

Effect of Inorganic Fillers in Binary Processing Aids on the Rheology of a Metallocene Linear Low-Density Polyethylene

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ABSTRACT: Inorganic fillers including porous diatomite, flaky talc, and spherical calcium carbonate were blended with polyethylene glycol (PEG) to prepare binary processing aids, and the effect of varied binary processing aids on the melt flow properties and extrudates distortion of a metallocene linear low-density polyethylene (mLLDPE) was studied. It was found that the binary processing aids exhibit better effect on viscosity reduction of mLLDPE than that obtained when PEG was added alone. The morphology of inorganic fillers influences the effect of binary processing aids. The diatomite/PEG binary processing aid shows the

most noticeable effect, followed by the talc/PEG binary processing aid, and then the calcium carbonate/PEG binary processing aid. The influence of particle size of the diatomite on the effectiveness of the diatomite/PEG binary processing aid was also studied. The mechanism for the improved effect of binary processing aids on reducing viscosity of mLLDPE was proposed. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 1824–1829, 2005

Key words: fillers; morphology; rheology; metallocene catalysts; polyethylene

INTRODUCTION

Linear low-density polyethylenes (LLDPE) are used in industry to manufacture films, pipes, sheets, and profiles. The molecular structural parameters, such as molecular weight and molecular weight distribution (MWD), and the type, amount, and distribution of short chain branchings (SCB) are key factors determining physical and mechanical properties of LLDPE.¹ For a given average molecular weight, the processability of LLDPE resins is essentially influenced by the molecular weight distribution and the long chain branching (LCB).

LLDPE produced by metallocene technology generally exhibits molecular structure with narrow molecular weight distribution, quite random comonomer distribution, and uniform SCB distribution. Metallocene linear low-density polyethylene (mLLDPE) ex-

hibits better physical properties than conventional LLDPE, while it is more difficult to process because of narrow MWD and absence of LCB. The mLLDPE processing often exhibits high viscosity, very little shear-thinning, and low critical shear rate for the onset of melt fracture (sharkskin, gross fracture).²

The rheological properties of mLLDPE can be controlled to the desirable level through selective incorporation of LCB or bimodal MWD.^{3–9} It was found that incorporation of LCB or bimodal MWD increases the zero shear rate viscosity and the shear-thinning behaviors of mLLDPE, thus making the polymer melt less viscous in the range of high shear rates and increasing the bubble stability in blowing film operation of mLLDPE. The processability of mLLDPE can also be improved after it is blended with small amounts of LDPE.^{5,10}

Another way to improve the rheological properties of mLLDPE is the application of polymer processing aids (PPA), such as fluoropolymer and organic silicon compound. This kind of processing aid has been widely used to improve the processability of LLDPE.^{10–15} When fluoropolymer or organic silicon compound is blended into mLLDPE, the additives will accumulate and form a slip layer on the die wall surface, acting as a die lubricant to promote the slip-page of main polymer melts and delay the onset of extrudates distortion. The benefit of those additives is not immediately evident, but becomes so after finite

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periods of extrusion. Liquid crystal polymer (LCP) was used as a flow modifier for polyethylene.^{16,17} The significant viscosity reduction of the PE/LCP blend can be attributed to the interlayer slippage of the main polymer on deformed LCP droplets under shear flow. However, LCP has poor compatibility and interphase adhesion with PE, and the processing temperature of common aromatic LCP is much higher than those used for PE processing. Therefore, there is a considerable increase in the energy consumption required, and the possibility of PE thermal degradation.

Boron nitride has also been used as a PPA for mLLDPE.^{18–22} It was found that the boron nitride addition eliminates the sharkskin fracture and postpones the gross fracture at high shear rates, but this new PPA has no effect on the rheological properties of mLLDPE.

In this study, inorganic fillers with different morphology and particle size were blended with PEG for the preparation of inorganic filler/PEG binary processing aids. The effect of binary processing aids on the rheological properties and the extrudates distortion of mLLDPE was examined.

EXPERIMENTAL

Materials

mLLDPE with a melt index of 1 was obtained from Qilu Petrochemical Corp. (Zibo, China). The diatomite with particle size of 5 μm and 38 μm was obtained from NaHui desiccating agent company (Shanghai, China). The molecular weight of polyethylene glycol (PEG) is 6000. Talc and calcium carbonate with particle size of 5 μm were applied without further treatment.

Sample preparation

The inorganic filler/PEG binary processing aids (denoted as BPA) with weight ratio of 2 : 1 were prepared on a two-roll mill for 20 min at 70°C and then pelletized for further application. The diatomite/PEG binary processing aid prepared from diatomite with particle size of 5 μm is denoted as BPA-1, and that obtained from diatomite with particle size of 38 μm is denoted as BPA-2. Talc/PEG and calcium carbonate/PEG binary processing aids are denoted as BPA-3 and BPA-4, respectively. Figure 1 shows the morphology of diatomite with particle size of 5 μm and that of BPA-1. A lot of orifice was observed on diatomite particles. After the blending of diatomite with PEG, the surface of diatomite was coated with PEG and a certain amount of PEG was pressed into the orifices of diatomite.

Test specimens of mLLDPE/additives and pure mLLDPE were prepared on a two-roll mill for 10 min at 120°C. One to five parts (by weight) additives were

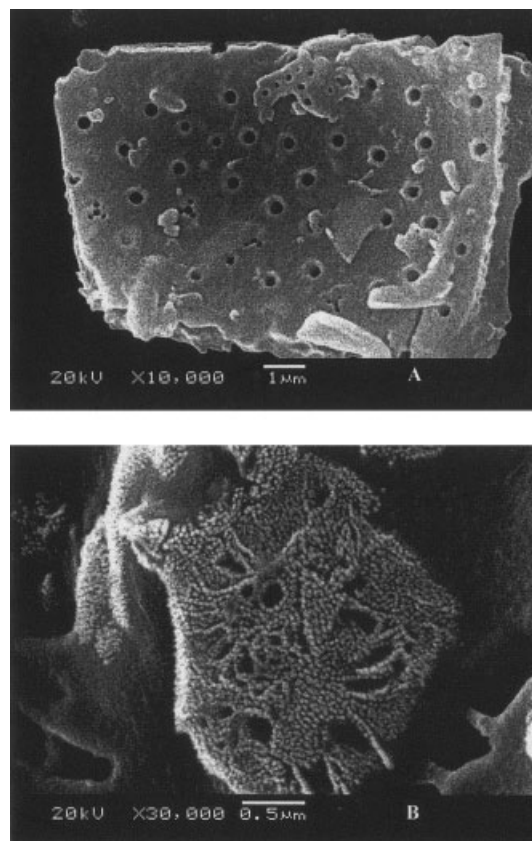


Figure 1 SEM micrographs of diatomite particles and diatomite/PEG binary processing aid: (A) diatomite particles; (B) diatomite/PEG binary processing aid.

added into hundred parts resin (phr) of mLLDPE for the preparation of blends.

Rheological experiments

The measurements of melt flow properties were performed by using a constant rate type capillary rheometer (Gottfert Rheograph 2002, Gottfert, Postfach, Germany) with a round hole die with diameter of 1 mm and length-to-diameter ratio (L/D) of 30. The entrance angle of the die is 180 degrees. Entrance pressure losses were negligible for such a long capillary die and no Bagley correction was applied. The flow properties of these specimens were measured under the range of apparent shear rates from 10 to 3000 s^{-1} at 190°C. The whole range of shear rates was obtained in a single measurement for each specimen. Before each fresh measurement, the barrel and die were extruded with pure mLLDPE to remove the PEG layer on the die wall. It was found that the PEG layer is removed after one extrusion of mLLDPE.

Scanning electron microscopy

The diatomite morphology was observed by a scanning electron microscope (JSM-5900 LV from JEOL,

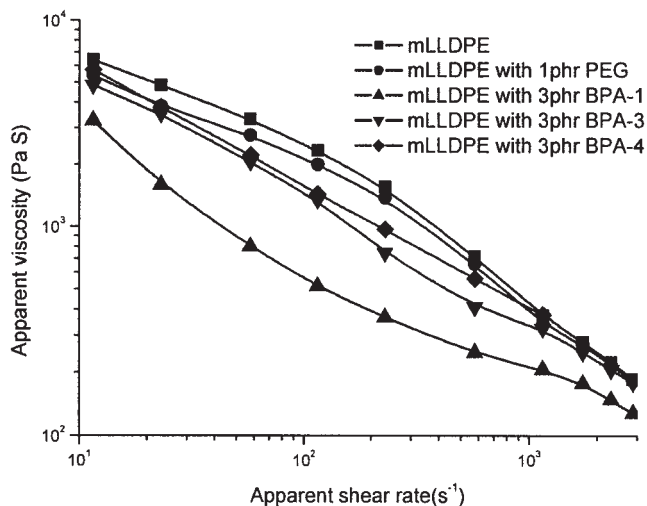


Figure 2 Plots of log apparent viscosity versus log apparent shear rate of pure mLLDPE and mLLDPE/additives.

Japan). The extrudates of mLLDPE and mLLDPE/BPA blends were also examined to detect surface defects. Extrudate specimens obtained at the shear rate of 115.2 s^{-1} were fractured in liquid nitrogen and then coated with silver before examination.

RESULTS AND DISCUSSION

Rheological properties of mLLDPE/BPA blends

The rheological properties of mLLDPE/PEG, mLLDPE/BPA, and pure mLLDPE were examined, as shown in Figure 2. The addition of BPA is 3 phr in each mLLDPE/BPA blend, so the amount of PEG contained in mLLDPE/BPA blends is the same as that of the mLLDPE/PEG blend, that is, 1 phr PEG is contained in the above blends. It can be seen that both the PEG addition and the BPA addition decrease mLLDPE viscosity. PEG is well known for its low viscosity and lubricating property, so such a viscosity reduction of the mLLDPE/PEG blend is expected. It is interesting to note that all mLLDPE/BPA blends are less viscous than the mLLDPE/PEG blend, though the same amount of PEG is contained in those blends. The incorporation of inorganic fillers doesn't decrease the effectiveness of PEG; on the contrary, BPA has a synergistic effect on viscosity reduction of mLLDPE. BPA addition also obviously improves the shear-thinning behavior and the flow properties of mLLDPE.

The morphology of inorganic fillers was found to influence the rheological properties of mLLDPE/BPA blends, as shown in Figure 2. BPA-1, which was prepared from PEG with porous diatomite filler, exhibits the best effect on viscosity reduction of mLLDPE. BPA-4, which was prepared from PEG with spherical calcium carbonate filler, has the least effect on reducing mLLDPE viscosity. While BPA-3, which was pre-

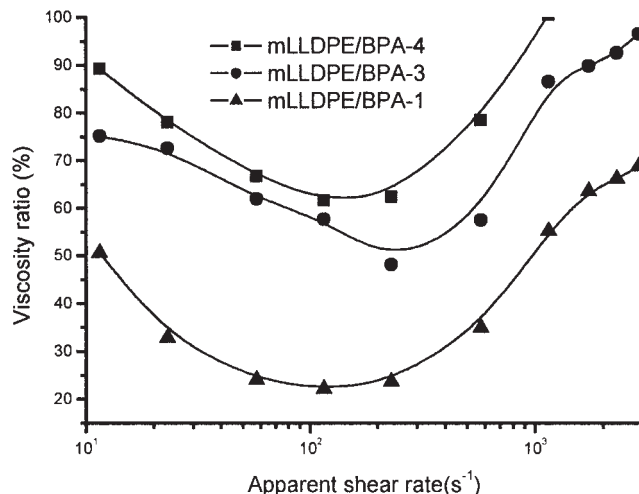


Figure 3 Shear rate dependence of viscosity ratios of mLLDPE/BPA to pure mLLDPE.

pared from PEG with flaky talc filler, shows better effect than BPA-4, it has less effect than BPA-1.

The viscosity ratios of mLLDPE/BPA blends to pure mLLDPE at constant apparent shear rates are shown in Figure 3. When the apparent shear rate is 115.2 s^{-1} , the viscosity ratio of mLLDPE/BPA-3 blend and mLLDPE/BPA-4 blend is 57.7% and 61.6%, respectively. The viscosity ratio of the mLLDPE/BPA-1 blend is extremely lower than that of the other blends—only 22.3%. With apparent shear rate increased to 230.4 s^{-1} , the viscosity ratio of mLLDPE/BPA-1, mLLDPE/BPA-3, and mLLDPE/BPA-4 is 23.6%, 48.1%, and 62.3%, respectively.

The rheological properties of mLLDPE blended with 5phr BPA-1, BPA-3, and BPA-4, respectively, are shown in Figure 4. The effect of BPA on viscosity

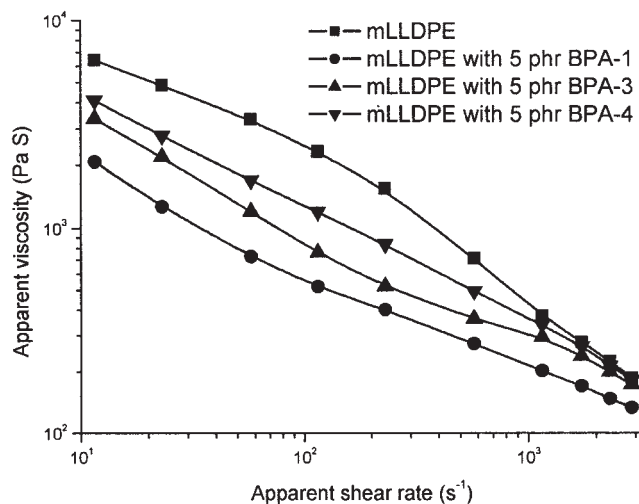


Figure 4 Plots of log apparent viscosity versus log apparent shear rate of mLLDPE blends with 5 phr BPA.

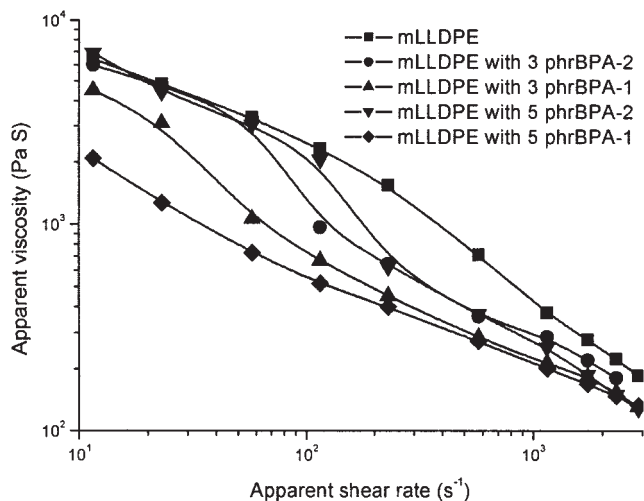


Figure 5 Plots of log apparent viscosity versus log apparent shear rate of mLLDPE/BPA-1 and mLLDPE/BPA-2.

reduction of mLLDPE increases in the order of BPA-4, BPA-3, and BPA-1. The experimental result is consistent with that obtained from Figure 2. The binary processing aid prepared from porous diatomite with PEG exhibits the best effect on improving processability of mLLDPE.

Effect of particle size of diatomite on the rheology of mLLDPE/BPA blends

The rheological properties of mLLDPE blends with the diatomite/PEG binary processing aid were influenced by the particle size of diatomite, as shown in Figure 5. BPA-1, which was obtained by blending diatomite having small particle size (5 μm) with PEG, shows noticeable effect on viscosity reduction of mLLDPE. BPA-2, which contains diatomite with particle size of 38 μm , exhibits less effect on viscosity reduction of mLLDPE than BPA-1 does. The dependence of mLLDPE melt viscosity on the content of BPA-2 is not obvious for the mLLDPE/BPA-2 blend, as compared to that of the mLLDPE/BPA-1 blend.

Sharkskin fracture of mLLDPE/BPA

The influence of BPA on extrudates distortion of mLLDPE was examined, as can be seen in Figure 6 and Figure 7. During the extrusion of pure mLLDPE, it is observed that the range of apparent shear rate for the smooth extrudates is quite narrow (Fig. 6). The surface of extrudates of mLLDPE exhibits sharkskin fractures at apparent shear rate of 57.6 s^{-1} , and the magnitude of sharkskin fracture increased with apparent shear rates. The gross fracture is shown on extrudates of mLLDPE between 230.4 s^{-1} and 2880 s^{-1} . The sharkskin melt fracture, which occurred at very low appar-

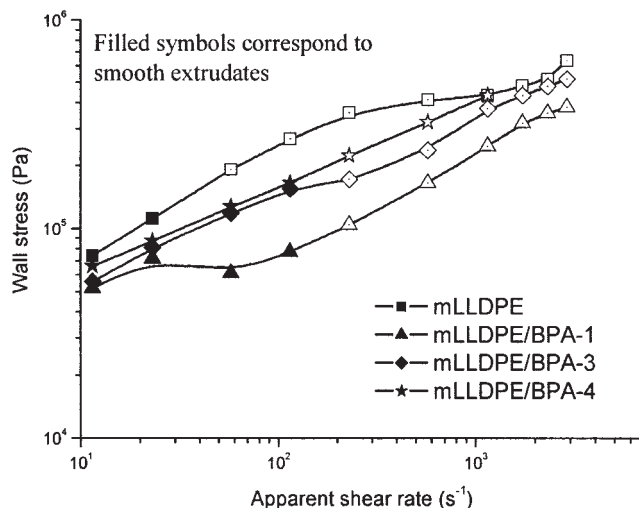


Figure 6 Plots of log wall stress versus log apparent shear rate of mLLDPE blends with 3 phr BPA.

ent shear rate, limits the processing operation of mLLDPE at high shear rates and thus the rate of production. In our work, it was found that the BPA addition eliminates the sharkskin fracture of mLLDPE. The maximum apparent shear rate for smooth extrudates is increased to 115.2 s^{-1} . The improvement of extrudates appearance of mLLDPE/BPA-3 and mLLDPE/BPA-4 is better than that of mLLDPE/BPA-1. With apparent shear rate increased to 230.4 s^{-1} , the extrudates of the mLLDPE/BPA blends exhibit gross fracture.

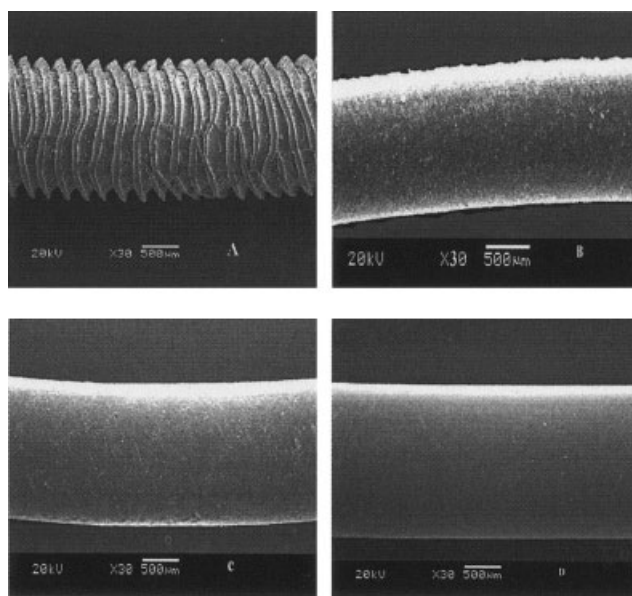


Figure 7 SEM micrographs of extrudate specimens of mLLDPE and mLLDPE/BPA blends at 115.2 s^{-1} : (A) virgin resin; (B) mLLDPE/BPA-1; (C) mLLDPE/BPA-3; (D) mLLDPE/BPA-4.

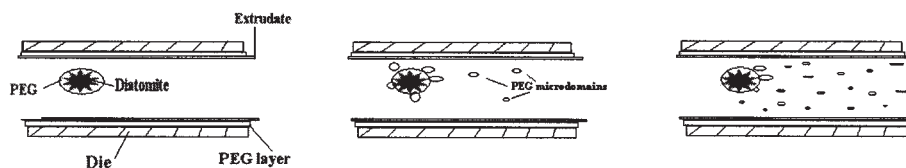


Figure 8 Wall slippage and interlayer slippage of mLLDPE/BPA-1 blend under shear flow.

The incorporation of rigid inorganic fillers often makes polymer melt more viscous. The influence of inorganic fillers on melt rheological properties depends on their shape, content, particle size, and surface treatment.^{23–25} The inorganic fillers with spherical, plate like, and tubular or rather cylindrical morphologies, whose specific surface areas were increased in order, increases the viscosity of polymer melt in sequence. It is considered that, under shear flow, flaky filler or fillers with cylindrical shapes offer much higher resistance to rotation than spherical filler in a viscous medium. Filler with the same particle size but different morphology and surface area was used to fill in HDPE.²⁵ It was found that filler with greater surface area makes the matrix more viscous than one with low surface area does.

However, our experimental results are not the same as those obtained by others. First, the incorporation of inorganic fillers didn't decrease the effect of PEG on reducing viscosity of mLLDPE. On the contrary, inorganic filler/PEG binary processing aids exhibit better effect than PEG does. Second, diatomite with porous structure and greater specific surface area endows the diatomite/PEG binary processing aid (BPA-1) with the most obvious effect on reducing mLLDPE viscosity, followed by BPA-3, which was prepared from flaky talc inorganic filler with PEG. BPA-4 with spherical calcium carbonate inorganic filler has the least effect on reducing viscosity of mLLDPE.

During the extrusion of the mLLDPE/PEG blend, PEG would accumulate and form a slip layer on the surface of the die, promoting wall slippage of the mLLDPE melt. Consequently, the viscosity of mLLDPE is decreased. However, mLLDPE added with BPA exhibits lower viscosity than the mLLDPE/PEG blend does, though those blends contain the same amount of PEG. It is concluded that the improved effect of BPA on viscosity reduction of mLLDPE can't be entirely attributed to the wall slippage of mLLDPE. The mechanism for BPA reducing viscosity of mLLDPE is different from that of PEG.

During the preparation of inorganic filler/PEG binary processing aids, part of PEG will coat on the surface of fillers and interact with polar groups on the surface of inorganic fillers. After the blending of mLLDPE with BPA, an encapsulation structure with a core of inorganic filler and shell of PEG lubricant is formed. Because of low viscosity, low friction coefficients of

PEG, and its immiscibility with polyethylene, the interlayer slippage of the mLLDPE melt on the PEG layer coating of the surface of inorganic particles would be promoted during the extrusion of mLLDPE/BPA blends. At the same time, some of the PEG, which isn't absorbed by inorganic fillers, coats the surface of the die wall and induces wall slippage of the main polymer, reducing the viscosity of mLLDPE and delaying the onset of sharkskin fracture. So the greater viscosity reduction of mLLDPE/BPA blends can be attributed to the interlayer slippage and the wall slippage of the main polymer.

It is assumed that, in the preparation of BPA-1, a certain amount of PEG was pressed into the orifices of diatomite (Fig. 1B). During the extrusion of the mLLDPE/BPA-1 blend, part of the PEG contained in the orifices of diatomite would break away and form PEG microdomains in the mLLDPE matrix. Those PEG microdomains deformed under shear flow and thus induced the interlayer slip of the mLLDPE matrix on deformed PEG microdomains.¹⁶ Figure 8 shows the possible mechanism for the BPA-1 to reduce mLLDPE viscosity.

CONCLUSION

Inorganic filler/PEG binary processing aids have better effect on viscosity reduction of mLLDPE than PEG has. The effect of inorganic filler/PEG binary processing aids is influenced by the morphology of inorganic fillers. The binary processing aid with porous diatomite filler (BPA-1) exhibits the best effect on viscosity reduction of mLLDPE, followed by the binary processing aid with flaky talc filler (BPA-3), and then the binary processing aid with spherical calcium carbonate (BPA-3). When 3 phr BPA-1 is incorporated, the mLLDPE viscosity is decreased by 77.9% at apparent shear rate of 115.2 s^{-1} . The improved effect of the inorganic filler/PEG is correlated with the interlayer slippage of mLLDPE on the PEG layer coating the inorganic fillers surface. In the extrusion of mLLDPE/BPA-1, the interlayer slippage of the main polymer on PEG microdomains is also a key factor reducing the viscosity of mLLDPE. The mechanism for inorganic filler/PEG binary processing aids to reduce viscosity of mLLDPE needs further examination.

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References

1. Kazatchkov, I. B.; Bohnet, N.; Goyal, S. K.; Hatzikiriakos, S. G. *Polym Eng Sci* 1999, 39, 8049.
2. Cheng Yang, L.; Wang, J.; Jiasong, H. E. *Polymer* 2002, 43, 3811.
3. Han, C. D.; Villamizar, C. A. *J Appl Polym Sci* 1978, 22, 1677.
4. Gabriel, C.; Munstedt, H. *Rheolo Acta* 2002, 41, 232.
5. Wood-Adams, P. M.; Dealy, J. M.; Degroot, A. W.; Redwine, O. D. *Macromolecules* 2000, 33, 7489.
6. Costeux, S.; Wood-Adams, P.; Beigzadeh, D. *Macromolecules* 2002, 35, 2514.
7. Yan, D.; Wang, W. J.; Zhu, S. *Polymer* 1999, 40, 1737.
8. Kim, Y. S.; Chung, C. I.; Lai, S. Y.; Hyun, K. S. *J Appl Polym Sci* 1996, 59, 125.
9. Fernandez, M.; Vega, J. F. *Macromol Rapid Commun* 2000, 21, 973.
10. Migler, K. B.; Lavallee, C.; Dillon, M. P.; Wooda, S. S.; Gettinger, C. L. *J Rheol* 2001, 45, 565.
11. Migler, K. B.; Son, Y.; Qiao, F.; Flynn, K. *J Rheol* 2002, 46, 383.
12. Lo, H. H. K.; Chan, C.-M. *Polym Eng Sci* 1999, 39, 721.
13. Eonseok, L.; White, J. L. *Polym Eng Sci* 1999, 39, 327.
14. Xing, K. C.; Schreiber, H. P. *Polym Eng Sci* 1996, 36, 337.
15. Gang, H.-G.; Cuculo, J. A.; Nam, S.; Crater, D. H. *J Appl Polym Sci* 1995, 55, 1465.
16. Whitehouse, C.; Lu, X. H.; Gao, P.; Chai, C. K. *Polym Eng Sci* 1997, 37, 1944.
17. Lin, Y. G.; Lee, H. W.; Winter, H. H. *Polymer* 1993, 34, 4703.
18. Rosenbaum, E. E.; Randa, S. K.; Hatzikiriakos, S. G.; Stewart, C. W.; Henry, D. L.; Buckmaster, M. *Polym Eng Sci* 2001, 40, 179.
19. Seth, M.; Hatzikiriakos, S. G.; Clere, T. M. *Polym Eng Sci* 2002, 42, 743.
20. Kazatchkov, I. B.; Yip, F.; Hatzikiriakos, S. G. *Rheol Acta* 2000, 39, 583.
21. Seth, M.; Hatzikiriakos, S. G. *J Vinyl Addit Techn* 2001, 7, 90.
22. Myung, L. S.; Kim, J. G. *J Vinyl Addit Techn* 2002, 8, 118.
23. Wu, G.; Song, Y. *J Appl Polym Sci* 2003, 88, 2160.
24. Li, L.; Masuda, T. *Polym Eng Sci* 1990, 30, 841.
25. Joseph, R.; McGregor, W. J.; Martyn, M. T.; Tanner, K. E.; Coates, P. D. *Biomaterials* 2002, 23, 4295.