Effect of Mixing Conditions on the Rheological and Optical Properties of Chemically Modified Poly(ethylene terephthalate-*co*-ethylene isophthalate)

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ABSTRACT: The optical properties and rheological properties were studied for binary reactive blends composed of poly(ethylene terephthalate-*co*-ethylene isophthalate) [P(ET–EI)] and a styrene–acrylate based copolymer with glycidyl functionality. The blade rotation speed in the internal mixer greatly affected the structure and properties for the blend system. Intensive mixing at a high rotation speed enhanced the optical transparency because of the reduced particle size of the dispersed phase. The graft copolymer generated by the reaction between P(ET–EI) and the modifier was responsible for the fine morphology. Furthermore, the copolymer also enhanced the elastic nature in the molten state because it acted as a long-chain branched polymer. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 107: 2665–2670, 2008

Key words: blends; mixing; polyesters; rheology; structure–property relations

INTRODUCTION

Reactive modification is one of the most important technologies for polyesters, such as poly(ethylene terephthalate) (PET), poly(butylene terephthalate) (PBT), and biomass-based polyesters, for enhancing their processability and mechanical properties.[1–4] It is known that transesterification reaction often occurs in blends containing PBT because the residual titanium-based catalyst in PBT is still active in many cases.[2] According to intensive studies on PBT/polycarbonate blends carried out by Devaux and coworkers,[2,5–7] transesterification was detected by infrared spectroscopy, NMR, and solubility in methylchloride. Furthermore, the resultant blends showed dimensional stability, excellent heat resistance, and high levels of impact strength.

Some PET blends have also shown transesterification, although the possibility is significantly lower than that in PBT blends. Suzuki et al.[8] and Wang et al.[9] found that morphology in blends of PET and polycarbonate was dependent on the mixing conditions, that is, the degree of the transesterification. According to these authors,[8,9] prolonged mixing enhanced the reaction and, thus, the homogenization of the phase-separated structure. Similar results were reported by Kanoh et al.[10] for the rheological characterization of binary blends of PET and polyester-based polyurethane. Furthermore, Ignatov et al.[11] demonstrated that only one-step extrusion was enough to produce a compatibilized blend when a catalyst was used. With regard to the catalyst for the transesterification reaction, Yoda[12] carried out pioneering studies and found that acetate compounds with various metals, such as Zn, Pb, Hg, and Co, were quite effective in the reaction. Recently, it has been learned that titanium catalyst, which was not studied by Yoda, is one of the most effective catalysts.[3,6,11,13] Furthermore, it has been reported that the addition of certain phosphites can be used to control the reaction.[3,7,11] Such kinds of techniques on reaction control will make it possible to use transesterification for the material design of high-performance polyesters.

Furthermore, terminal hydroxyl and carboxyl groups of polyesters can be used as reactive sites with various types of functionalities, such as glycidyl, isocyanate, maleic acid, and oxazoline.[1–3] In particular, various reactive compounds with at least two functional groups capable of addition reactions with hydroxyl or carboxyl groups are frequently used to enhance the elastic nature of molten resins because poor melt elasticity is one of the most serious problems for polycondensation polymers and biomass-based polyesters.[4,14,15] The reactive compounds are sometimes called *melt-strength enhancers* or *chain extenders.* Bikiaris, Karayannidis, and coworkers[16–19]

studied the chain extension of PET and PBT with glycidyl compounds. Xanthos and coworkers[18–21] studied extensively the rheological properties of PET mixed with various reactive compounds and successfully obtained modified PET with a high melt strength, which was available for extrusion foaming.

In our previous article,[22] we showed that the rheological properties of poly(ethylene terephthalate-co-ethylene isophthalate) [P(ET–EI)] were greatly modified by the addition of a small amount of styrene–acrylate based copolymer with glycidyl functionality. Furthermore, the enhanced melt elasticity was attributed mainly to the generation of long-chain branches, which was contrary to previous work on PET with pyromellitic dianhydride,[23] one of the most popular chain extenders. Because of the generation of long-chain branches, heat sagging was reduced, and the Barus effect was prominent at extrusion.[22] We also found in our previous study that the addition of the reactive modifier, however, caused a loss of transparency in the extrudates, which was due to light scattering from the dispersed particles with different refractive indices.[22,24]

In this study, the relation between the mixing conditions in an internal mixer and the structure of the blend was investigated in detail to design a high-performance polyester with good transparency and appropriate rheological properties.

EXPERIMENTAL

Sample preparation

The polymers used in this study were P(ET–EI) with 20 wt % ethylene isophthalate and styrene–acrylate based copolymer with glycidyl functionality commercially available from Toagosei (Arufon UG4030) (Tokyo, Japan). The epoxy equivalent was 1.8 mequiv/g. The molecular weights of the materials as a polystyrene standard were as follows: number-average molecular weight (M_n) = 5.5×10^4 and weight-average molecular weight (M_w) = 8.7×10^4 for P(ET–EI) and $M_n = 5.1 \times 10^3$ and $M_w = 1.5 \times 10^4$ for the modifier. Moreover, the refractive indices of the materials, evaluated by an Abbe refractometer (Atago, NRA-IT Tokyo, Japan), were as follows: 1.575 for P(ET–EI) and 1.530 for the modifier. Furthermore, as demonstrated in a previous article,[22] the fully molten state was obtained at 210°C for P(ET–EI).

The melt mixing of P(ET–EI) with 1, 4, and 10 wt % modifier was performed by an internal batch mixer (Toyoseiki, Labo-plastmill, Tokyo, Japan) at various blade rotation speeds: 30, 60, 90, and 120 rpm. The temperature in the mixer was controlled at either 210 or 240°C. Furthermore, the residence time in the mixer was 3 or 10 min. Before mixing, both materials were dried *in vacuo* at 90°C for 2 h. The obtained blends were compressed into flat sheets with 0.3 mm thickness by a

compression-molding machine (Tester Sangyo, table-type test press SA-303-I-S) at 210°C and at 10 MPa.

Measurements

The optical transparencies of the sheets were evaluated at room temperature by a haze machine (Toyoseiki, direct reading haze meter). *Haze* is defined as the percentage of total transmitted light passing through the specimen that is scattered from the incident beam by more than 2.5°; it is often used in industry as a measure of the turbidity of a film specimen.

The morphology of the blends was examined by scanning electron microscopy (SEM; Hitachi, S4100, Tokyo, Japan). Fractured surfaces of the blend samples were prepared by breaking in liquid nitrogen and sputter coating with Pt–Pd.

The oscillatory shear moduli, such as storage modulus (G') and loss modulus (G''), were measured by a cone-and-plate type rheometer (UBM, MR500) (Mukoh, Japan) at 210°C under a nitrogen atmosphere.

Furthermore, the drawdown force was measured with a capillary rheometer (Yasudaseiki, 140 SAS-2002) (Nishinomiya, Japan), equipped with a circular die with the following dimensions: length = 8 mm, diameter = 2.095 mm, and entrance angle = $\pi/2$. The temperature in the capillary reservoir cylinder and the die was kept at 210°C, and the down speed of the plunger was 10 mm/min, which yielded a 6.28-s^{-1} shear rate. An extruded strand was vertically pulled through a tension detector (Nidec-Shimpo, tension meter PLS) (Nishinomiya, Japan) by a set of rotating wheels at a rate of 40 m/min; this corresponded to a draw ratio of about 20. The detailed conditions are described in ref. 15.

The molecular weight and its distribution of the blends were investigated by gel permeation chromatography (GPC; Tosoh, HLC-8020, Tokyo, Japan) with TSK-GEL GMHXL (Tosoh, Tokyo, Japan) as a polystyrene standard. In GPC measurements, the sample was first dissolved into hexafluoroisopropanol at a concentration of 10 mg/mL. Then, the solution was diluted by chloroform at a concentration of 1 mg/mL. The measurements were carried out by injection of the diluted solution at 40°C at a flow rate of 1.0 mL/min.[22]

RESULTS AND DISCUSSION

Effect of the blade rotation speed

In our previous study,[22] we demonstrated that a small amount of the modifier enhanced the elastic properties in the molten state and consequently depressed heat sagging at extrusion. The extruded strand, however, lost optical transparency, which restricted the applications. In this study, therefore, the effect of blade rotation speed on the transparency was investigated first. Figure 1 shows the haze level for the sam-
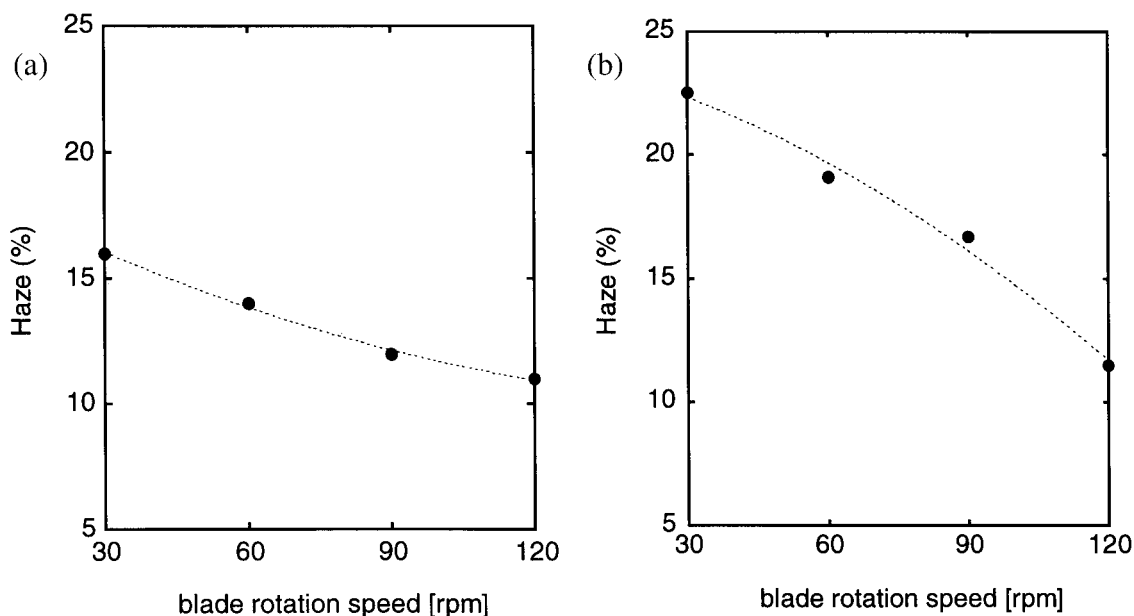
Figure 1 Haze values for the blends with (a) 1 and (b) 4 wt % modifier as a function of the blade rotation speed.

ples prepared at various blade rotation speeds in the internal mixer at 210°C for 3 min.

It was clear that the high-speed mixing enhanced the transparency to a great extent regardless of the modifier content. Furthermore, the haze values of the blends with 10 wt % modifier were 66.8% at 30 rpm and 17.8% at 120 rpm.

The effect of the modifier content on the transparency was quite significant when the blade rotation speed was low. On the other hand, the blends obtained at high shear conditions showed relatively low values of haze. In particular, the haze level of the blend with 1 wt % modifier at 120 rpm (11.0%) was close to that of the pure P(ET–EI) (10.2%).

The light scattering resulting from the dispersed particles with different refractive indices was responsible for the light scattering.[24–28] Figure 2 shows SEM pictures for the blends containing 4 and 10 wt % modifier. As shown in the figure, the samples prepared at low shear rates had larger dispersed particles regardless of the modifier content. Although the number of dispersed particles increased with the modifier content, the size of the particles was not so different as long as the blade rotation speed was the same, which suggests that the shear rate played a dominant role in the morphology. The particle size obtained at 120 rpm was approximately 100 nm regardless of the modifier content, which was smaller than the wavelength of visible light. This was responsible for the transparency.

The rheological properties of the obtained samples were evaluated by a cone-and-plate rheometer and a capillary rheometer equipped with a tension detector. Figure 3 shows the frequency dependence of the oscillatory shear moduli at 210°C for the blends with 4 wt

% modifier. With increasing blade rotation speed, G' greatly increased, especially at low frequencies with slight enhancement of G'', which indicated the generation of a prolonged relaxation time mechanism. The enhancement of the elastic nature, which is necessary for various processing techniques such as film processing, foaming, blow molding, and thermoforming, was well demonstrated by the plot of G' versus G'' as illustrated in Figure 4. This plot, called a *Cole–Cole plot*, was originally used for dynamic dielectric properties by Cole and Cole[29] and was then used for viscoelastic properties considering the analogy.[30] In this figure, the data located upper region demonstrate strong elasticity compared to viscosity.[30,31]

Furthermore, the blade rotation speed drastically affected the drawdown force, as shown in Table I. In the case of the samples blended at high rotation speeds, stretching could not be carried out at a draw ratio of 20 because the extruded strand exhibited brittle rupture due to high elongational stress. The considerable increase in the drawdown force was attributed to the marked strain-hardening behavior in elongational viscosity.[32–35]

As demonstrated, the blends obtained at high blade rotation showed excellent transparency and high levels of drawdown force.

To clarify the mechanism of the rheological change, GPC measurements were carried out. As a result, it was confirmed, but is not presented here, that the GPC curves of the modified P(ET–EI) were almost the same as that of the pure P(ET–EI) regardless of the mixing conditions. Consequently, the average molecular weights were almost independent of the blade rotation speed, as shown in Figure 5. The experimental results suggest that the enhancement of melt elas-
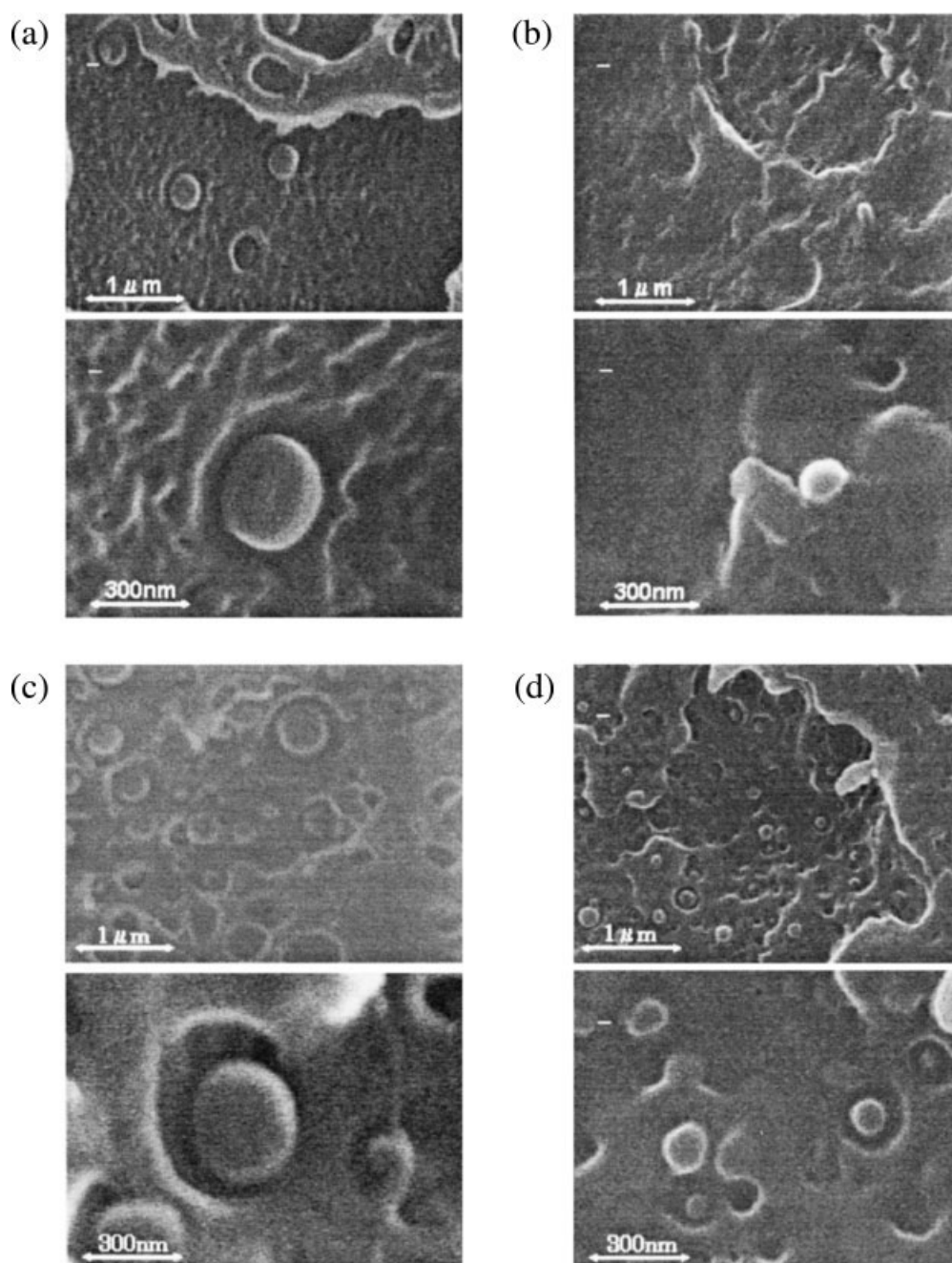
Figure 2 SEM pictures of the blends: (a) 4 wt % at 30 rpm, (b) 4 wt % at 120 rpm, (c) 10 wt % at 30 rpm, and (d) 10 wt % at 120 rpm.

ticity by the modifier was mainly due to the generation of long-chain branches, as discussed in our previous article.[22]

Effects of other mixing conditions

The obtained results demonstrate that the blade rotation speed had a great effect on the morphology and, thus, the optical and rheological properties and processability. The mixing at high blade rotation speed provided the following situations:[36–38] (1) an increase in the degree of distributive mixing (extensive mixing), in which applied strain had a decisive role due to the large strain (products of shear rate and residence time); (2) an increase in the degree of dispersive mixing (intensive mixing), in which applied stress had a decisive role due to a high level of applied stress; and (3) an increase in the resin temperature due to viscous dissipation that was proportional to the products of shear stress (σ) and shear viscosity (η), that is, $\sigma\eta = \eta\dot{\gamma}^2$, where $\dot{\gamma}$ is the shear rate. To clarify the effect of high-speed mixing, further experiments on the following were carried
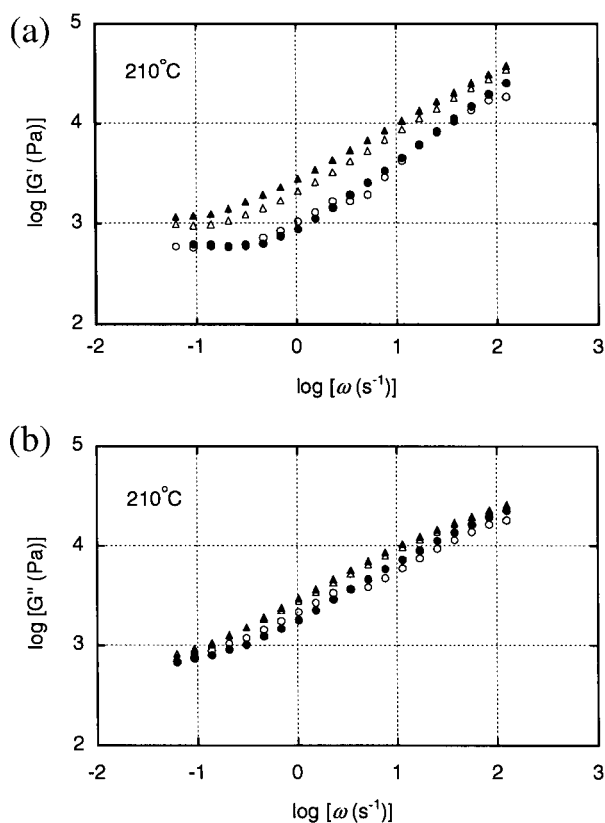
Figure 3 Frequency ω dependences of (a) G' and (b) G'' for the blends with 4 wt % modifier mixed at various blade rotation speeds: (○) 30, (●) 60, (△) 90, and (▲) 120 rpm. The temperature was 210°C.

out: (1) the effect of the residence time in the mixer to check the effect of distributive mixing, that is, applied total strain, and (2) the effect of resin temperature in the internal mixer.
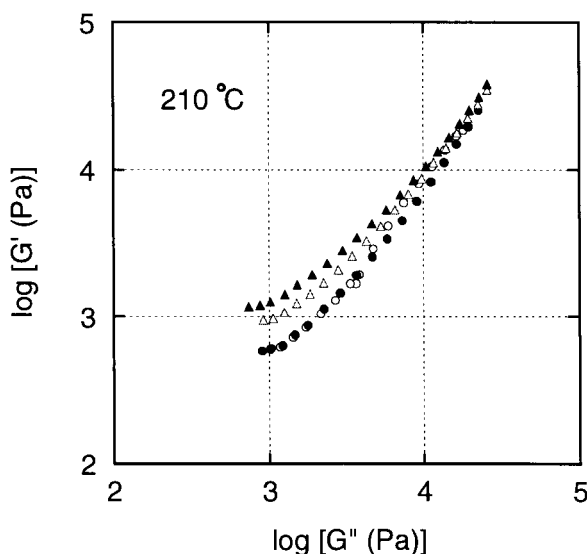
TABLE I
Drawdown Force for the Samples Obtained at Various Blade Rotation Speeds

Modifier content (%)	Blade rotation speed (rpm)	Drawdown force (mN)
0	30	15[a]
1	30	45[a]
1	60	60[a]
1	90	105[a]
1	120	105[a]
4	30	600[b]
4	60	1500[b]
4	90	>2000[c]
4	120	>2000[c]

[a] The draw ratio was 20.
[b] The draw ratio was 5.
[c] The draw ratio was 2.

Table II shows the haze values for the samples with 4 wt % modifier mixed at various conditions. The table indicates that both mixing time and temperature had little or no effect on the optical transparency, that is, morphology. Therefore, we concluded that the dispersive mixing was required to produce the transparent products. The dispersive mixing, which led to a large deformation and/or breakup of dispersion, was responsible for the contact of an immiscible pair of P(ET–EI) and the modifier, which accelerated the reaction between them. In other words, intensive stress was required to overcome the interfacial tension between the polymers and/or the cohesive force of the dispersed particles. The generated graft copolymer played an important role as the compatibilizer, which led to a finer morphology. Furthermore, the
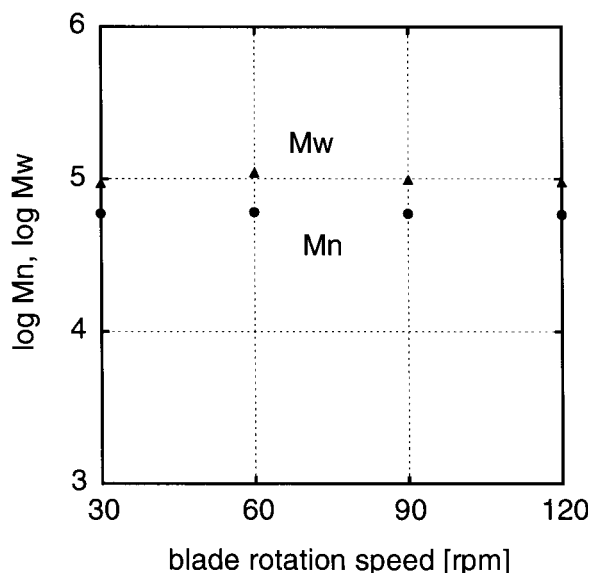

Figure 4 Cole–Cole plot for the blends with 4 wt % modifier mixed at various blade rotation speeds: (○) 30, (●) 60, (△) 90, and (▲) 120 rpm.

Figure 5 Effect of the blade rotation speed on (●) M_n and (▲) M_w for the blends with 4 wt % modifier.

TABLE II
Haze Values for the Samples Obtained Under Various Mixing Conditions

Mixing temperature (°C)	Mixing time (min)	Haze (%)
210	3	15.0
210	10	13.2
240	3	16.0

The modifier content was 4 wt %.

graft copolymer, in which graft chains acted as long-chain branches, enhanced the melt elasticity to a great extent.

CONCLUSIONS

The effect of the mixing conditions, such as blade rotation speed, resin temperature, and residence time in the mixer, on its structure and properties were studied for P(ET–EI) modified by a styrene–acrylate based copolymer with glycidyl functionality. The optical transparency was greatly improved by mixing at a high blade rotation speed in an internal mixer, which was attributed to the depression of the dispersed particle size. Furthermore, the transparent blends also exhibited a high level of melt elasticity, such as drawdown force. As a result, the high-speed mixing was preferred from the viewpoints of rheological properties, that is, processability, and the optical properties. This was due to the enhancement of dispersive mixing, which led to more contacts between both phases and, thus, the reaction.

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