

Effect of Diatomite/Polyethylene Glycol Binary Processing Aids on the Rheology of a Metallocene Linear Low-Density Polyethylene

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ABSTRACT: Flow performance of metallocene linear low-density polyethylene (mLLDPE) containing small amounts of polyethylene glycol (PEG) diatomite and diatomite/PEG binary processing aids respectively was investigated. The mLLDPE melt viscosity is increased by the addition of diatomite, but is decreased by addition of PEG or the diatomite/PEG binary processing aids. It was also found that the viscosity reduction of mLLDPE with the addition of diatomite/PEG binary processing aid was significantly greater than that obtained with the addition of only PEG. The flow curves of mLLDPE containing diatomite/PEG binary pro-

cessing aid show extremely lower value and stronger dependence on shear rate than the others. It is suggested that the rheological improvement of mLLDPE with diatomite/PEG binary processing aids resulted not entirely from the wall slip promoted by PEG; the intrinsic structure may have changed under the application of shear flow. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1546–1552, 2004

Key words: rheology; polyethylene (PE); metallocene catalysts; additive; immiscibility

INTRODUCTION

New types of linear low-density polyethylene (LLDPE) based on the metallocene catalyst technology have been introduced recently in the market. The single site characteristics of metallocenes, with the catalyst site being identical, are known to produce materials having narrow molecular weight distribution ($M_w/M_n \approx 2$), with essentially a random comonomer distribution and narrow composition distribution. Meanwhile, these new catalysts open the possibility of designing polyethylene structure at the molecular level, making product properties controllable and presenting an opportunity for further studies in gaining a better understanding of molecular structure–properties relationships.

Narrow molecular weight distribution (MWD) and absence of long chain branching (LCB) result in better mechanical and optical properties.^{1–5} On the other hand, polymers having such characteristics become more difficult to process than conventional ones. The

mLLDPE melts often exhibit high viscosity, very little shear-thinning, and low critical shear rate at which melt fracture (sharkskin, gross fracture) appears.⁵ In industrial processing, the extrusion of mLLDPE would exhibit higher melt pressure, motor load, and viscosity and low output, which make the market penetration slower than expected.

To improve the processability of mLLDPE, the rheological properties of mLLDPE blends with LDPE, HDPE, and PP have been studied.^{5,6} mLLDPE with LCB or bimodal MWD were also produced and their steady-state and dynamic rheological properties were thoroughly studied.^{2,7–10} It was found that mLLDPE with LCB or bimodal MWD possesses higher zero shear rate viscosity and a greater degree of shear-thinning, which makes the melt less viscous at higher shear rates.

Fluoropolymer polymer processing aids (PPAs), which have been widely used to improve the processability of LLDPE,^{11–12} are also used in mLLDPE processing.^{13–14} Certain fluoropolymers act as die lubricants, allowing the host polymer melts to slip along the die wall and thus delaying the onset of melt flow instability such as sharkskin melt fracture. A certain induction time is needed before these effects are fully obtained, that is, time for complete coating of die wall by the fluoropolymer. This renders the use of fluoropolymers expensive.

Boron nitride has also been used as PPA for mLLDPE. It was found that trace Boron nitride addition

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eliminates sharkskin melt fracture and postpones the gross melt fracture to higher shear rate. It was also reported that this new PPA has no effect on the rheological properties of the mLLDPE melt examined.^{15–19}

In this paper, the processability of an mLLDPE resin containing small amounts of PEG diatomite and diatomite/PEG binary processing aid respectively is examined. The results show that the diatomite/PEG binary processing aid reduces the apparent melt viscosity and increases the shear-thinning characteristics of the melt dramatically compared to the effect when PEG is added alone. To study the mechanism by which these processing aids significantly reduce the viscosity of the mLLDPE melts, rheological measurements were carried out using a capillary rheometer.

EXPERIMENTAL

Materials

The mLLDPE used in this work was supplied as pellets by Qilu Petrochemical Corp. (Zibo, China) and had a melt index of 1.0 g/10min. The diatomite with particle size of about 5 μ m was supplied by NaHui desiccating agent company (Shanghai, China). PEG having molecular weight of about 6000 and polyethylene wax were used as additives without further treatment.

Sample preparation

The binary processing aids (BPA) based on diatomite/PEG hybrids and diatomite/polyethylene wax hybrids were prepared on two-roll mill for 20min at 70°C, and then pelletized for further application. The diatomite/PEG hybrids with weight ratios of 1:2, 1:1, and 4:1 are denoted as BPA-a, BPA-b, BPA-c, and BPA-d respectively. The diatomite/polyethylene wax hybrid with weight ratio of 2:1 is denoted as BPA-e. The mLLDPE blends with processing aid addition being 1–5 per hundred resin (phr) by weight were prepared on two-roll mill for 10min at 120°C.

Rheological experiments

The rheological measurements were performed by a constant rate capillary rheometer (Gottfert Rheograph 2002, Germany) and using a die having a diameter D equal to 1 mm and a length-to-diameter ratio, $L/D = 30$. The die had an entrance angle of 180°. Entrance pressure losses are assumed to be negligible for such a long capillary die and therefore no Bagley correction was applied. The flow properties of these specimens were measured over a range of apparent shear rates of 10 to 3000 s^{-1} at the temperature of 190°C. The rheological data were calculated directly by the rheometer. The apparent shear rate ($\dot{\gamma}_w$), the wall shear stress (τ_w),

and the apparent viscosity (η_a) were obtained using the formulas:

$$\tau_w = \frac{\Delta p D}{4L} \quad (1)$$

$$\dot{\gamma}_w = \frac{32Q}{\pi D^3} \quad (2)$$

$$\eta_a = \frac{\tau_w}{\dot{\gamma}_w} \quad (3)$$

where Q is the volumetric flow rate; D and L are the capillary diameter and length, respectively; Δp is the pressure drop along the capillary.

Transient capillary experiments at the apparent shear rate of 115.2 s^{-1} were performed for pure mLLDPE, mLLDPE/PEG, and mLLDPE/BPA-d, and the extrusion pressure was recorded as a function of time. For the extrusion of pure mLLDPE, one filling of the rheometer barrel (about 10 min of run time at 115.2 s^{-1}) was enough for a steady state. For the extrusion of mLLDPE blends, it was necessary to refill the rheometer barrel up to three times to reach a steady state.

Scanning electron microscopy

The cross-sectional morphology of the mLLDPE/BPA extrudates was examined by a scanning electron microscope (JSM-5900 LV, JEOL, Japan). 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

Influence of BPA-c on the mLLDPE melts viscosity

The rheological behavior of mLLDPE containing 1phr PEG, 2 phr diatomite, and 3phr BPA-c are shown in Figure 1. All blends exhibit non-Newtonian and shear-thinning behavior. When diatomite or PEG was added alone, they influence the processability of mLLDPE slightly. The apparent shear stress of mLLDPE/diatomite is little higher than that of pure mLLDPE. The mLLDPE/PEG blend exhibits lower values of apparent shear stress compared to that of pure mLLDPE. However, the diatomite/PEG hybrid shows synergistic effect on improving the processability of mLLDPE. When BPA-c was blended with mLLDPE, the rheological behavior of mLLDPE/BPA-c is significantly different from that of the other blends. The apparent shear stress is reduced dramatically and its dependence on apparent shear rate is increased in the whole range of shear rates studied. Comparison of flow behavior of mLLDPE/PEG and mLLDPE/BPA-c, that is, test specimens containing the same amount of

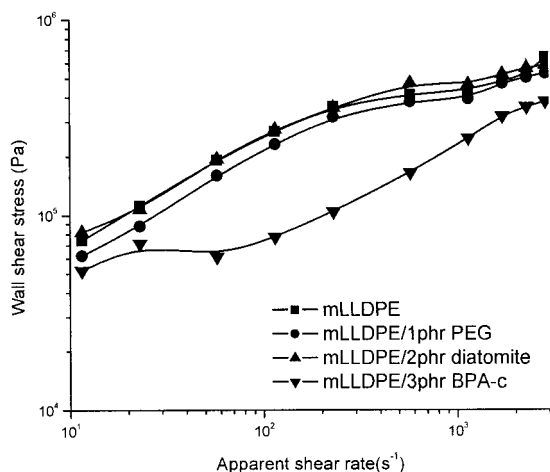


Figure 1 Plots of log wall shear stress versus log apparent shear rate of mLLDPE/additives.

PEG, has shown that the effect of BPA-c on shear stress reduction of mLLDPE was significantly greater than that of PEG. PEG is often used as lubricant, which can act like a fluoropolymer PPA to promote mLLDPE melt slippage on die wall, so it is reasonable to expect such an apparent shear stress reduction for mLLDPE/PEG blend. However, the dramatic reduction with the addition of BPA-c is quite surprising.

For multicomponent polymer systems, it was recommended that the plot of apparent viscosity versus apparent shear stress should be used for the illustration of melts rheological properties.¹⁰ The relationship between apparent viscosity and apparent shear stress for mLLDPE/PEG, mLLDPE/diatomite, and mLLDPE/BPA-c respectively, is shown in Figure 2. Diatomite addition increases the viscosity of mLLDPE, and PEG addition decreases the viscosity slightly. How-

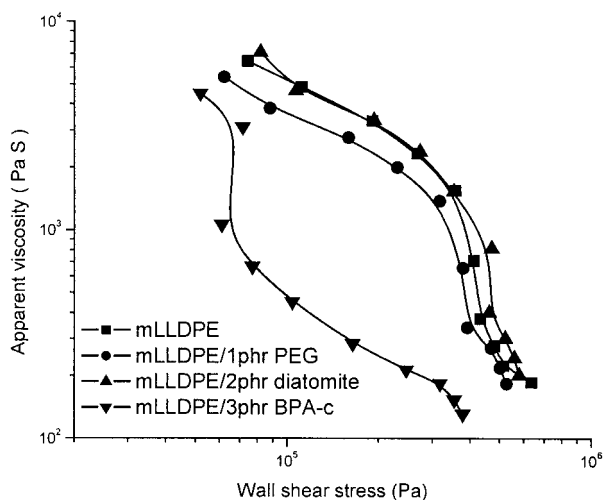


Figure 2 Plots of log apparent viscosity versus log wall shear stress of mLLDPE/additives.

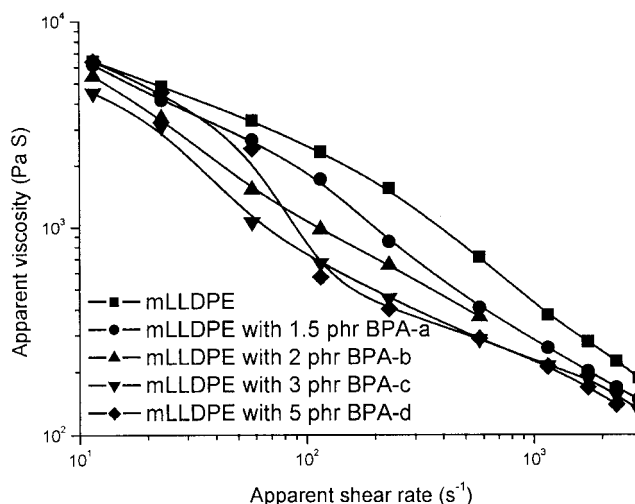


Figure 3 Plots of log apparent viscosity versus log shear rate of mLLDPE/BPA blends.

ever, the BPA-c reduces the viscosity of mLLDPE dramatically, which causes the processing windows of mLLDPE to expand significantly.

The rheological properties of mLLDPE/BPA blends with varied diatomite/PEG BPA

The rheological properties of mLLDPE blends with varied diatomite/PEG BPAs were also studied. The addition of BPA-a, BPA-b, BPA-c, and BPA-d are 1.5, 2, 3, and 5 phr respectively, so the same amount of PEG (1 phr) is contained in mLLDPE/BPA-a, mLLDPE/BPA-b, mLLDPE/BPA-c, and mLLDPE/BPA-d blends, and the amount of diatomite contained is increased gradually from mLLDPE/BPA-a to mLLDPE/BPA-d. As can be seen in Figure 3, all diatomite/PEG BPAs increase the degree of shear-thinning and improve the flow performance of mLLDPE. However, BPAs with varied weight ratio of diatomite to PEG have different benefit on reducing the viscosity of mLLDPE. The effect of BPAs is improved with the weight ratio of diatomite to PEG increasing. The BPA-a (weight ratio of diatomite to PEG is 1:2) addition has the least effect on viscosity reduction of mLLDPE, while BPA-c (weight ratio of diatomite to PEG is 2:1) and BPA-d (weight ratio of diatomite to PEG is 4:1) exhibit the best effect. And mLLDPE/BPA-d, which contains the highest content of filler, presents a yield-like behavior with increasing shear rates and exhibits the lowest viscosity at high shear rates.

Filler addition often increases the viscosity of matrix. The more filler added, the more the viscosity increases. But in our work, it is interesting that, when the amount of PEG is constant in mLLDPE/BPA blends, the viscosity of mLLDPE melt decreased with increasing content of diatomite. Moreover, the more

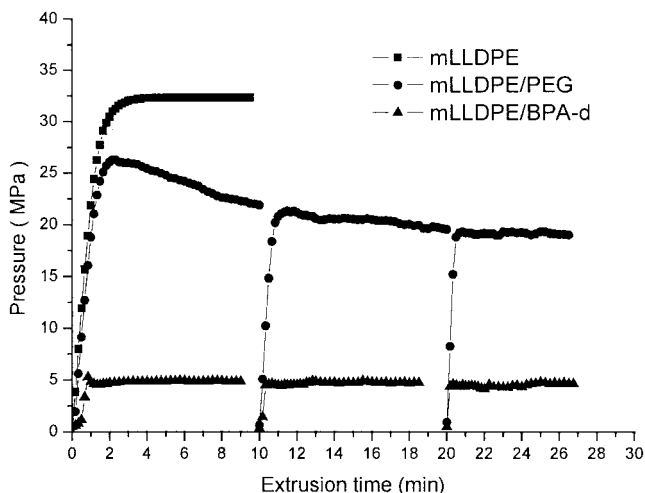


Figure 4 Extrusion pressure versus time for mLLDPE, mLLDPE/PEG, and mLLDPE/BPA-d in a capillary extrusion: $\dot{\gamma} = 115.2 \text{ sec}^{-1}$.

diatomite in the blend, the more the viscosity of matrix decreased.

Transient capillary experiments for mLLDPE/PEG and mLLDPE/BPA-d

Figure 4 illustrates the transient capillary experiments results of mLLDPE, mLLDPE/PEG, and mLLDPE/BPA-d. For the pure mLLDPE, the extrusion pressure builds up and reaches a steady state value rapidly. For the mLLDPE/PEG blend, during the first run the pressure initially increases, goes through a maximum, and then gradually decreases. However, it was not possible to obtain steady state during run No. 1. A steady-state value was obtained during run No. 3. It is interesting to note that the maxima in run Nos. 1–3 gradually decrease, and that the maximum pressure in the second run is at the point where the previous one ended. Such behavior has been observed previously in the capillary extrusion of LLDPE when a small amount of fluoropolymer is included as a processing aid.²⁰ The gradual decrease of the load in these experiments was associated with gradual coverage of the wall with the processing aid and the gradual increase of slippage of the polymer melt over fluoropolymer layer on the die wall surface.

The experiment results for the mLLDPE/BPA-d blend, which don't show a time dependent effect, are not the same as that of mLLDPE/PEG and pure mLLDPE. The pressure builds up rapidly and then decreases rapidly to the steady state values in each run. A pressure maximum, which appears in each run, is much lower than that of mLLDPE/PEG. And the time for a steady state to be reached in each run is quite short for mLLDPE/BPA-d. So it is concluded that the enhanced effect of BPA-d at high shear rates can't be

due to the gradual increase of slippage of the polymer over PEG layer. The interior structure may be changed at high shear rates.

Comparison of diatomite/polyethylene wax BPA (BPA-e) and diatomite/PEG BPA (BPA-c)

The influence of PEG, polyethylene wax (PEW), and their corresponding BPAs on rheological properties of mLLDPE was also studied and the results are shown in Figure 5. It can be seen that, when the PEW or the PEG is added alone, the viscosity of mLLDPE decreases only slightly, and the mLLDPE/PEG and mLLDPE/PEW blends have almost the same flow behavior. However, the BPA-e and BPA-c, which are composed of diatomite with PEW and diatomite with PEG respectively, show quite different effect on viscosity reduction of mLLDPE. The diatomite/PEW BPA (BPA-e) exhibits the same effect as that of PEW, whereas diatomite/PEG BPA (BPA-c) has more obvious effect on viscosity reduction of mLLDPE than PEG. The BPA-c addition decreased the viscosity of mLLDPE significantly.

Figure 6 shows the influences of the content of BPA-c and BPA-e on the rheological properties of mLLDPE. The increase of BPA-e content has little influence on viscosity reduction of mLLDPE matrix. However, an increasing addition of BPA-c increases the shear-thinning effect of mLLDPE melts. A small amount of BPA-c (1phr), although a little influence on the rheological properties of mLLDPE at low shear rates, increases the shear-thinning behavior and thus decreases the viscosity of mLLDPE obviously at high shear rates. With BPA-c content further increased to 3 phr and 5 phr, the viscosity of mLLDPE reduces even further.

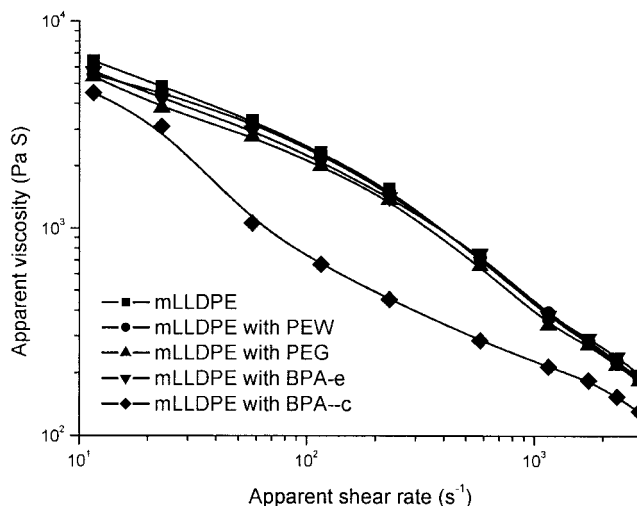


Figure 5 Plot of log apparent viscosity versus log apparent shear rate for mLLDPE/PEG, mLLDPE/PEW, mLLDPE/BPA-c, and mLLDPE/BPA-e.

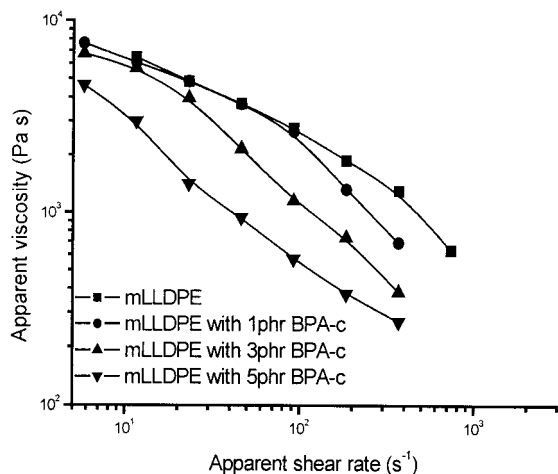
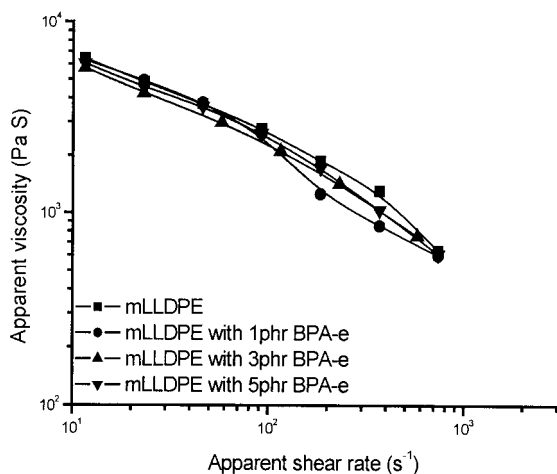


Figure 6 Plots of log apparent viscosity versus log shear rate of mLLDPE/BPA-e blends and mLLDPE/BPA-c blends.

We calculate the viscosity ratios of mLLDPE/BPA-c blends to pure mLLDPE, and the curves of viscosity ratio versus apparent shear rate are plotted in Figure 7. It is clear that the BPA-c addition decreases the mLLDPE melt apparent viscosity and increases the shear-thinning behavior of the matrix. The more the BPA-c is added, the more the viscosities of polymer melts are reduced. When 3phr BPA-c is added to mLLDPE matrix, the melt viscosity ratio of mLLDPE/BPA-c to pure mLLDPE is 88.3% at the apparent shear rate of 11.52 s^{-1} and it decreases to 29.5% at 368.64 s^{-1} . When BPA-c addition is further increased to 5phr, the corresponding viscosity ratio is 46.6% and 20.8% respectively. It is clear that the BPA-c is a very effective flow modifier for the extrusion of mLLDPE.

Morphology observation

SEM micrographs of mLLDPE containing 3phr BPA-c are shown in Figure 8. The pretreatment of diatomite

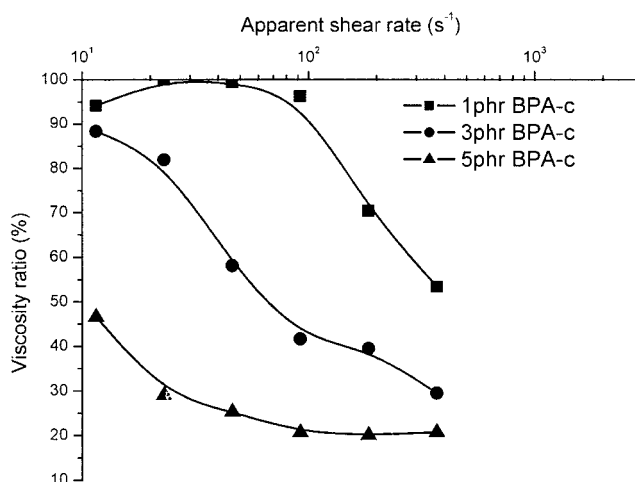


Figure 7 Shear rate dependence of viscosity ratios of mLLDPE/BPA-c blends.

with PEG shows a uniform dispersion of diatomite in the mLLDPE matrix. The diatomite was finely dispersed in mLLDPE matrix and no obvious aggregation was found.

DISCUSSION

To explain the synergistic effect of diatomite with PEG on the flow performance of mLLDPE during the capillary extrusion, the following possible mechanism can be discussed:

1. Wall slip: Wall slip might be a factor in these extrusion experiments, because some amounts of PEG, which is often used as lubricant for the extrusion of polyolefins, was included in these mLLDPE blends.
2. Internal slip: PEG migration toward die wall surface will be constrained by diatomite, and this part of PEG is located in interior of poly-

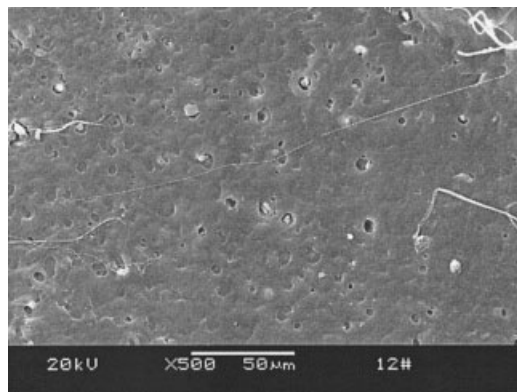


Figure 8 SEM micrographs of extrudate of mLLDPE with 3phr BPA-c at the apparent shear rate of 115.2 s^{-1} .

mer melt, thus promoting the internal slippage of mLLDPE on surface of PEG microdomains.

When only PEG was added into mLLDPE, the PEG would migrate toward die wall and coat the die wall surface, thus acting as die lubricant and promoting the slippage of extrudate on lubricant layer. So the viscosity reduction of mLLDPE/PEG was due to wall slippage of mLLDPE over PEG layer.

When diatomite/PEG BPA was blended into mLLDPE, a certain amount of PEG was also incorporated in these blends. It is reasonable to attribute the great viscosity reduction of mLLDPE/BPA to wall slip. However, it is clear that the rheological behavior of mLLDPE/BPA-c is quite different from that of mLLDPE/PEG, as can be seen in Figure 1 and Figure 2. PEG addition has little effect on reducing the apparent viscosity and wall stress of host polymer melt, whereas the apparent viscosity, extrusion pressure, and the wall stress of mLLDPE/BPA are extremely lower than that of mLLDPE/PEG, and the time for a steady state to be reached is much shorter for the extrusion of mLLDPE/BPA-d, even though these blends contain the same amount of PEG. It is suggested that the mechanism for diatomite/PEG BPA to decrease the mLLDPE viscosity is different from that of PEG processing aid; the BPA may act as an internal lubricant (plasticizer).

Addition of inorganic filler often modifies the flow behavior of polymer melts. The influence of fillers on melt rheological properties depends on their shape, content, particle size, and surface treatment. The incorporation of rigid filler often makes polymer melt more viscous. Especially when the filler content exceeds a critical content and a physical network is formed, the viscosity of the composite increases significantly. The interface between filler and matrix also influences the rheological properties of the composite. It has been reported that surface treatment of fillers with coupling agents improves the rheological properties because of the plasticizing and lubricating effect of the coupling agents.^{21,22}

Because diatomite possesses porous structure and contains polar groups on its surface, the PEG and diatomite have good affinity. After the blending of diatomite with PEG, most of the PEG would be pressed in orifice of diatomite or absorbed on diatomite surface, and this part of PEG cannot migrate toward die wall in extrusion of mLLDPE/BPA. So the PEG migrated to the interface between die wall and polymer melt is less for mLLDPE/BPA than that of mLLDPE/PEG. This may weaken the wall slippage of mLLDPE/BPA. However, an encapsulated structure may be formed with rigid core of diatomite and shell of PEG in mLLDPE/BPA blends. Meanwhile, under the application of shear flow, some of the PEG will be

broken away from the orifice or the surface of diatomite, and then dispersed in mLLDPE matrix in the form of microdomains. Because of the immiscibility of PEG with mLLDPE and its lubrication property, the interfacial adhesion strength between PEG domains and mLLDPE matrix is weak, and the PEG layer coating on the diatomite surface would decrease the interaction of filler with matrix. The weak interfacial adhesion would promote the interface slip of mLLDPE melt on the surface of diatomite and PEG microdomains.²³ At the same time, the shear rate gradient would make the rigid filler act as ball bearing in melt, which also decreases the flow resistance of mLLDPE melt.

When the amount of PEG (1phr) is constant in mLLDPE/BPA blends, the diatomite content is increased from mLLDPE/BPA-a to mLLDPE/BPA-d in turn. The number of encapsulation of PEG/diatomite, which is located in interior of mLLDPE melt, is increased when BPA with high weight ratio of diatomite to PEG is added into mLLDPE. So the more internal slip is induced and further the viscosity of matrix is decreased.

It is known that the compatibility of PEW with mLLDPE is better than that of PEG with mLLDPE.²⁴ The interfacial adhesion of diatomite with matrix for mLLDPE/BPA-e is strengthened compared to that of mLLDPE/BPA-c. With the application of shear field, this stronger interfacial adhesion depresses the internal slip of mLLDPE on the surface of diatomite and thus decreases the degree of viscosity reduction of mLLDPE melts.

CONCLUSION

Small amounts of diatomite/PEG BPA added to mLLDPE were found to reduce the viscosity dramatically as well as increase the shear-thinning behavior of the host polymer melt. The apparent shear viscosity was found to depend on the diatomite/PEG BPA content significantly. However, the diatomite/PEW BPA has little influence on the viscosity reduction of mLLDPE. The origin for this significant viscosity reduction of mLLDPE in the presence of diatomite/PEG hybrid is not only due to the wall slip induced by PEG, but is also related to the change in the melt intrinsic structure response to flow field.

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