

# Melt Rheological Properties of Reactive Compatibilized HDPE/PET Blends

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Received 10 October 2007; accepted 29 December 2007

DOI 10.1002/app.28031

Published online 6 March 2008 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Melt rheological properties of high density polyethylene and poly(ethylene terephthalate) (HDPE/PET) blends compatibilized by an ethylene-butyl acrylate-glycidyl methacrylate terpolymer (EBAGMA) were studied by means of a HAAKE torque rheometer and a capillary rheometer. The phase morphology of the blends was evaluated by a scanning electron microscope (SEM). The results showed that the melts of blends behave pseudoplasticity. The addition of EBAGMA strengthens the interfacial adhesion between HDPE and PET and improves the phase dispersion due to reactive compatibilization. It was

observed that the balance torque, melt viscosity, and sensitivity of melt viscosity to shear rate of the melts increase with increasing content of EBAGMA, but the melt flow index and activation energy decrease. At the same time, the plasticizing time is shortened indicating that the processability of the compatibilized blends has been improved. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 3559–3564, 2008

**Key words:** high-density polyethylene; poly(ethylene terephthalate); blends; rheology; compatibilization

## INTRODUCTION

High-density polyethylene (HDPE) and poly(ethylene terephthalate) (PET) are widely used thermoplastics polymers. HDPE is relatively inexpensive and exhibits good flexibility, ease of processing, and crystallizing but possesses the disadvantages of low mechanical properties and thermal stability. On the other hand, PET engineering plastic is rigid, more thermally and chemically stable but brittle and exhibits poor processability. Blending of HDPE with PET offers an interesting route to achieve new materials with promising property combinations by optimizing their properties.<sup>1</sup> However, the immiscibility of HDPE and PET in the melt state leads to the blends with poor interfacial adhesion, unstable phase morphology, and bad mechanical properties of the blends, which limit their practical use.<sup>2,3</sup> Reactive compatibilization is the most promising way to improve the compatibility of PE/PET blends by the addition of suitable graft or block copolymers with reactive groups,<sup>4,5</sup> for example, maleic anhydride (MA) or glycidyl methacrylate (GMA). During melt blending, these compatibilizers with functional groups can react with the component of blends, giving rise to *in situ* compatibilization resulting in the reduction of interfacial tension and improvement of

phase dispersion and adhesion between two phases. The ethylene-butyl acrylate-glycidyl methacrylate terpolymer (EBAGMA) is expected to act as a reactive compatibilizer between the polar PET and non-polar HDPE. Kaci et al.<sup>6</sup> reported that the addition of small amounts of this terpolymer to the binary LDPE/PET blends reduces the size of PET with a finer dispersion and increases the tensile properties and impact strength. Our previous studies<sup>7,8</sup> had shown that the mechanical properties of HDPE/PET blends, prepared by melt extrusion, improved effectively by adding small quantities (5 phr) of EBAGMA. Furthermore, the blends possess good thermally stimulated shape memory effect with the improvement of interactions between two phases. However, rheological effects of the incorporation of the compatibilizer to the PE/PET blends is a subject that has not been discussed in depth.

Polymer rheological properties help to formulate a polymer system in respect to its processing characteristics. These also give an insight into the physical properties and morphology of the system because there is an interplay between the processing conditions, structures, and properties.<sup>9</sup> In this article, the terpolymer EBAGMA was used as the reactive compatibilizer to HDPE/PET blends, and melt rheological properties of the blends were studied by means of a HAAKE torque rheometer and a capillary rheometer. Morphology of the blends and effects of the compatibilizer content, shear rate, and temperature on melt viscosity of the blends have been discussed.

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## EXPERIMENTAL

### Materials

In this study, HDPE used was DGDA6098 produced by Qilu Petro-Chemical, China. The melt flow rate (MFR) of this polymer was 1.58 g/10 min (at 190°C/10 kg), and the density was 0.95 kg/m<sup>3</sup>. PET with an intrinsic viscosity of 0.67 dL/g was supplied by Yanshan Petro-Chemical, China. EBAGMA terpolymer consisted of 66.75 wt % ethylene, 28 wt % butyl acrylate, and 5.25 wt % GMA, which was supplied by DuPont (Belgium) under the trade name Elvaloy PTW. The main characteristics of the terpolymer were a MFR of 12 g/10 min measured by the method of ASTM 1238 and a melting point of 72°C.

### Preparation of blends

Before use, PET and EBAGMA were dried in a drying cabinet at 130°C for about 4 h and at 50°C for about 6 h, respectively. The HDPE/PET blends with and without the EBAGMA terpolymer were prepared by melting extrusion, which was carried out in a single-screw extruder (Brabender PLE330) with a diameter of 19 mm and a length to diameter ratio ( $L/D$ ) of 25. HDPE, PET, and EBAGMA in a given ratio were introduced into the hopper of the extruder at a screw speed of 35 r min<sup>-1</sup> and the barrel temperature (from the feeding zone to the die) of 200, 245, 265, and 250°C. The screw profile was made up of conveying and kneading elements to ensure melting, mixing, shearing, and good dispersing of the components. The strands obtained from the extruder were cooled in air and then cut into small granules in a granulator and dried (8 h at 80°C). The compositions of HDPE/PET/EBAGMA blends were 100/0/0, 0/100/0, 90/10/0, 90/10/3, 90/10/5, and 90/10/8.

### Morphology analysis

The morphology of the blends was examined using a JSM-6380 scanning electron microscope (SEM), made in Japan. The samples were freeze fractured in liquid nitrogen and sputter coated with gold before analysis.

### FTIR analysis

FTIR spectra of HDPE, PET, EBAGMA, and HDPE/PET/EBAGMA (90/10/5) blend were obtained using a VECTOR22 spectrometer (Bruker, Germany).

### Torque rheology test

The processing rheological properties of HDPE/PET/EBAGMA blends were first investigated by a

HAAKE torque rheometer (PolylabRC-300P, Haake Machine, Germany). HDPE, PET, and EBAGMA that had been weighted according to the compositions were added together in the mixing chamber at 260°C with rotors rotating at 30 rpm and mixed for 10 min. The variation of torque moment during melt mixing was recorded against the time of blending.

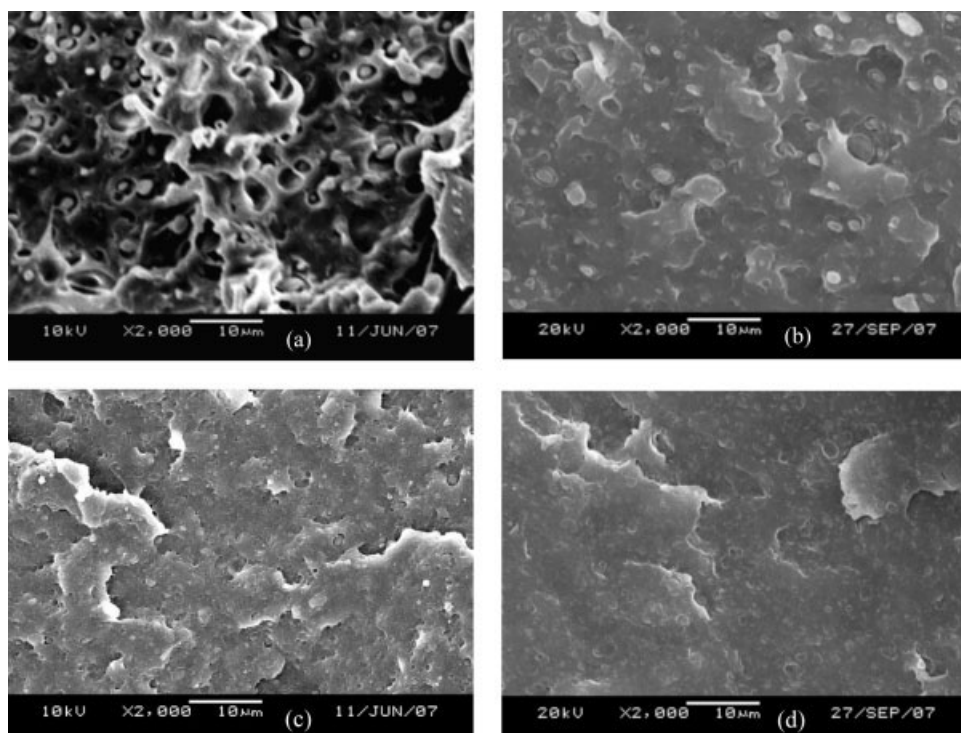
### Capillary rheological measurement

Capillary rheological properties were investigated with a capillary rheometer (RH2000, Rosand Precision, UK) at three temperatures (250, 260, and 270°C) with shear rates varied from 20 to 5000 s<sup>-1</sup>. The ratio of length to diameter ( $L/D$ ) and the diameter of the capillary were 35 and 1 mm, respectively. The samples were preheated for 5 min at a test temperature before measuring. The apparent shear viscosity ( $\eta_a$ ) and the apparent shear rate ( $\dot{\gamma}'_w$ ) were calculated from the experimental data using the conventional expression.<sup>10,11</sup> The Bagley correction is neglected for the  $L/D$  ratio of the capillary is 35. The Rabinowitsch correction for non-Newtonian behavior was made.

## RESULTS AND DISCUSSION

### Morphology

SEM micrographs of the blends, which are uncompatibilized and compatibilized with EBAGMA, are shown in Figure 1. It is obvious that the blends display two-phase structure, that is, the droplets of PET dispersed in the continuous HDPE phase. The uncompatibilized blend (a) shows a typical morphology of a phase segregation structure with the appearance of sharp dispersed particles and discrete interface between the two phases due to the poor interfacial adhesion. In comparison, blends with the compatibilizer show well-dispersed PET particles inside the HDPE matrix. The particle size reduces and adherence between the two phases is promoted with increasing the content of EBAGMA as illustrated in Figure 1(b–d). These results indicate the effectiveness of the EBAGMA terpolymer to create an interfacial adhesion between the PET and HDPE. This could ascribe the chemical interactions that presumably result from the reactions of the hydroxyl and carboxyl groups of PET with the epoxy group of GMA of the EBAGMA terpolymer. Figure 2 shows FTIR spectra of HDPE, PET, EBAGMA, and HDPE/PET/EBAGMA (90/10/5) blend. The oxirane absorption of GMA in pure EBAGMA appears at 912 cm<sup>-1</sup>, and the disappearance of the oxirane absorption at 912 cm<sup>-1</sup> in the HDPE/PET/EBAGMA blend is an evidence for the reactions.

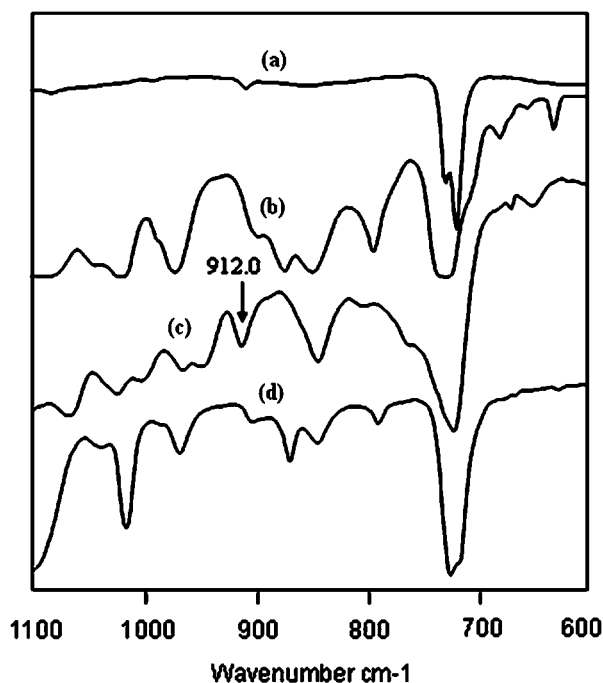


**Figure 1** SEM photographs of fracture surface of the blends: (a) HDPE/PET (90/10); (b) HDPE/PET/EBAGMA (90/10/3); (c) HDPE/PET/EBAGMA (90/10/5); and (d) HDPE/PET/EBAGMA (90/10/8).

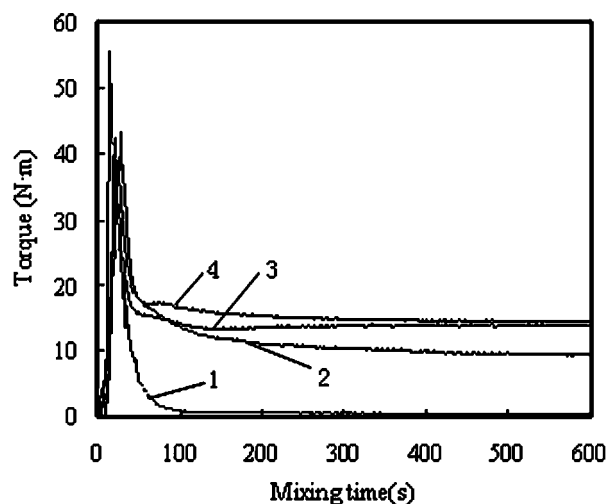
**Processing rheological properties**

A torque rheometer, which provides quantitative information on the flow behavior of the blends by re-

ording of torque varying with time, is widely used to monitor the chemical reaction during reactive melt mixing.<sup>12</sup> The torque variation as a function of mixing time and plasticizing times for HDPE, PET, and HDPE/PET blends is shown in Figure 3 and Table I, respectively. It can be noticed that the plasticizing time of PET is longer, and its balance torque is smaller compared to HDPE. It is the result of the



**Figure 2** FTIR spectra of HDPE, PET, EBAGMA, and HDPE/PET/EBAGMA blend: (a) HDPE; (b) PET; (c) EBAGMA; and (d) HDPE/PET/EBAGMA (90/10/5).



**Figure 3** Torque variation as a function of mixing time at 260°C for HDPE, PET, and HDPE/PET blends: (1) PET, (2) HDPE/PET (90/10), (3) HDPE/PET/EBAGMA (90/10/5), and (4) HDPE.

**TABLE I**  
**Values of the Balance Torque and Plasticizing Time**  
**of the Samples**

HDPE/PET/ EBAGMA	Plasticizing time (s)	Balance torque (N m)
100/0/0	65	14.8
0/100/0	100	0.5
90/10/0	120	10.1
90/10/3	80	12.9
90/10/5	65	13.8
90/10/8	45	15.5

molecular chain rigidity, high melting point, and narrow processing temperature of PET. However, the balance torque of the HDPE/PET binary blend is between the two homopolymers, whereas, the plasticizing time increases, which means that blending of HDPE and PET possesses the bad processability due to the incompatibility of them. After adding the reactive compatibilizer EBAGMA, the plasticizing time decreases and the balance torque increases with increasing the content of EBAGMA. It indicates that the addition of EBAGMA promotes the processing rheological properties of the HDPE/PET blends. Because the balance torque is associated with melt viscosity during processing, the increase of torque may be accounted for the improvement of interactions between PET and HDPE due to the effect of reactive compatibilization. Consequently, the interfacial adhesion between two phases of the blends is strengthened evidently, causing the increase in balance torque and reduce in plasticizing time. Therefore, the molding processing properties of the blends could be improved in certain degree.

### Capillary rheological properties

#### Melt flow curve

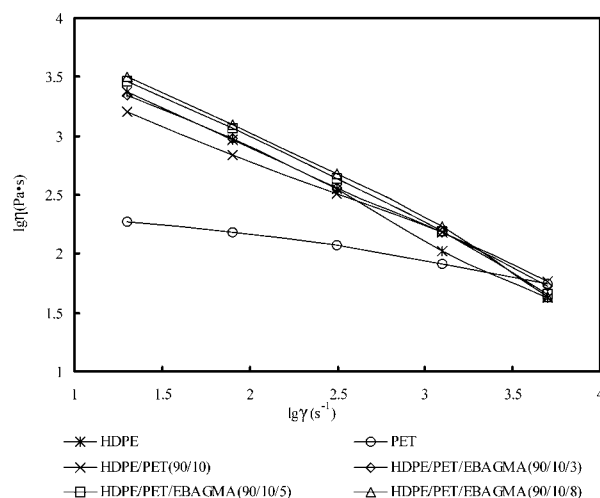
Figure 4 shows logarithmic plots of melt viscosity versus shear rate at 260°C for HDPE, PET, and HDPE/PET/EBAGMA blends. It is evident that the melt viscosity decreases with increasing the shear rate, indicating that the melts of all these samples belong to pseudoplastic fluids and have the flow properties of shear thinning and conform to the equation of power-law fluid. As shown in Figure 4, the shear thinning of pure PET is less than pure HDPE and other blends. It can be ascribed that the molecular chains of PET are rigid and hence hard to tangle each other, whereas HDPE with flexible chains possesses much more entanglements than PET. With the addition of EBAGMA, it can also be found that the melt viscosity increases with an increase of the compatibilizer content within the low shear rate range due to the improvements of phase

structure and interfacial adhesion between PET and HDPE.

In addition, as shown in Figure 4, the sensitivity of melt viscosity to shear rate of the compatibilized blends is stronger than the uncompatibilized blends, especially at the range of high shear rate. This can be explained for these reasons as follows: first, the phase interface of the compatibilized blends is difficult to be destroyed in the region of lower shear rates because of the strong chemical interactions between the two phases. With increasing the shear rate, it becomes easy to be broken up, especially in the high shear rate region. Second, the terpolymer EBAGMA itself is a flexible polymer and possesses a high sensitivity of melt viscosity to shear rate. As a result, the sensitivity of melt viscosity to shear rate increases with the addition of EBAGMA indicating that the melt rheological properties of the compatibilized HDPE/PET blends can be improved by changing the shear rate. Meanwhile, the improvement of rheological processing properties of the blends can also be observed by the phenomenon of the rough surfaces of extruded uncompatibilized blends compared to the smooth surfaces of extruded blends compatibilized by EBAGMA in the melt extrusion processing.

#### Flow behavior index

The melt flow behavior can be described by power law, which is expressed as  $\eta = K\dot{\gamma}^{n-1}$ . Table II shows the flow behavior index ( $n$ ) values at 260°C calculated by using the equation.  $n < 1$  is a characteristic of non-Newtonian, that is, the pseudoplastic behavior of the blends. Values of  $n$  decrease with an increase of shear rate and/or EBAGMA content implying the shear sensitivity increases (see Table II).



**Figure 4** Melt viscosity of HDPE, PET, and the blends as a function of shear rate at 260°C.

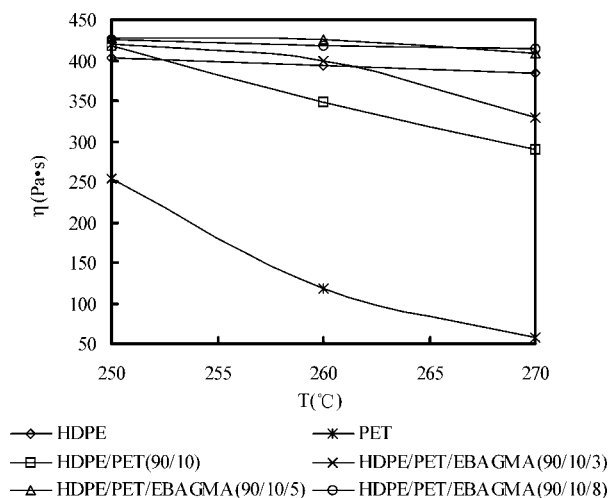
**TABLE II**  
 Values of Flow Behavior Index  $n$  of the Samples at 260°C

HDPE/PET/ EBAGMA	Flow behavior index ( $n$ )				
	20 s <sup>-1</sup>	80 s <sup>-1</sup>	300 s <sup>-1</sup>	1300 s <sup>-1</sup>	5000 s <sup>-1</sup>
100/0/0	0.37	0.32	0.27	0.22	0.17
0/100/0	0.64	0.59	0.54	0.49	0.45
90/10/0	0.54	0.48	0.42	0.36	0.30
90/10/3	0.48	0.41	0.34	0.27	0.19
90/10/5	0.45	0.38	0.31	0.24	0.17
90/10/8	0.38	0.33	0.27	0.21	0.15

This indicates that the shear rate and EBAGMA content both increase the pseudoplasticity of the blending melts, which is consistent with the conclusions drawn from Figure 4.

#### Flow activation energies

Controlling the processing temperature is an important means to regulate the flowability of polymer melts. In general, melt viscosity of polymer decreases monotonously with an increase in the temperature. The melt viscosity of the blends as a function of temperature at the shear rate (values at 300 s<sup>-1</sup>, see Fig. 5) from 250 to 270°C demonstrated that increasing temperature improves the flow behavior of the melts. It is due to the fact that when the temperature increases, the melt free volume increases, causing an enhancement of chain segments motion and a reduction of interactions between chain segments. As a result, the melt viscosity decreases with the increase in the temperature. However, the effect of temperature on melt viscosity is also dependent on the shear rate, which will be discussed in a subsequent section.



**Figure 5** Melt viscosity of HDPE, PET, and the blends as a function of temperature at the shear rate of 300 s<sup>-1</sup>.

**TABLE III**  
 Activation Energies of the Samples at Various Shear Rates

HDPE/PET/ EBAGMA	$E_{\eta}$ (kJ/mol)			
	20 s <sup>-1</sup>	80 s <sup>-1</sup>	300 s <sup>-1</sup>	1300 s <sup>-1</sup>
100/0/0	14.47	13.05	5.40	2.82
0/100/0	502.81	474.62	176.03	103.10
90/10/0	88.47	69.51	43.32	30.52
90/10/3	68.18	45.4	29.02	25.69
90/10/5	28.44	22.78	5.40	4.66
90/10/8	7.82	8.40	3.33	1.50

The temperature dependence of melt viscosity can be stated using the following Arrhenius equation:

$$\eta = Ae^{E_{\eta}/RT} \quad (1)$$

where  $\eta$  is the melt viscosity,  $A$  is a constant related to the structure, and  $E_{\eta}$ ,  $R$ , and  $T$  are the activation energy for viscous flow, universal gas constant, and absolute temperature, respectively. Flow activation energy,  $E_{\eta}$  at the different shear rate, which can be calculated from the slope obtained by linear regression of  $\ln \eta$  versus  $1/T$  drawn from Figure 5 is shown in Table III.

$E_{\eta}$  is the energy that needs to be consumed for breaking up the interactions among the chain segments when the melt flows. It reflects the dependence of melt viscosity on temperature. The higher the  $E_{\eta}$  is, the more pronounced the dependence is. As shown in Table III, it is clear that the activation energy for viscous flow decreases with increase in shear rate. It is assigned to the reason that the shearing favors destroying the coupling point of the entanglement structures of components and the interactions between two phases of the blends. Meanwhile, the activation energy decreases as the EBAGMA content from 0 to 8 phr, implying that the temperature sensitivity of the blends decreases due to the chain flexibility of EBAGMA. Obviously, the compatibilized blends can achieve a steady flow within a wider range of temperature and facilitate the blends molding processing.

## CONCLUSIONS

1. The addition of the reactive compatibilizer EBAGMA to the HDPE/PET blends increases the interactions between two phases progressively and improves the phase dispersion of the blends, due to the epoxy groups of EBAGMA react with the hydroxyl and carboxyl groups of PET in the melt extrusion processing.
2. The balance torque of the HDPE/PET/EBAGMA blends increases with an increase in the EBAGMA content, and the plasticizing time

is shortened, which improves the processing rheological properties of the blends.

3. The capillary rheological test showed that the melts of HDPE/PET/EBAGMA blends behave pseudoplasticity. Increasing the EBAGMA content, the melt viscosity and the sensitivity of viscosity to shear rate increase, whereas the flow behavior index decreases.
4. The activation energy for viscous flow reduced with an increase in both EBAGMA content and shear rate.

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