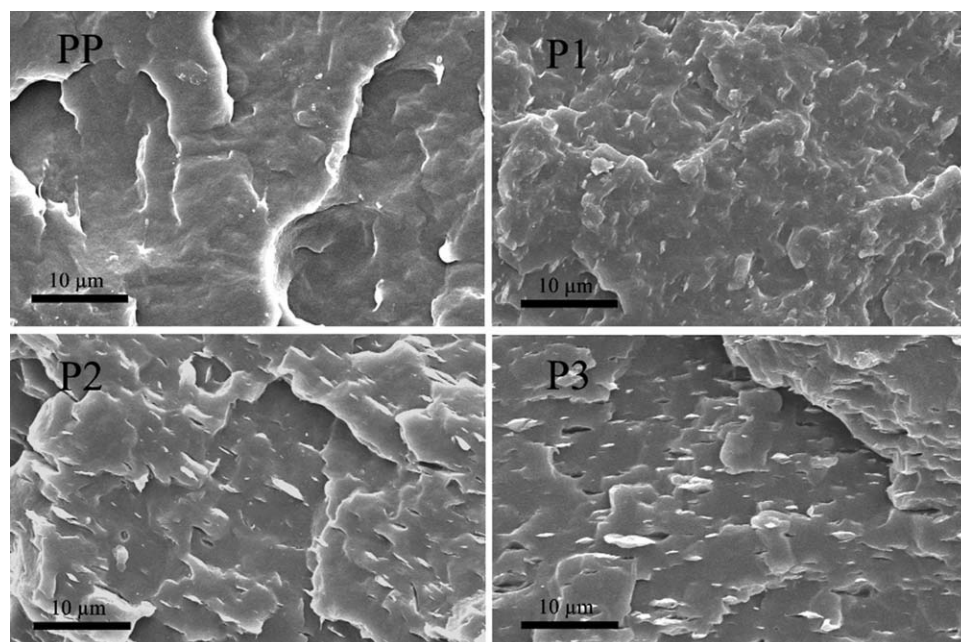


Figure 5 SEM micrographs of the fractured surface of PP and the PP nanocomposites.

from where the agglomerates were removed; this indicated that the crack propagated along the PP/MMT interface. As discussed earlier, the adhesion between the clay and the matrix was lower in the P3 nanocomposite. This lower adhesion led to more effective microvoid formation in this material and resulted in a higher impact strength.

PP is a semicrystalline polymer, and its properties are strongly influenced by the crystalline phase. Nevertheless, all of the nanocomposites showed no significant change in the melting temperature (ranging from 162 to 164°C), crystallization temperature (ranging from 114 to 115°C), or crystallinity (ranging from 49 to 54%) when compared to pristine PP (115°C, 163°C, and 49%, respectively). In addition to the crystallinity degree, the crystal forms were important in determining the PP properties. It is well-known that the monoclinic form (α) presents a higher modulus, and the trigonal one (β) leads to a higher impact strength. Medellin-Rodriguez et al.²³ detected the formation of β -crystalline structures in PP/clay nanocomposites and observed that the α form was the predominant structure, but the low clay concentration induced the formation of β -crystalline structures.

The β form in the crystalline phase of PP nanocomposites could increase the impact strength of these materials. However, the characteristic peaks of the β -crystalline structures were not observed in our XRD analysis.

Clay can also be an active nucleating agent in PP/MMT nanocomposites, as observed by many authors.^{15,19} However, the nucleating activity is very low or absent when no macromolecular compatibilizer is used.²⁴ In a previous study,¹¹ we examined the nucleation activity of MMT in the PP matrix, and the results show that the clay was an effective nucleating agent only when the adhesion energy between the filler and matrix was high.

All of these results indicate that the interactions between the clay and the matrix were lower in samples P2 and P3 than in sample P1; this lower interaction provided additional energy dissipation processes, which increased the impact strength significantly. Other samples were prepared with up to 10 wt % PPG, but the balance between the flexural modulus and impact strength was not satisfactory because the impact strength presented a slight increase and the flexural modulus presented a high decrease; this indicated that the ratio OMMT to PPG of 5 : 1 was the most appropriate one.

CONCLUSIONS

PP nanocomposites were obtained by melt processing with an MMT suspension. The nanocomposites

presented a higher modulus than pristine PP. The use of polar molecules as swelling agents increased the interlayer distance and the dispersion level of the clay in the PP/MMT nanocomposites. The increase in the interlayer distance was related to the intercalation of the MEK and PPG molecules into the clay galleries due to favorable polar interactions. In the same manner, these polar molecules modified the interactions between PP and clay, probably because they adhered to the external clay surface and reduced the load transfer efficiency from the matrix to the clay. This, consequently, decreased the material modulus. On the other hand, the lower adhesion between PP and clay resulted in additional energy dissipation processes during the fracture, which increased the impact strength of the nanocomposites obtained with the MMT suspension. The clay addition caused no significant changes in the PP melting temperature, crystallization temperature, or crystallinity. Finally, the solvent-assisted extrusion process related here successfully produced nanocomposites with superior impact properties, similar to rubber-toughened PP, but without the inconvenience of a decreased flexural modulus.

The authors thank Braskem S. A., Capes, Fapergs/Pronex, Cnpq and Finep for financial and technical support.

References

- Calcagno, C. I. W.; Mariani, C. M.; Teixeira, S. R.; Mauler, R. S. *Compos Sci Technol* 2008, 68, 2193.
- Vaia, R. A.; Giannelis, E. P. *Macromolecules* 1997, 30, 7990.
- Ray, S. S.; Okamoto, M. *Prog Polym Sci* 2003, 28, 1539.
- Lertwilmolnun, W.; Vergnes, B. *Polymer* 2005, 46, 3462.
- Vermogen, A.; Masenelli-Varlot, K.; Seguela, R.; Duchet-Rumeau, J.; Boucard, S.; Prele, P. *Macromolecules* 2005, 38, 9661.
- Dennis, H. R.; Hunter, D. L.; Chang, D.; Kim, S.; White, J. L.; Cho, J. W.; Paul, D. R. *Polymer* 2001, 42, 9513.
- Wang, K.; Wang, L.; Wu, J. S.; Chen, L.; He, C. B. *Langmuir* 2005, 21, 3613.
- Dal Castel, C.; Bianchi, O.; Oviedo, M. A. S.; Liberman, S. A.; Mauler, R. S.; Oliveira, R. V. B. *Mater Sci Eng C* 2009, 29, 602.
- Fornes, T. D.; Paul, D. R. *Polymer* 2003, 44, 4993.
- Sheng, N.; Boyce, M. C.; Parks, D. M.; Rutledge, G. C.; Abes, J. I.; Cohen, R. E. *Polymer* 2004, 45, 487.
- Dal Castel, C.; Pelegrini, T., Jr.; Barbosa, R. V.; Liberman, S. A.; Mauler, R. S. *Compos A* 2010, 41, 185.
- Ding, C.; Jia, D. M.; He, H.; Guo, B. C.; Hong, H. Q. *Polym Test* 2005, 24, 94.
- Garcia-Lopez, D.; Picazo, O.; Merino, J. C.; Pastor, J. M. *Eur Polym J* 2003, 39, 945.
- Lopez-Quintanilla, M. L.; Sanchez-Valdes, S.; de Valle, L. F. R.; Medellin-Rodriguez, F. J. *J Appl Polym Sci* 2006, 100, 4748.
- Kim, D. H.; Park, J. U.; Cho, K. S.; Ahn, K. H.; Lee, S. J. *Macromol Mater Eng* 2006, 291, 1127.
- Liberman, S. A.; Silva, L. P.; Pelegini, T., Jr.; Barbosa, R. V.; Mauler, R. S. *Int. Pat. WO/2007/009200* (2007).

17. Bu, H. S.; Cheng, S. Z. D.; Wunderlich, B. *Makromol Chem Rapid Commun* 1988, 9, 75.
18. Perrin-Sarazin, F.; Ton-That, M.-T.; Bureau, M. N.; Denault, J. *Polymer* 2005, 46, 11624.
19. Burgentzlé, D.; Duchet, J.; Gérard, J. F.; Jupinb, A.; Fillon, B. *J Colloid Interface Sci* 2004, 278, 26.
20. Dubnikova, I. L.; Berezina, S. M.; Antonov, A. V. *J Appl Polym Sci* 2004, 94, 1917.
21. Liang, J. Z. *J Appl Polym Sci* 2002, 83, 1547.
22. Yuan, Q.; Misra, R. D. K. *Polymer* 2006, 47, 4421.
23. Medellín-Rodríguez, F. J.; Mata-Padilla, J. M.; Hsiao, B. S.; Waldo-Mendoza, M. A.; Ramirez-Vargas, E.; Sanchez-Valdes, S. *Polym Eng Sci* 2007, 47, 1889.
24. Chiu, F.-C.; Lai, S.-M.; Chen, J.-W.; Chu, P.-H. *J Polym Sci Part B: Polym Phys* 2004, 42, 4139.