

# An investigation on recycled PET/PP and recycled PET/PP-EP compatibilized blends: Rheological, morphological, and mechanical properties

# Adriana Martinelli Catelli de Souza, Caren Barbosa Caldeira

Materials Engineering Department, Centro Universitário da FEI, São Bernardo do Campo, São Paulo, Brazil Correspondence to: A. Souza (E-mail: amcsouza@fei.edu.br)

**ABSTRACT:** The effectiveness of P(E-*co*-MA-*co*-GMA) as a compatibilizer for recycled PET/PP and recycled PET/PP-EP (polypropylene (ethylene-propylene) heterophase copolymer) blends was investigated by means of morphological (scanning electron microscopy), rheological (small amplitude oscillatory shear), mechanical (tensile, flexural and impact tests), and thermal (differential scanning calorimetry) properties. Compatibilizer concentration ranged from 1 to 5 wt % with respect to the whole blend. All blends were obtained in a 90/10 composition using a twin screw extruder. Compatibilization effects for PETr/PP-EP were more pronounced due to ethylene segments present in both PP-EP and P(E-*co*-EA-*co*-GMA). PETr/PP-EP has shown greater dispersed phase size reduction, a more solid-like complex viscosity behavior and larger storage modulus at low frequencies in relation to PETr/PP blend. For both investigated blends, mechanical properties indicated an improvement in both elongation at break and impact strength with increasing compatibilizer content. PETr/PP-EP blends showed improved performance for the same level of compatibilizer content. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41892.

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# INTRODUCTION

Due to their ability to combine the properties of their components in a unique product, polymer blends have proven to be one of the most efficient ways to satisfy new requirements for materials properties.<sup>1</sup> Nowadays, research in polymer blends focuses mainly on blends containing engineering plastics, biodegradable polymers, recycled polymers, and the fundamental understanding of how to control the morphology of these materials, as the properties of these materials are directly related to their morphology.

Poly(ethylene therephthalate) (PET) is one of the most recycled plastics in the world due to its wide range of applications: textiles, carpets, bottles, packaging, films, and so forth. PET recycling has several advantages as compared to other polymers from the standpoint of energy consumption, water consumption, environmental impact, social benefits, among others. However, PET chains present ester groups which are extremely hygroscopic and a dimethylene sequence which is highly reactive with oxygen above the PET melting temperature. As a consequence, recycled PET undergoes hydrolytic and thermal degradation<sup>2,3</sup> resulting in a decrease in molar mass that, in turn, deteriorates thermal, rheological and mechanical properties.<sup>4</sup> In the case of mechanical properties, impact resistance is highly affected.

Some studies have reported that mixing PETr with other polymers, polyolefins for example, can be an alternative to improve its properties.  $^{5-10}$ 

Unfortunately, PET and polyolefins are immiscible resulting in blends with poor adhesion among its phases, coarse morphology, and consequently poor mechanical properties. The compatibility of these blends can be improved commonly by reactive compatibilization processes where copolymers can be formed in situ during melt-blending by using suitable polymers containing functional groups (e.g., carboxyl, anhydride, epoxy, etc.) capable of reacting with PET end groups.<sup>7,11</sup> Several studies have shown that copolymers containing epoxy functions present the strongest compatibilizing effect as compared to polymer bearing maleic anhydride or acrylic acid functions. The epoxy functions can react with hydroxyl and carboxyl end groups of PET while maleic anhydride and acrylic acid functions only react with the hydroxyl functions.<sup>11</sup> Moreover, PET/polyolefin compatibilization will be more effective if the compatibilizer presents compatible molecular segments with polyolefin molecules.

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Polymer/copolymer	Trade name	Manufacturer	Wt %	Melt flow index (g/10 min)	Density (g/cm <sup>3</sup> )	Zero shear stress viscosity (Pa.s)
PP homopolymer	HP 550K	Braskem	-	3.5ª	0.905	1843
PP-EP heterophase Copolymer	EP 200K	Braskem	Ethylene: 12.5 to 13.5	3.6ª	0.903	1798
P(E-co-MA-co-GMA)	Lotader AX 8900	Arkema	MA:24 GMA:8	6.0 <sup>b</sup>	0.940	-
PETr	-	Clodam	-	21.0 <sup>c</sup>	1.330	91

Table I. Main Characteristics of the Polymers Used in this Study

<sup>a</sup>2.16 kg/230°C.

<sup>b</sup>2.16 kg/190°C.

°2.16 kg/260°C.

Some studies regarding PETr/PP, PETr/PE, and PETr/ ethylenepropylene rubber (EPR) blends have been conducted.<sup>5–14</sup> Nevertheless, no study about PET/polypropylene (ethylene-propylene) heterophase copolymer (PP-EP) has been addressed. PP-EP heterophase copolymer consists mainly of a polypropylene matrix with embedded ethylene–propylene copolymer domains.<sup>15,16</sup>

The aim of this work is a comparative investigation on P(E-*co*-EA-*co*-GMA) effectiveness as a compatibilizer for recycled PET (PETr)/PP and recycled PET (PETr)/PP-EP blends. A systematic blend morphologies investigation, as well as their influences on the rheological and mechanical properties, was performed to establish the correlation of ethylene sequences presence both in the compatibilizer and the polyolefin (in the case of PETr/PP-EP blend) or just in the compatibilizer (in the case of PETr/PP blend).

# EXPERIMENTAL

# Materials

Recycled material from PET bottles (PETr) (supplied by Clodam, Brazil) (as matrix) and commercial grade polypropylene (PP) and polypropylene (ethylene-propylene) heterophasic copolymer (PP-EP) (supplied by Braskem, Brazil) (as dispersed phase) as well as a compatibilizer Poly(ethylene-*co*-methyl acrylate-*co*-glycidyl methacrylate (P(E-*co*-EA-*co*-GMA), type Lotader AX 8900, commercial product of Arkema (France) were used. Table I summarizes the main characteristics of the polymers used in this study.

Table	II.	Composition	of	PETr/PP-EP	and	PETr/PP	Blends

Blend	PETr (wt %)	PP (wt %)	PP-EP (wt %)	P(E-co-MA-co-GMA) (wt %)
PETr/PP-EP	90	-	10	-
PETr/PP-EP/1L	89	-	10	1
PETr/PP-EP/3L	87	-	10	3
PETr/PP-EP/5L	85	-	10	5
PETr/PP	90	10	-	-
PETr/PP/1L	89	10	-	1
PETr/PP/3L	87	10	-	3
PETr/PP/5L	85	10	-	5

# **Experimental Procedures**

PETr/PP and PETr/PP-EP blends were prepared in a Haake PolyLab 900/Rheomix PTW16 twin-screw extruder (Haake—Germany). The temperature profile, starting from the feeding zone to the die, was 250, 260, 270, 270, 260, 245°C and the rotation speed of the screws was 150 rpm. Both the genuine blends and the ones to which the copolymer was added were prepared in two steps. The compatibilizer was first mixed with the minor phase (PP or PP-EP). PP homopolymer and PP-EP copolymer were subjected to the same processing in order to undergo the same thermo mechanical history. Next, the first mixture was added to PETr (matrix) according to proportions shown in Table II. Prior to extrusion, PETr was dried at 150°C for approximately 6 h.

Samples for tensile (ASTM D-638, Type I), flexural and impact tests were obtained by injection molding (Battenfeld HM 60/ 350—Austria) using the same injection conditions for all investigated blends in this work (heating cylinder temperature profile of 245–280°C; injection pressure: 65 MPa; mold temperature: 50°C).

Tensile and flexural tests were performed at room temperature using an Instron 5567 universal tester, according to standard conditions (ASTM D-638 and ASTM D-790, respectively). Charpy impact tests were performed using notched samples according to ASTM D256 (pendulum weight of 2.19 kg). For all mechanical tests conducted, at least 10 specimens of each material were tested. All samples were conditioned for one week at 23°C and 50% relative humidity prior to testing.

Blend morphologies were characterized by scanning electron microscopy (SEM) using a CanScan model CS3200LV microscope (England). Fracture surfaces from impact tests were analyzed. The samples were coated with gold using an Edwards sputter coater. Several micrographs were taken for each blend. Dispersed phase diameter distribution was characterized by measuring the diameter of about 800 particles for each sample using Analysis-Olympus software. To calculate the average diameter, Saltikov's correction was used.<sup>17</sup>

Differential scanning calorimetry (DSC) tests were carried out using a TA Instruments calorimeter DSC-Q20 under a nitrogen atmosphere. Samples taken from impact test specimens were heated at a scanning rate of 10°C/min from 25 to 280°C. DSC



data from the first heating cycle were considered, because blend mechanical properties are determined by crystallinity obtained during the injection molding cycle.

PP degree of crystallinity  $(X_c\%)$  was determined according to:

$$X_c \% = \frac{\Delta H_m}{\Delta H_{\rm mo} \times \omega} \times 100\% \tag{1}$$

where  $\Delta H_m$  is the measured enthalpy of melting,  $\omega$  the weight fraction of the blend components and  $\Delta H_{\rm mo}$  the enthalpy of melting of 100% crystalline polymer. The enthalpy of melting of 100% crystalline PP was considered 208 J/g.<sup>18</sup> The PP-EP degree of crystallinity was not calculated since EPR concentration in the block copolymer was not specified by the supplier.

In the case of PETr which presented a peak of cold crystallization during first heating DSC tests, the initial degree of crystallinity ( $X_c$ %) of PETr (related to PETr crystallization obtained during injection molding cycle) was determined according to:

$$X_c \% = \frac{\Delta H_m - \Delta H_{cc}}{\Delta H_{mo} \times \omega} \times 100\%$$
<sup>(2)</sup>

where  $\Delta H_{cc}$  is the measured enthalpy of cold-crystallization. The enthalpy of melting of 100% crystalline PET was considered 140 J/g.<sup>19</sup>

Dynamic frequency sweep tests were performed using a controlled strain rheometer ARES (TA Instruments) under dry nitrogen atmosphere at 270°C. A plate-plate configuration was used with a gap size of 0.9 mm and a plate diameter of 25 mm. The measurements were carried out in the linear viscoelastic region at frequencies from 100 to 0.1 rad/s. Prior to experiments, dynamic strain sweep tests were performed at 270°C for neat PP, PP-EP, and PETr samples and blends. The strain value was set at 5% to validate the linear viscoelastic region. In addition, time sweep tests for neat PP, PP-EP and PETr samples were performed at 270°C for 600 s (duration of dynamic frequency sweep tests). It was observed that the complex viscosity of these polymers remained constant throughout the period [.] examined, indicating thermal stability during the tests. Before all rheological experiments, the specimens were dried at 100°C for 24 h in a vacuum oven at approximately 100Pa.

Fourier transform infrared spectroscopy (FTIR) spectra were obtained using a Nicolet-560 FTIR spectrometer. Samples for infrared analysis were thin films prepared by hot pressing. Resolution of 2 cm<sup>-1</sup> and 32 scans were used.

# **RESULTS AND DISCUSSION**

### Reactive Compatibilization—FTIR Spectroscopy

Figure 1 shows FTIR spectra of P(E-*co*-EA-*co*-GMA), uncompatibilized PETr/PP-EP and compatibilized PETr/PP-EP at 5 wt % of P(E-*co*-EA-*co*-GMA). The absorption bands of the epoxy group (C-O-C) in P(E-*co*-EA-*co*-GMA; located at 846, 912, and 996 cm<sup>-1</sup>)<sup>20</sup> were not present in PETr/PP-EP compatibilized blend spectrum. This behavior could indicate that chemical reactions occurred between the epoxy group in P(E-*co*-EA-*co*-GMA) and hydroxyl (-OH) or carboxyl -COOH) in PETr, resulting in a P(E-*co*-EA-*co*-GMA)-*co*-PETr copolymer as described in Figure 2. Similar behavior was observed for PETr/PP blends.



**Figure 1.** FTIR spectra of P(E-*co*-EA-*co*-GMA), uncompatibilized PETr/PP-EP and compatibilized PETr/PP-EP at 5 wt % of P(E-*co*-EA-*co*-GMA).

In addition to chemical reactions between P(E-*co*-EA-*co*-GMA) and PETr, physical interactions may occur between PP or PP-EP and the ethylene segments of P(E-*co*-EA-*co*-GMA). The effects of these physical interactions on morphological, rheological, and mechanical properties of PETr/PP-EP and PETr/PP are discussed in the next sections.

# Morphological Characterization

All blends, compatibilized or not, presented droplet dispersion morphology. Figure 3(a,b) shows morphologies of uncompatibilized PETr/PP-EP (90/10) and compatibilized PETr/PP-EP (90/10) at 5 wt % of P(E-*co*-EA-*co*-GMA), respectively. Table III reports the volume average diameter  $(d_v)$ , the number average diameter  $(d_n)$ , and the polydispersity  $(d_v/d_n)$  for the different investigated blends.

The number average diameter  $(d_n)$  and the volume average diameter  $(d_v)$  were calculated from the following equations:<sup>21</sup>

$$d_n = \frac{\sum_i n_i d_i}{\sum_i n_i} \tag{3}$$

$$d_{\nu} = \frac{\sum_{i} n_{i} d_{i}^{4}}{\sum_{i} n_{i} d_{i}^{3}} \tag{4}$$

where  $n_i$  is the number of particles with diameter  $d_i$ .

The diameter reduction  $(d_v R \text{ and } d_n R)$  for a given compatibilizer concentration was calculated using the following equation:<sup>22</sup>

$$dR = \frac{d_o - d_c}{d_o} \times 100\% \tag{5}$$

where  $d_o$  is the average diameter of the dispersed phase of the uncompatibilized blend ( $d_{vo}$  or  $d_{no}$ ) and  $d_c$  is the average diameter of the dispersed phase of the blend at a given concentration **c** of the compatibilizer ( $d_{vc}$  or  $d_{nc}$ ). These values are shown in Table III.

For both PETr/PP-EP and PETr/PP blends, the dispersed phase average diameters ( $d_v$  and  $d_n$ ) and polydispersity decreased as a



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where X= -O- or -O-CH<sub>2</sub>CH<sub>2</sub>-O-

Figure 2. Possible reaction between P(E-co-EA-co-GMA) and PET.

function of increasing compatibilizer concentration. This behavior may be attributed to the presence of the compatibilizer that interacts with the blend components leading to interfacial ten-



Figure 3. PETr/PP-EP blends morphology: uncompatibilized (a), compatibilized at 5wt % P(E-*co*-EA-*co*-GMA) (b).

sion reduction and coalescence suppression. Although the dispersed phase diameter of the PETr/PP blends was initially smaller than PETr/PP-EP blends, the effectiveness of compatibilizer was more pronounced for PETr/PP-EP blends: the reduction in diameter was 58% for PETr/PP-EP blends compared to 49% for PETr/PP blends, both compatibilized with 5 wt % of P(E-*co*-EA-*co*-GMA). The polydispersity showed the same trend.

# **Rheological Characterization**

Figure 4(a,b) shows the storage (G), loss (G) moduli and the complex viscosity ( $\eta^*$ ), respectively, as functions of frequency at 270°C for the neat constituents of PETr/PP-EP and PETr/PP blends.

The rheological curves of PP and PP-EP presented the same magnitude. The zero shear stress viscosities of PP and PP-EP, determined using the rheological data fitted to Carreau's model<sup>23</sup> (Table I), presented similar values. The storage and loss modulus and the complex viscosity of PETr were lower than that of PP and PP-EP for the measured frequency range. PETr displayed a pseudo-Newtonian behavior for the whole frequency range and did not present the transition from a liquid-like to a solid-like behavior.

 Table III. Morphology Quantification for PETr/PP-EP and PETr/PP

 Blends

Blend	$d_{ m v}$ ( $\mu$ m)	d <sub>n</sub> (μm)	d <sub>v</sub> /d <sub>n</sub>	d <sub>v</sub> R (%)	d <sub>n</sub> R (%)
PETr/PP-EP	3.69	1.50	2.46	-	-
PETr/PP-EP/1L	2.76	1.35	2.05	25	10
PETr/PP-EP/3L	1.69	0.91	1.86	54	39
PETr/PP-EP/5L	1.54	0.86	1.78	58	43
PETr/PP	3.29	1.21	2.72	-	-
PETr/PP/1L	2.61	1.04	2.51	21	14
PETr/PP/3L	1.88	0.98	1.92	43	19
PETr/PP/5L	1.69	0.90	1.88	49	26





Figure 4. Storage (*G*), loss (*G*<sup>"</sup>) moduli (a) and the complex viscosity ( $\eta^*$ ) (b), as functions of frequency at 270°C for the neat constituents of the PETr/PP-EP and PETr/PP blends.

Figure 5(a,b) shows the storage modulus (*G*<sup>°</sup>) and complex viscosity ( $\eta^*$ ) as functions of frequency at 270°C, respectively, of uncompatibilized and compatibilized PETr/PP-EP and PETR/PP blends at P(E-*co*-EA-*co*-GMA) different concentrations. All blends presented an intermediate behavior between their components and did not present the transition from a liquid-like to a solid-like behavior, since at high frequencies, the matrix behavior is dominant. Compatibilized PETr/PP-EP and PETr/PP blends showed an increase in storage modulus with increasing compatibilizer concentration at low frequencies. This increase in elasticity has already been observed by several researchers in different compatibilized blends and is related to the role of compatibilizer in reducing dispersed phase size, narrowing the polydispersity, and inducing interactions, at the interface, between blend components.<sup>24–28</sup>

Comparing PETr/PP-EP and PETr/PP compatibilized blends at 1 wt % P(E-*co*-EA-*co*-GMA), storage modulus presented the same magnitude at low frequencies. For higher P(E-*co*-EA-*co*-GMA) concentrations (3 and 5 wt %), PETr/PP-EP blends showed the highest storage modulus at low frequencies when compared to PETr/PP blends for the same level of compatibilizer content.

Compatibilized PETr/PP-EP and PETr/PP blends showed an increase in complex viscosity with increasing compatibilizer concentration at low frequencies. The complex viscosity of uncompatibilized blends, PETr/PP-EP, and PETr/PP blends containing 1 wt % P(E-*co*-EA-*co*-GMA) presented a typical Newtonian plateau at low frequencies, whereas for higher P(E-*co*-EA-*co*-GMA) concentrations, the blends exhibited a shear thinning behavior. PETr/PP-EP blends compatibilized with 3 and 5 wt % P(E-*co*-EA-*co*-GMA) presented a stronger shear thinning effect



**Figure 5.** Storage modulus (G) (a) and the complex viscosity ( $\eta^*$ ) (b), as functions of frequency at 270°C of uncompatibilized and compatibilized PETr/PP-EP and PETr/PP blends at different P(E-*co*-EA-*co*-GMA) concentrations.

	PETr						PP-EP or PP		
	<i>T</i> <sub>g</sub> (°C)	T <sub>cc</sub> (°C)	$\Delta H_{\rm cc}$ (J/g)	T <sub>m</sub> (°C)	$\Delta H_m$ (J/g)	X <sub>c</sub> (%)	T <sub>m</sub> (°C)	$\Delta H_m$ (J/g)	X <sub>c</sub> (%)
PETr/PP-EP	69.4	124.0	26.0	248.4	44.9	15.0	165.0	6.8	-
PETr/PP-EP/1L	69.2	123.7	26.5	248.6	46.8	16.1	165.0	7.0	-
PETr/PP-EP/3L	68.5	122.9	27.0	248.2	49.4	17.8	164.9	7.0	-
PETr/PP-EP/5L	68.6	122.3	27.3	248.3	49.9	17.9	164.8	7.1	-
PETr/PP	69.7	128.7	25.8	247.9	44.8	15.1	161.8	7.2	34.6
PETr/PP/1L	69.4	128.2	26.1	248.1	46.9	16.5	162.0	7.0	33.7
PETr/PP/3L	68.7	127.1	27.0	248.0	50.1	18.3	161.7	7.1	34.1
PETr/PP/5L	68.5	127.0	27.0	248.2	50.0	18.3	161.6	7.2	34.6

Table IV. DSC Results of the First Heating Scan

as compared to PETr/PP blends. Good agreement exists between morphological observations and rheological response of blends studied.

The rheological behavior observed could indicate that ethylene segments present in both PP-EP and P(E-*co*-EA-*co*-GMA) copolymers enhanced interpolymer interactions in PETr/PP-EP blends, resulting in an increase in elasticity<sup>24–28</sup> and viscosity.<sup>29</sup>

# **Thermal Properties**

Table IV summarizes DSC results obtained during the first heating scan. T<sub>cc</sub> of PETr within PETr/PP-EP blends presented lower values as compared to  $T_{cc}$  of PETr within PETr/PP blends whereas the enthalpy of melting  $(\Delta H_m)$  of PETr within PETr/ PP-EP and PETr/PP blends did not present differences. The ethylene sequences affect  $T_{cc}$  of PETr, but do not promote an increase in crystallinity. For compatibilized PETr/PP-EP and PETr/PP blends, T<sub>cc</sub> of PETr and PETr degree of crystallinity presented a slight decrease and a slight increase, respectively, with increasing P(E-co-EA-co-GMA) concentration. This behavior might indicate that P(E-co-EA-co-GMA) copolymer acted as heterogeneous nucleating agent and increased PETr crystallization. No significant differences were observed in  $T_g$  and  $T_m$  of PETr within the blends. Probably, the slight increase in PETr degree of crystallinity was not sufficient to promote changes in these temperatures.  $T_m$  of PP within the blends presented lower values as compared to  $T_m$  of PP-EP. No differences were observed in  $T_m$  and in the enthalpy of melting  $(\Delta H_m)$  of PP-EP and PP within the blends containing P(E-co-EA-co-GMA), indicating that PP or PP-EP crystallization was not influenced by the presence of P(E-co-EA-co-GMA).

# **Mechanical Properties**

Table V presents the tensile, impact and flexural properties of PETr, PP-EP, PP neat polymers and Figures 6–9 present the

mechanical properties of PETr/PP and PETr/PP-EP blends as a function of P(E-*co*-EA-*co*-GMA) concentration.

Impact strength and elongation at break of PETr/PP-EP and PETr/PP blends increased with increasing P(E-*co*-EA-*co*-GMA) concentration, indicating its effectiveness as compatibilizer for the investigated blends. The elastomeric nature of P(E-*co*-EA-*co*-GMA) may also affect toughness and ductility. Located at the matrix/dispersed phase interface, P(E-*co*-EA-*co*-GMA) acted both as compatibilizer and softening agent.

When P(E-*co*-EA-*co*-GMA) was added to PETr/PP-EP blends, elongation at break and impact strength showed a marked increase as compared to those corresponding to compatibilized PETr/PP blends, where a slight increase was observed. This is another indication that the ethylene segments present in both PP-EP and P(E-*co*-EA-*co*-GMA) copolymers enhanced interpolymer interactions in PETr/PP-EP/P(E-*co*-EA-*co*-GMA) blends, leading to more compatible blends than PETr/PP/P(E-*co*-EA-*co*-GMA) blends. The morphology and the rheological curves observed for these blends corroborated this behavior. Similar behavior was observed by Martínez *et al.*<sup>30</sup> where a comparative study of PP/EVA and PP-EP/EVA blends showed that the presence of ethylene segments in both PP-EP and EVA resulted in a more efficient compatibilization.

Young modulus and yield strength values presented a decrease with increasing P(E-*co*-EA-*co*-GMA) concentration. This behavior could be explained by the elastomeric nature of P(E-*co*-EA-*co*-GMA) copolymer that acted as a softening agent. The copolymer could enhance plastic flow in the matrix caused by extensive interaction of shear stress fields around PP or PP-EP particles.<sup>31</sup> Consequently, the matrix could yield locally at lower stress than expected, resulting in a decrease in Young modulus and yield strength with increasing compatibilizer concentration.

Table V. Tensile, Impact, and Flexural Properties of PETr, PP-EP, and PP Neat Polymers

	Young modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (J/m)	Flexural modulus (MPa)	Flexural strength (at 5% def.) (MPa)
PETr	2672 (±162)	57.9 (±0.5)	>100	17.0 (±1.7)	2426 (±14)	87.3 (±0.5)
PP-EP	1135 (±125)	20.4 (±0.3)	>100	-	1003 (±10)	29.2 (±0.7)
PP	1295 (±112)	28.9 (±0.9)	>100	28.9 (±0.9)	1205 (±45)	39.4 (±1.2)





**Figure 6.** Tensile properties of PETr/PP and PETr/PP-EP blends as a function of P(E-*co*-EA-*co*-GMA) concentration: Young modulus and yield strength.



**Figure 7.** Tensile properties of PETr/PP and PETr/PP-EP blends as a function of P(E-*co*-EA-*co*-GMA) concentration: elongation at break.



**Figure 8.** Impact strength of PETr/PP and PETr/PP-EP blends as a function of P(E-*co*-EA-*co*-GMA) concentration.



**Figure 9.** Flexural properties of PETr/PP and PETr/PP-EP blends as a function of P(E-*co*-EA-*co*-GMA) concentration.

In this case, the softening effect was more effective than the increase in PETr crystallinity observed by DSC analysis. Similar observations were reported by Pracella *et al.*<sup>32</sup> on PET/PE/E-GMA, Friedrich *et al.*<sup>33</sup> on PET/PP/E-GMA, Chiu and Hsiao<sup>34</sup> on PET/PP/POE-g-MA and by Armat and Moet<sup>31</sup> on PA/PE/SEBS-MA.

Flexural modulus and flexural strength also decreased with increasing P(E-*co*-EA-*co*-GMA) concentration. The reduction in flexural properties could be again attributed to the elastomeric nature of P(E-*co*-EA-*co*-GMA) copolymer that acted as a softening agent for PETr/PP-EP and PETr/PP blends.

# CONCLUSIONS

In this study, a comparative investigation of morphological, rheological, and mechanical properties of PETr/PP and PETr/PP-EP blends compatibilized or not with P(E-*co*-EA-*co*-GMA) was performed.

P(E-*co*-MA-*co*-GMA) acted as a compatibilizer for PETr/PP and PETr/PP-EP blends, but its effectiveness as compatibilizer was more pronounced for PETr/PP-EP blends.

All blends, compatibilized or not, presented droplet dispersion morphology. For both PETr/PP-EP and PETr/PP blends, the dispersed phase diameters and polydispersity decreased as a function of increasing compatibilizer concentration. The reduction in droplet diameter of PETr/PP-EP compatibilized blends was more pronounced compared to PETr/PP blends for the same compatibilizer content.

At 3 and 5 wt % of P(E-*co*-MA-*co*-GMA), the complex viscosity of PETr/PP-EP blends exhibited a more solid-like behavior as compared to PETr/PP blends. PETr/PP-EP blends showed the largest storage modulus at low frequencies.

DSC studies revealed that P(E-*co*-EA-*co*-GMA) copolymer acted as heterogeneous nucleating agent for PETr, promoting a decrease in  $T_{cc}$  and a slight increase in crystallization. The slight increase in PETr crystallization was not sufficient to promote changes *in*  $T_g$  and  $T_m$  of PETr within the blends. PP or PP-EP crystallization was not affected by P(E-*co*-EA-*co*-GMA) addition.



The mechanical properties of PETr/PP and PETr/PP-EP blends were markedly affected by P(E-*co*-EA-*co*-GMA). Located at the matrix/dispersed phase interface, P(E-*co*-EA-*co*-GMA) acted both as compatibilizer and softening agent due to its elastomeric nature, resulting in a decrease in Young and flexural modulus, a decrease in yield and flexural strength and an increase in impact strength and elongation at break with increasing compatibilizer concentration. PETr/PP-EP blends showed improved performance in elongation at break and impact strength for the same compatibilizer content.

Morphological, rheological, and mechanical properties indicated that ethylene segments present in both PP-EP and P(E-*co*-EA-*co*-GMA) copolymers enhanced interpolymer interactions in PETr/PP-EP/P(E-*co*-EA-*co*-GMA) blends, leading to more compatible blends than PETr/PP/P(E-*co*-EA-*co*-GMA) blends.

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### REFERENCES

- Utracki, L. A. Commercial Polymer Blends, 1st ed.; Chapman and Hall: London, Weinhein, New York, Tokyo, Melborne, Madras, 1998.
- 2. Srithep, Y.; Javadi, A.; Pilla, S.; Turng, L. S.; Gong, S.; Clemons, C.; Peng, J. *Polym. Eng. Sci.* **2011**, *51*, 1023.
- 3. Pirzadeh, E.; Zadhoush, A.; Haghighat, M. J. Appl. Polym. Sci. 2007, 106, 1544.
- 4. Badía, J. D.; Vilaplana, F.; Karlsson, S.; Ribes-Greus, A. Polym. Test. 2009, 28, 169.
- Zhang, H.; Zhang, Y.; Guo, W.; Xu, D.; Wu, C. J. Appl. Polym. Sci. 2008, 109, 3546.
- 6. Benhamida, A.; Kaci, M.; Cimmino, S.; Silvestre, C.; Duraccio, D. *Macromol. Mater. Eng.* **2009**, *294*, 122.
- 7. Pracella, M.; Pazzagli, F.; Galeski, A. Polym Bull. 2002, 48, 67.
- 8. Loyens, W.; Groeninckx, G. Polymer 2002, 43, 5679.
- 9. Pracella, M.; Rolla, L.; Chionna, D.; Galeski, A. J. Appl. Polym. Sci. 2005, 98, 2201.
- Pluta, M.; Bartczak, Z.; Pawlak, A.; Galeski, A.; Pracella, M. J. Appl. Polym. Sci. 2001, 82, 1423.
- Pietrasanta, Y.; Robin, J. J.; Torres, N.; Boutevin, B. Macromol. Chem. Phys. 1999, 200, 142.

- 12. El-Nashar, D. E.; Maziad, N. A.; Sadek, E. M. J. Appl. Polym. Sci. 2008, 110, 1929.
- Kaci, M.; Banhamida, A.; Cimmino, S.; Silvestre, C.; Carfagna, C. Macromol. Mater. Eng. 2005, 290, 987.
- 14. Lepers, J. C.; Favis, B. D.; Lacroix, C. J. Polym. Sci. A2 1999, 37, 939.
- 15. Doshev, P.; Lach, R.; Lohse, G.; Heuvelsland, A.; Grellmann, W.; Radusch, H. J. *Polymer* **2005**, *46*, 9411.
- 16. Li, R.; Zhang, X.; Zhao, Y.; Hu, X.; Zhao, X.; Wang, D. *Polymer* **2009**, *50*, 5124.
- 17. Underwood, E. E. Quantitative Stereology; Addison Wesley: Reading, MA, **1970**.
- Brandrup, J.; Immergut, E. H. Polymer Handbook, 3rd ed.; Wiley: New York, 1989.
- Ghanbari, M.; Heuzey, M. C.; Carreau, J. P.; Ton-That, M. T. Polym. Int. 2013, 62, 439.
- 20. Kalfoglou, N. K.; Skafidas, D. S.; Kallitsis, J. K. Polymer 1995, 36, 4453.
- 21. Tol, R. T.; Groeninckx, G.; Vinckier, I.; Moldenaers, P.; Mewis, J. *Polymer* **2004**, *45*, 2587.
- 22. Souza, A. M. C.; Demarquette, N. R. Polymer 2002, 43, 3959.
- 23. Carreau, J. P.; De Kee, D.; Chhabra, R. Rheology of Polymeric Systems Principles and Applications; Carl Hanser: Munich, Germany, **1997**.
- 24. Jacobs, U.; Fahrlander, M.; Winterhalter, J.; Friedrich, C. J. Rheol. 1999, 43, 1495.
- 25. Van Hemelrijck, E.; Van Puyvelde, P.; Velankar, S.; Macosko, C. W.; Moldenaers, P. J. Rheol. **2005**, 49, 783.
- 26. Yee, M.; Souza, A. M. C.; Valera, T. S.; Demarquette, N. R. *Rheolog. Acta* **2009**, *48*, 527.
- 27. Wu, D.; Zhang, Y.; Yuan, L.; Zhang, M.; Zhou, W. J. Polym. Sci. A2 2010, 48, 756.
- Souza, A. M. C.; Calvão, P. S.; Demarquette, N. R. J. Appl. Polym. Sci. 2013, 129, 1280.
- 29. Yi, X.; Xu, L.; Wang, Y. L.; Zhong, G. J.; Ji, X.; Li, Z. M. *Eur. Polym. J.* **2010**, *46*, 719.
- 30. Martínez, B. M. H.; Vargas, E. R.; Rodriguez, F. J. M.; Garcia, R. C. *Eur. Polym. J.* **2005**, *41*, 519.
- 31. Armat, R.; Moet, A. Polymer 1993, 34, 977.
- 32. Pracella, M.; Rolla, L.; Chionna, D.; Galeski, A. *Macromol. Chem. Phys.* **2002**, *203*, 1473.
- Friedrich, K.; Evstatiev, M.; Fakirov, S.; Evstatiev, O.; Ishii, M.; Harrass, M. Compos. Sci. Technol. 2005, 65, 107.
- 34. Chiu, H. T.; Hsiao, Y. K. J. Polym. Res. 2006, 13, 153.

