

## **Influence of intercalated montmorillonite/polyethylene glycol binary processing aids on the rheological and mechanical properties of metallocene linear low-density polyethylene**

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### **Summary**

Organomodified Na<sup>+</sup>-montmorillonite/polyethylene glycol (PEG) processing aids were prepared. Melt compounding was used to prepare nanocomposites of exfoliated montmorillonite platelets dispersing in a metallocene linear low-density polyethylene (mLLDPE) matrix. The extent of intercalation of PEG into montmorillonite layers and clay platelet exfoliation in the mLLDPE matrix was studied by X-ray diffraction. The influence of montmorillonite/PEG binary processing aids on the rheological properties and sharkskin melt fracture of mLLDPE was studied using a capillary rheometer and scanning electron microscope (SEM). The crystallization and melting characters were also studied by differential scanning calorimetry (DSC) and X-ray diffraction.

The montmorillonite/PEG binary processing aids could reduce the viscosity of mLLDPE. Meanwhile, the critical apparent shear rate of the onset of sharkskin melt fracture of mLLDPE was increased by adding the aids. Also the nanocomposite prepared with the montmorillonite/PEG processing aids had better mechanical properties than pure mLLDPE. And the crystallinity, crystallization temperature, crystallization rate and melting temperature of mLLDPE/BPA nanocomposites were increased by adding the binary processing aids, and crystallization of mLLDPE became more complete.

### **Introduction**

Metallocene Linear low-density polyethylene (mLLDPE) is more and more used in industry to manufacture films, pipes, sheets and profiles owing to its better mechanical and optical properties, but the processing of mLLDPE often shows high melt viscosity and sharkskin melt fracture because of the narrow molecular weight distribution and absence of long chain branching (LCB).[1]Therefore, the productivity in many polymer processes such as calendaring, extrusion, film-blowing, and wire-coating is reduced.

Our laboratory has reported the effect of micro-diatomite/polyethylene glycol binary processing aids on the rheology of metallocene linear low density polyethylene. It is found that the binary processing aids can increase the shear-thinning behavior and decrease the melt viscosity significantly. Meanwhile, the critical apparent shear rate of the onset of sharkskin melt fracture of mLLDPE was increased. [2, 3] Our interest is focused on whether nanoscale inorganic fillers can reduce the melt viscosity of high melt viscosity polymer such as mLLDPE and also promote the mechanical and other properties of the matrix.

The polymer/layered silicate nanocomposite containing low levels of exfoliated clays such as montmorillonite has a structure consisting of platelets with at least one dimension in the nanometer range. The platelet aspect ratio exceeds 300, giving rise to a high degree of polymer/clay surface interaction, which results in barrier and mechanical properties that are far superior to those of the base material. A lot of work are concentrated on the melt intercalation, flammability properties, reinforcement of matrix, while the rheological application of montmorillonite is infrequent. [4-12]

In this paper, the idea whether the polyethylene glycol (PEG) could intercalated into the layers of montmorillonite and whether montmorillonite/PEG could reduce the melt viscosity of mLLDPE and also promote the mechanical properties with small amount was developed. Furthermore, the paper studied the influence of exfoliated montmorillonite on the rheological, mechanical, crystallization and melting properties of mLLDPE.

## Experimental

### *Materials*

Two organomodified sodium montmorillonite (OMMT) clays were used as received: Nanolin DK1(DK1) and Nanolin DK1N(DK1N) by Zhejiang Feng Hong clay mineral Corporation. DK1 and DK1N are natural montmorillonite modified with a quaternary ammonium salt and the polarity of DK1N is stronger than DK1. Metallocene linear low-density polyethylene (PE, Elite 5100, MFI=0.85g/10min) was supplied by DOW Chemical Corp. (USA) and polyethylene glycol with the molecular weight 6000 was supplied by Liaoning Aoke chemical Corp. (China).

### *Preparation of m-LLDPE/montmorillonite film*

The binary processing aids based on intercalation of PEG into montmorillonite were prepared by stirring and heating them in alcohol and then dried for further application. The DK1/PEG mixture with the weight ratio of 1:1, 2:1 are denoted as BPA-1, BPA-2. The DK1N/PEG mixture with the weight ratio of 1:1 is denoted as BPA-3. The montmorillonite/PEG binary processing aids (BPA) and mLLDPE were blended in a twin screw extruder (SHJ-20, Nanjing Jie Ante Co., China) with 180, 190, 190 and 190°C as the temperature of first, second, third and die area respectively, and the blends were blown into film on a Haake Rheocord torque rheometer (Haake Rheocord 90, Germany), connected to a film blowing machine at 190°C. The extrusion speed was fixed at 30 rpm; and the extrusion temperature from the feed section to the die was fixed at 180, 190, 190 and 190°C. The film thickness, blow-up ratio, and frost-line height were 50 μm, 2.5 : 1, and 15cm, respectively.

### *Rheological Experiments*

The rheological measurements were performed by using a capillary rheometer (Gottfert Rheograph 2002, Germany) and a round die, with a diameter of 1mm and a length-to-diameter ratio (L/D) of 20. The die has an entrance angle of 180°. Entrance pressure loss was negligible for such a long capillary die and no Bagley correction was applied. The flow properties of specimens were measured over a range of apparent shear rates from 10 s<sup>-1</sup> to 3000s<sup>-1</sup> at a temperature of 190°C. The rheologic data were calculated directly on the rheometer.

### *X-ray diffraction (XRD)*

The extent of polyethylene glycol intercalation into the silicate layers and the clay exfoliation in the composites were determined by X-ray diffraction. XRD experiments were conducted using a Philips X-ray generator (Ni filter, Cu-K $\alpha$  radiation  $\lambda=0.154\text{nm}$ ) with 40kV accelerating voltage and 40mA current. The powder samples and film samples with a thickness of 0.05mm were scanned using 2 $\theta$  range from 1.0 to 60° at a rate of 2°/min. The direction of X-ray is parallel to the film surface. Measurements were recorded at every 0.02°. For comparative purpose, the XRD patterns were represented in terms of relative intensities.

### *Thermal properties*

The thermal properties were measured using a differential scanning calorimeter (NETZSCH DSC 204, Germany). Nitrogen flow rate is 50ml/min. The samples were heated to 160°C and kept at 160°C for 5min to remove the thermal history of the material. Then, the samples(5–10 mg) were cooled in the first scan from 160 to 60°C at a rate of 10°C/min, kept at 60°C for 5 min, and heated at the same rate to 160°C for the second scan. The melting temperatures and the enthalpies of melting were determined from the second scan. Mass crystallinity was calculated according to

$$wc = \Delta Hm / \Delta Hm_0 \quad (1)$$

where  $\Delta Hm$  is the melting enthalpy obtained from the DSC melting endothermic peak and  $\Delta Hm_0 = 293 \text{ J g}^{-1}$  is the melting enthalpy of 100% crystalline polyethylene.

### *Mechanical properties*

The tensile and tearing properties were tested on the Instron universal testing machine (Instron 4302, UK) with the tensile speed of 200mm/min at room temperature. The samples were prepared by cutting blowing films into tensile and tearing specimens according to GB 13022-91 and GB/T 1130-91 respectively.

## **Results and Discussion**

### *The extent of PEG intercalation into OMMT*

The XRD patterns for DK1, DK1N and their binary processing aids intercalated by PEG were compared in Fig.1 and Fig.2. Fig.1 shows the interlayer d-spacing for BPA-1, BPA-2 have increased from 2.29nm to 3.38nm, 3.21nm respectively. And Fig. 2 shows the interlayer d-spacing for BPA-3 has increased from 2.22nm to 3.23nm. The increase

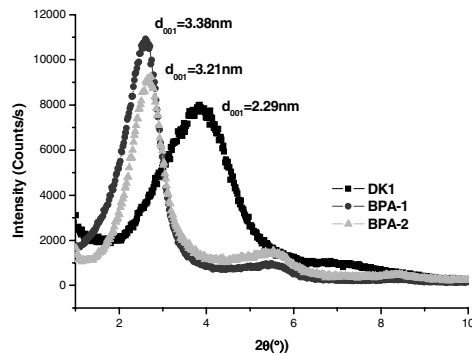


Fig. 1 XRD patterns of BPA-1, BPA-2 and DK1

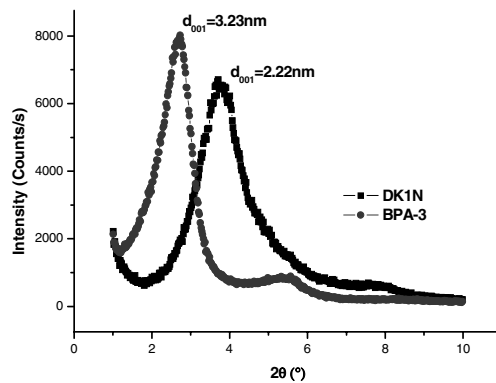


Fig. 2 XRD patterns of BPA-3 and DK1N

in d-spacing for BPA confirmed that the silicate layers had expanded because of intercalation of polyethylene glycol chains into the layers of organomodified montmorillonite and indicated that there exist interaction between PEG and organomontmorillonite layers.

Nature montmorillonite consists of silicate layers with high aspect ratio; its d-spacing is just about 1 nm and there are strong polarity and interlayer force between layers. It is difficult for polymers to intercalate into the silicate layers. DK1 and DK1N were obtained by modifying nature montmorillonite with quaternary ammonium halide, polarity of montmorillonite was weakened to match the polarity of PEG, and the d-spacing of modified montmorillonite was swelled to higher extent compared to the d-spacing of nature montmorillonite, which is favor for the PEG molecular chains to intercalate into the montmorillonite layers. The intercalation of PEG into the layers of DK1 (DK1N) and hence the layer swelling is most important for reducing the viscosity of mLLDPE and the exfoliation of the silicate layers in the latter extrusion process.

#### *Influence of BPA on the rheology properties of mLLDPE*

The influence of BPA-1, BPA-2 and BPA-3 on the rheological properties of mLLDPE is showed in Fig. 3. Usually, the incorporation of rigid filler often makes polymer melt more viscous, especially when the filler content exceeds a critical point and a physical

network is formed, the viscosity of the composite increases significantly. But it is interesting to note that the viscosity of mLLDPE is reduced significantly with the BPA addition. The shearthinning behavior of the mLLDPE/BPA blend is increased obviously at low apparent shear rates but is inconspicuous at high apparent shear rates. As the weight content of BPA in mLLDPE increases from 1 wt% to 5wt%, the viscosity reduction effect becomes better (Fig. 3).

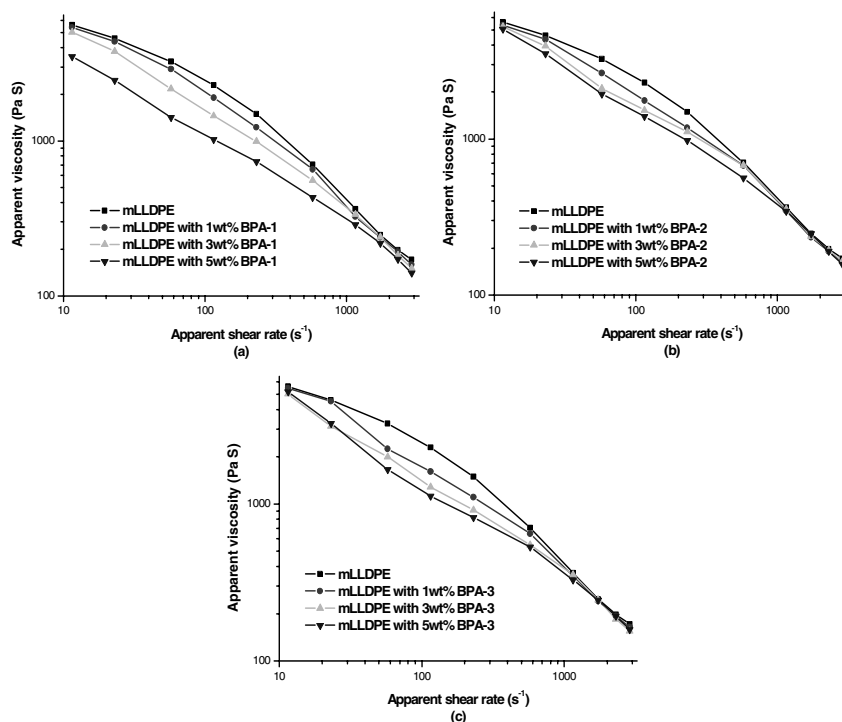


Fig. 3 (a) Plot of log apparent viscosity versus log shear rate of mLLDPE with different wt% BPA-1 (b) Plot of log apparent viscosity versus log shear rate of mLLDPE with different wt% BPA-2 (c) Plot of log apparent viscosity versus log shear rate of mLLDPE with different wt% BPA-3

The influence of BPA-1, BPA-2 and BPA-3 on the rheological properties of mLLDPE is compared in Fig. 4. All composites exhibit the non-Newtonian and shearthinning behaviors. BPA-1 and BPA-3 show better shearthinning effect than BPA-2. And BPA-1 exhibits a little better shearthinning effect than BPA-3. The possible reason for it is as following. PEG is well known for its low molecular weight, low friction coefficient, and partial miscibility with PE matrix. PEG is used to reduce the melt viscosity of the matrix, because it is partial miscible with mLLDPE and when it intercalates into montmorillonite layers and clings to the layers, the montmorillonite layers coated with PEG can slip in the mLLDPE matrix to reduce the viscosity of mLLDPE and also help the polymer chains to unwind. In order to make clear the mechanism of how BPA reduces the viscosity of mLLDPE, XRD was used to analyze the relationship between the exfoliation of montmorillonite and the viscosity reduction.

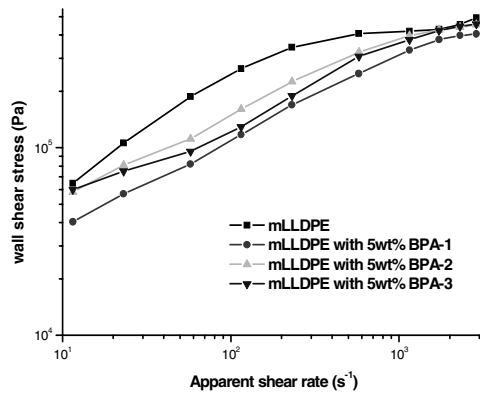


Fig. 4 Plot of wall stress versus apparent shear rate of mLLDPE blended with 5wt% BPA

Fig. 5a shows the composites with 0.5, 1 and 2 wt% BPA-1 are the delaminated nanocomposite with the layered clay structure dispersed throughout the polymer matrix, but the XRD diffraction shoulders with very wide and less intense peaks for the 3 and 4wt% BPA-1/mLLDPE composites suggest the possibility of a small amount of layer incoherence or a form of disordered intercalated structure. However, as seen from Fig. 5c, most composites prepared with BPA-3 are close to a fully exfoliated structure. As seen from Fig. 5b, the silicate layers haven't been completely exfoliated but exhibit the great layer swelling, and with the increase of content of BPA-2, the degree of layer swelling decreases.

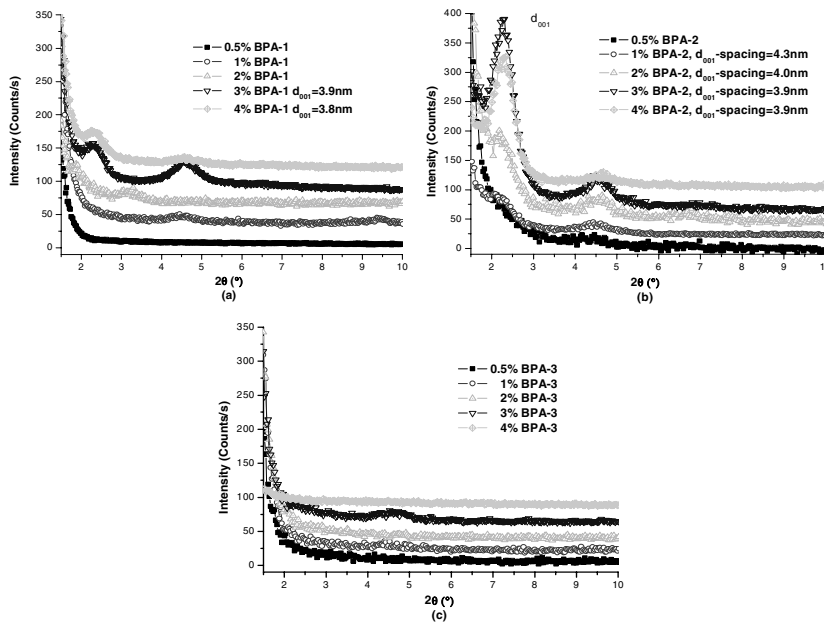


Fig. 5 (a) XRD patterns for mLLDPE/BPA-1 composites with different clay contents (b) XRD patterns for mLLDPE/BPA-2 composites with different clay contents (c) XRD patterns for mLLDPE/BPA-3 composites with different clay contents

The effect of viscosity reduction of BPA-1 and BPA-3 is better than BPA-2. BPA-1 and BPA-3 were prepared with more PEG than BPA-2; also we have confirmed that the d-spacings of BPA-1 and BPA-3 were increased by 1.09 and 1.01nm by PEG respectively. However, the d-spacing of BPA-2 was increased by 0.92nm (Fig. 1). This indicated that more PEG intercalated into the montmorillonite layers of BPA-1 and BPA-3 compared to BPA-2. Adequate intercalation of PEG molecules into the montmorillonite layers or coating the layers surface expedites the exfoliation of montmorillonite layers through the matrix, furthermore the slippage of the montmorillonite layers coated with PEG among the matrix and the reduction of the viscosity of the mLLDPE matrix. We could also conclude that better dispersion of BPA1 and BPA3 compared to BPA2 generated more BPA layers, which was good for reduction of melt viscosity. Another factor affecting the exfoliation of montmorillonite layers and the viscosity reduction may be the different polarity between BPA-1 and BPA-3 and the miscibility between the BPA and mLLDPE matrix. The organomontmorillonite intercalated by PEG and exfoliated by the melt blend indicated that there was a certain interaction between BPA and mLLDPE matrix. So the relationship between the miscibility of BPA to mLLDPE matrix and the melt viscosity reduction needs to be studied further.

#### *Influence of BPA on the melt fracture of mLLDPE*

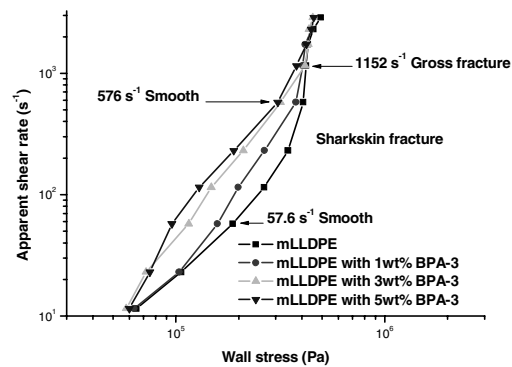


Fig. 6 Plot of log apparent shear rate versus log wall stress of mLLDPE with BPA-3

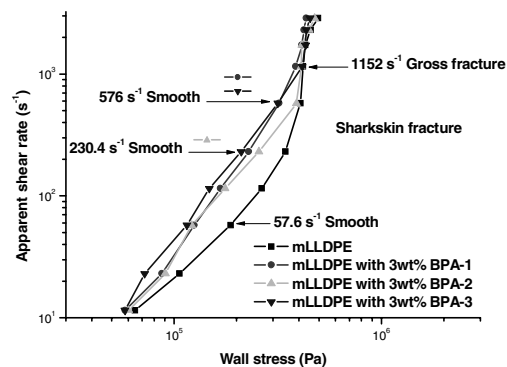


Fig. 7 Plot of apparent shear rate versus wall stress of mLLDPE with 3 wt% BPA

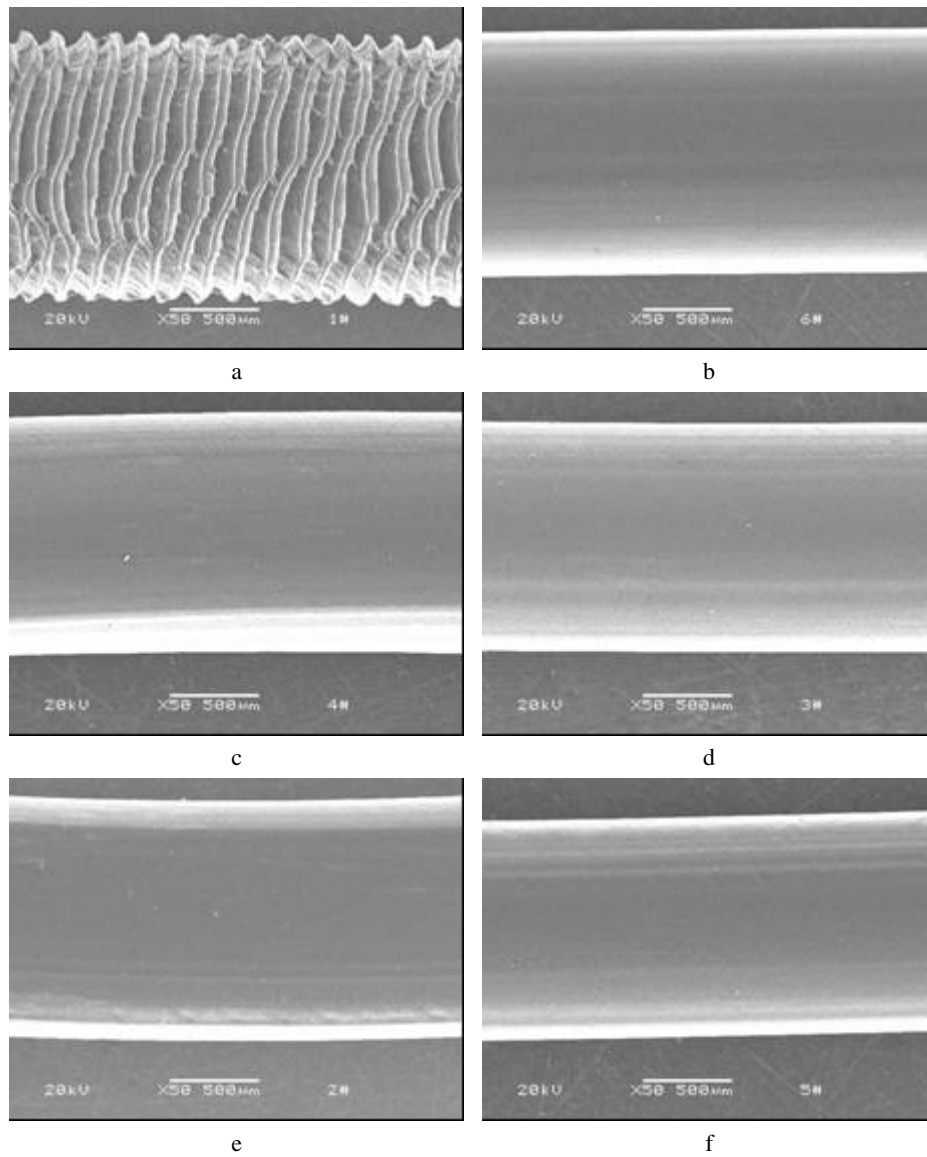


Fig. 8 SEM of extrudate specimens of mLLDPE and mLLDPE/BPA. a. Sharkskin fracture for virgin resin at  $\gamma = 115.2$ . b. Smooth extrudate for mLLDPE with 1 wt% BPA-3 at  $\gamma = 576 \text{ s}^{-1}$ . c. Smooth extrudate for mLLDPE with 3 wt% BPA-3 at  $\gamma = 576 \text{ s}^{-1}$ . d. Smooth extrudate for mLLDPE with 5 wt% BPA-3 at  $\gamma = 576 \text{ s}^{-1}$ . e. Smooth extrudate for mLLDPE with 3 wt% BPA-1 at  $\gamma = 576 \text{ s}^{-1}$ . f. Smooth extrudate for mLLDPE with 3 wt% BPA-2 at  $\gamma = 230.4 \text{ s}^{-1}$

Fig. 6 shows the plot of wall stress vs. apparent shear rate for mLLDPE and the mLLDPE/BPA blends. At low apparent shear rates, the extrudate surface of mLLDPE appears smooth. The extrudate surface shows sharkskin fracture at an apparent shear rate of  $115.2 \text{ s}^{-1}$ . As the apparent shear rate further increases to  $1152 \text{ s}^{-1}$ , the gross fracture occurs on the extrudate of mLLDPE. The incorporation of 1, 3 or 5 wt%



BPA-3 was found to retard the onset of surface defects in mLLDPE. The upper limit of the range of apparent shear rate for smooth extrudates of mLLDPE with different weight content of BPA-3 is increased to  $576 \text{ s}^{-1}$ , especially with 1 wt% BPA-3, the extrudate has a slipperly surface.

Fig.7 exhibits the plot of wall stress vs. apparent shear rate for blends prepared with three kinds of BPAs and mLLDPE. With 3 wt% BPA-1 or BPA-3, the upper limit of the range of the apparent shear rate for smooth extrudates was increased to  $576 \text{ s}^{-1}$ , while with 3 wt% of BPA-2, the maximum apparent shear rate for smooth extrudate was only increased by  $230.4 \text{ s}^{-1}$ . In other words, BPA-2 has less ability to improve the quality of extrudate surface. This result reflects BPA-1 and BPA-3 have better melt viscosity reduction effect than BPA-2. On the other hand, the extrudates of pure mLLDPE and mLLDPE/BPA blends were examined to detect surface defects by SEM in Fig. 8.

#### *Influence of BPA on the mechanical properties of mLLDPE*

Table 1 Mechanical properties of mLLDPE and mLLDPE/BPAs

Sample (composition in wt% )	Tensile Yield Strength (MPa)		Tensile Strength at break (MPa)		Tensile Young's Modulus (MPa)		Tearing Strength ( MPa )	
	MD	TD	MD	TD	MD	TD	MD	TD
mLLDPE	9.69	9.14	27.97	26.36	218.9	226	8.71	8.40
mLLDPE/BPA-1 97/3	11.12	10.35	31.37	28.89	249.4	267.7	8.98	8.29
mLLDPE/BPA-1 95/5	11.61	10.73	32.82	29.55	231.8	236.7	8.18	8.53
mLLDPE/BPA-2 97/3	11.76	10.36	33.01	29.23	251.5	251.6	7.98	9.34
mLLDPE/BPA-2 95/5	10.76	11.44	32.16	37.79	250.1	273.2	9.48	8.95
mLLDPE/BPA-3 99/1	11.44	10.45	32.79	28.63	244.6	279.3	8.42	9.18
mLLDPE/BPA-3 97/3	12.21	11.32	36.93	27.84	225.0	247.2	8.34	9.02
mLLDPE/BPA-3 97/5	11.22	10.96	31.86	30.29	235.6	268.8	9.26	8.19

Note: MD represents machine direction. TD represents transverse direction.

Tab. 1 shows the tensile yield strength, tensile strength at break, tensile young's modulus and tearing strength in the machine direction (MD) and transverse direction (TD) for the pure mLLDPE and mLLDPE/BPA films. The tensile yield strength, tensile strength at break and the tensile young's modulus of the composites are greatly increased not only in the machine direction but also in the transverse direction. There is no big difference in tearing strength.

The improvement of mechanical properties of the composites is believed to have relationship with the crystallization characters of the composites. Tab. 2 exhibits the melting and crystallization parameters of pure mLLDPE and mLLDPE/BPA composites.  $T_c$  and  $T_m$  are crystallizing temperature and melting temperature respectively.  $T_{\text{conset}}-T_c$  is the temperature range between the temperature at which composite starts to crystallize( $T_{\text{conset}}$ ) and  $T_c$ , it represents the overall crystallization rate.  $T_m(\text{endset-onset})$  is the melting range.  $T_c$  and  $T_m$  of mLLDPE/BPA composites are increased compared to the pure mLLDPE.  $T_m$  of PE has relationship with the crystal thickness. The increase of  $T_m$  indicates that the addition of BPA makes the crystal thickness of mLLDPE/BPA composites increase, therefore the yield strength

Table 2 Melting and crystallization parameters of pure mLLDPE and mLLDPE/BPAs Nanocomposite

samples	Tc(°C)	Tconset-Tc(°C)	Tm(°C)	Tm(endset-onset) °C	Crystallinity (%)
mLLDPE	105.48	2.95	123.90	12.76	24.2
mLLDPE/TPA-1 97/3	110.84	2.69	124.6	6.61	33.6
mLLDPE/TPA-1 95/5	110.26	2.34	123.99	7.27	32.1
mLLDPE/TPA-2 97/3	109.49	2.67	124.58	9.45	33.7
mLLDPE/TPA-2 95/5	109.29	2.68	124.59	9.05	32.7
mLLDPE/TPA-3 99/1	109.6	2.56	124.29	8.68	32.5
mLLDPE/TPA-3 97/3	109.0	2.73	124.79	9.28	33.0
mLLDPE/TPA-3 95/5	109.73	2.65	124.5	8.67	32.0
mLLDPE/TPA-6 95/5	109.11	2.82	125.19	7.5	32.1

of mLLDPE/BPA is increased, which is related to the crystal thickness[13]. Tconset-Tc becomes narrow, which indicates that the overall crystallizing rate increases. This means that the BPA dispersed among the matrix acts as a nucleating agent, and accelerates the crystallization rate of mLLDPE. Tm(endset-onset) becomes narrow indicates that mLLDPE/BPA composites crystallize more completely than pure mLLDPE. Furthermore, the crystallinity of mLLDPE is greatly increased by adding BPA. So the strength and modulus of mLLDPE/BPA composites have greatly increased. The tensile strength in the machine direction increases more greatly than in the transverse direction, which results from the polymer chain orientation along machine direction.

The tear behavior is highly influenced by the orientation distribution of the lamellar stacks with respect to the tearing direction. The preferential orientation of the lamellar stacks parallel to the MD is responsible for the low tear strength in the MD and the imbalance of tear strengths of the blown films between the MD and TD. As the polymer molecules exit the film die, the extensional forces applied tends to orient them along the direction of the stress. The relaxation of the extended conformation of these polymer chains simultaneously competes with their orientation before the crystallization process. Consequently, at high MD extension rates, a greater number of molecules are oriented along the MD before the onset of crystallization; it tends to offer lower resistance to tear propagation along the MD [14-18]. For most of the films, the TD tear strength exceeds the MD tear strength due to the higher preferential orientation of lamellar stacks to the MD. In our experiment, the tearing strength differences between the machine direction and the transverse direction are not obvious. The reason may be that the adding of BPA enhanced the tearing strength in the transverse direction. In another word, it compensates the tearing strength reduction generated by polymer chains orientation along the machine direction.

## Conclusion

The montmorillonite/PEG processing aids can be obtained by intercalating PEG into montmorillonite layers. The montmorillonite/PEG binary processing aids exhibit good effect on the viscosity reduction of mLLDPE and on their melt flow stability. The small amount of BPA is found to reduce mLLDPE melt viscosity dramatically and to

increase the critical apparent shear rate for the onset of sharkskin melt fracture. The reason for the melt viscosity reduction is that PEG molecular chains intercalate into montmorillonite layers and coat them. Therefore, the montmorillonite layers with PEG coating can slip in the matrix, reducing the friction between montmorillonite and matrix and helping polymer chains to unwind. The adding of montmorillonite/PEG binary processing aids to mLLDPE can also increase the crystallinity,  $T_c$  and  $T_m$ , make mLLDPE crystallize more completely. So the mechanical properties of the mLLDPE/BPA composites are increased.

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## References

- 1 Kazatchkov IB, Bohnet N, Goyal SK, Hatzikiriakos SG (1999) *Polym Eng Sci* 39: 8049.
- 2 Liu XL, Li HL (2004) *J Appl Polym Sci* 93: 1546.
- 3 Liu XL, Xie MJ, Li HL (2005) *J Appl Polym Sci* 96: 1824.
- 4 Alexandre M, Dubois P (2000) *Mater. Sci. Eng.* 28: 1.
- 5 Giannelis EP (1996) *Adv Mater* 8 (1): 29.
- 6 Giannelis EP, Krishnamoorti R, Manias E (1999) *Adv Polym Sci* 138: 107.
- 7 Gopakumar TG, Lee JA, Kontopoulou M, Parent JS (2002) *Polymer* 43: 5483.
- 8 Wang SF, Hu Y, Qu ZK, Wang ZZ, Chen ZY, Fan WC (2003) *Mater Lett* 57: 2675.
- 9 Morawiec J, Pawlak A, Shouf M, Galeski A, Piorkowska E, Krasnikowa N (2005) *European Polymer Journal* 41: 1115.
- 10 Zhai HB, Xu WB, Guo HY, Zhou ZF, Shen SJ, Song QS (2004) *European Polymer Journal* 40: 2539.
- 11 Liao B, Song M, Liang HJ, Pang YX (2001) *Polymer* 42: 10007.
- 12 Zhao CG, Qin HL, Gong FL, Feng M, Zhang SM, Yang MS (2005) *Polymer Degradation and Stability* 87: 183.
- 13 T Kazmierczak, A Galeski, A S Argon, (2005) *Polymer* 46:8926.
- 14 Krishnaswamy RK, Sukhadia AM (2001) *Polymer* 41: 9205.
- 15 Kim YM, Park JK (1996) *J Appl Polym Sci* 61: 2315.
- 16 Krishnaswamy RK, Lamborn MJ (2000) *Polym Eng Sci* 40(11): 2385.
- 17 Wang KH, Xu M, Choi YS, Chung IJ (2001) *Polym Bull* 46: 499.
- 18 Wang KH, Choi MH, Koo CM, Xu M, Chung IJ, Jang MC, Choi SW, Song HH (2002) *J Polym Sci Part B: Polym Phys* 40:1454.