

# Influence of the Reactive Processing of Recycled Poly(ethylene terephthalate)/Poly(ethylene-co-glycidyl methacrylate) Blends

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Received 13 October 2009; accepted 23 May 2010

DOI 10.1002/app.32836

Published online 11 October 2010 in Wiley Online Library (wileyonlinelibrary.com).

**ABSTRACT:** The effect of the amount of reactive additive and screw speed during extrusion on the morphological characteristics and mechanical performance of recycled poly(ethylene terephthalate)(RPET) was investigated. With an increase in the ethylene-glycidyl methacrylate copolymer (E-GMA) additive content, a gradual increase in the Izod impact strength of the RPET/E-GMA blends was initially recorded. Subsequent increases in the E-GMA content to above 13.5 wt % led to a drastic enhancement in the toughness of the blends. Meanwhile, the density of the

blends decreased with increasing amount of the additive E-GMA. The toughness and density of the blends were found to be dependent on the screw rotation speed during the extrusion. In addition, ductile and microporous structures were observed on the Izod impact fracture surfaces. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 50–55, 2011

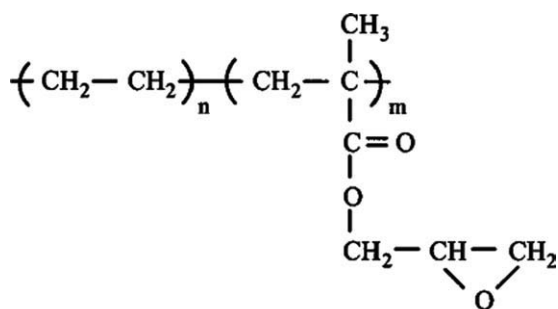
**Key words:** blending; impact resistance; injection molding; polyesters; recycling

## INTRODUCTION

Poly(ethylene terephthalate) (PET) is a widely used engineering plastic and is used in applications such as soft drink bottles. The success of this material in the bottling industry is mainly attributed to its transparency, thermal stability, chemical resistance, and excellent barrier properties. As a result, the amount of waste plastics is increasing all over the world. More than 50% of waste plastics are disposed of in landfills or by combustion. Landfills and combustion are no longer acceptable for the disposal of plastics because of serious environmental concerns and the low weight-to-volume ratio of plastics. Therefore, the recycling of waste plastics has received significant worldwide attention. There are mainly two recycling methods, that is, chemical<sup>1,2</sup> and physical<sup>3</sup> recycling. In chemical recycling, a lot of solvents are used to recycle plastics, and it is necessary to purify the plastics used, although a return the raw materials is possible. In physical recycling, plastics can be easily recycled to other plastic products.

However, the mechanical properties of recycled materials decrease because of the decomposition and degradation of the polymer chains. Some investigations into the control of the degradation in polymers during recycling have been performed by the creation of blends and/or the introduction of additives. Several such studies on the use of a third polymer component to compatibilize PET/polyolefin blends to improve the thermal stability of the blends have been reported in the literature. These include the use of an acrylic acid grafted polypropylene to compatibilize blends of PET and polypropylene through the *in situ* formation of a compatibilizer resulting from transesterification reactions.<sup>4</sup> Similar improvements in the toughness of such blends have been reported with the use an ethylene-glycidyl methacrylate copolymer [poly(ethylene-co-glycidyl methacrylate)(E-GMA)],<sup>5–9</sup> whereas other workers have found polyolefin ionomers to be effective compatibilizers for these systems.<sup>10–13</sup> For the same purpose, Mascia and coworkers<sup>14,15</sup> used coionomeric mixtures of either ethylene acrylic acid or methacrylic acid copolymers with a polyhydroxyether (phenoxy). Although many investigations have been done on blends involving PET and other polymers, very few have focused on the effects of the processing conditions (particularly, the screw speed during the extrusion

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**Poly(ethylene-co-glycidyl methacrylate)**  
(E-GMA)

**Figure 1** Chemical structure of E-GMA.

process), homogeneity, and mechanical performance of the blends.

On the other hand, it is known that together with stiffness and tensile strength, toughness is one of the main properties sought in polymers. A number of polymers show remarkable stiffness and strength relative to their density. A number of engineering and high-performance polymers also show a large unnotched impact strength, but most of them, including polycarbonate, PET, and poly(ether ether ketone), are clearly notch-sensitive. This leads to an insufficient notched impact strength, which limits the mechanical performance because the notched behavior is most closely related to service performance. Recently, much higher increases in impact strength have been obtained by compatibilization, which is usually attained by functionalization of the rubber phase.

Therefore, it is very important to develop a new approach for solving these underlying problems. The aim of this study was to produce recycled materials with high static and impact strengths by the blending of waste PET with a copolymer containing epoxy functional groups, that is, E-GMA. The structure and properties of these recycled poly(ethylene terephthalate)(RPET)-based blends prepared by reactive compounding were investigated on the basis of their mechanical performance and morphological characteristics.

## EXPERIMENTAL

### Materials

In this study, RPET was supplied by Yasuda Sangyo Co., Ltd., (Kyoto, Japan), and E-GMA was purchased from Sumitomo Chemicals Co., Ltd., (Tokyo, Japan), and acted as an impact modifier for RPET. The chemical structure of E-GMA is shown in Figure 1; it was compatible with RPET because of the presence of epoxy functional groups that could react and/or interact

with the carboxyl end groups of PET. Therefore, it could work as either a chain extender or impact modifier for PET.

### Sample preparation

The sample designation and the corresponding composition is shown in Table I. The RPET/E-GMA blends were compounded at E-GMA loadings of 0, 6, 9, 13.5, and 16 wt % in a twin-screw extruder (TEX30 HSS, Japan Steel Works Co., Ltd., Tokyo, Japan). The extruder barrel temperature was set between 250 and 260°C at screw speeds of between 100 and 300 rpm. The blends were dried with a dehumidifying drier at 80°C for 5 h before they were injection-molded (UM50, Po Yuen Co., Ltd., Hong Kong, China) into dumbbell specimens at barrel temperatures of 260–280°C and at an injection speed of 100 mm/s.

### Characterization

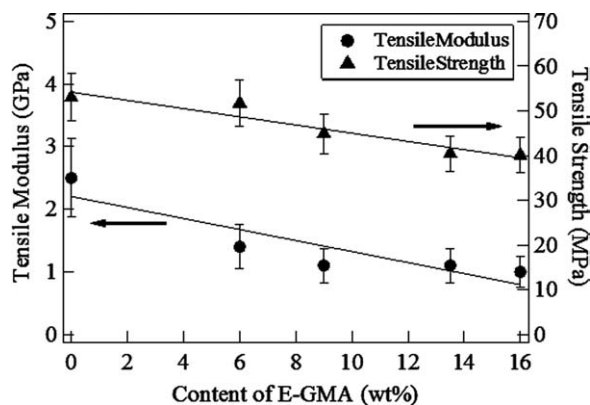
Tensile tests were performed with an Instron 4206 universal testing machine according to ASTM D 638. The gauge length of the specimens was 115 mm, and the tests were conducted at an extension rate of 50 mm/min. The Izod impact strength was determined for all specimens that were notched at a 2-mm depth. The impact specimens were obtained from the parallel regions of the dumbbell specimens. The tests were conducted with a Toyo Seiki Izod impact tester (Toyo Seiki Seisaku-sho, Ltd., Tokyo, Japan) according to ASTM D 256 with a pendulum of 5.50 J.

The morphology of the blends was characterized from notched impact fractured specimens with a scanning electron microscope (JEOL, JSM5200, JEOL Ltd., Tokyo, Japan). A gold coating was sputtered onto the specimens to enhance their conductivity.

Differential scanning calorimetry (DSC; DSC2920, TA Instruments, New Castle, Delaware) was conducted in a nitrogen atmosphere at a temperature

**TABLE I**  
**Compounding Conditions of the RPET/E-GMA Blends**

Sample number	RPET (wt %)	E-GMA (wt %)	Screw speed (rpm)
1	100	0	200
2	94	6	200
3	91	9	200
4	86.5	13.5	100
5	86.5	13.5	150
6	86.5	13.5	200
7	86.5	13.5	250
8	86.5	13.5	300
9	84	16	200



**Figure 2** Tensile modulus and strength as a function of the content of E-GMA. The screw speed in the extrusion was 200 rpm.

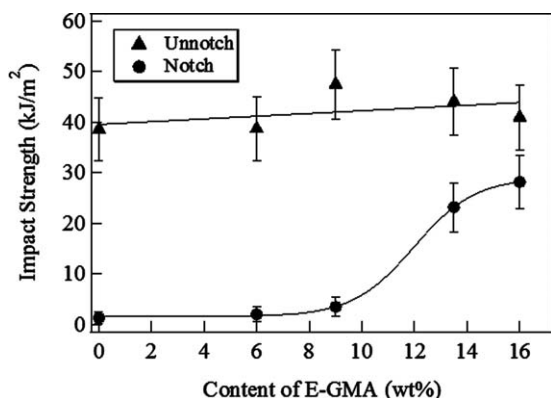
range of 30–280°C with a heating rate of 10°C/min for the purpose of investigating the thermal properties of the RPET/E-GMA blends.

A parallel-plate rheometer (AR1000, TA Instruments) was used to determine the viscosities of the RPET/E-GMA (86.5/13.5) compositions blended at various screw rotation speeds. The viscosity of the blends was determined at a temperature of 280°C under a range of angular frequencies of between 1 and 100 rad/s. The density of the RPET/E-GMA blends was measured with a pycnometer (Micromeritics Accpvc133, Shimadzu Co., Ltd., Kyoto, Japan).

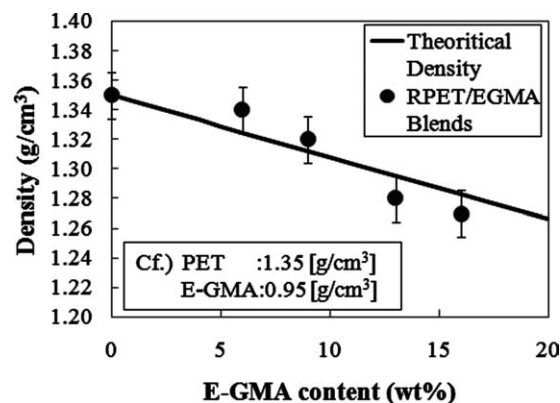
## RESULTS AND DISCUSSION

### Effect of the E-GMA content

Figure 2 shows the tensile modulus and strength of the RPET/E-GMA blends as a function of the E-GMA content. Both the tensile modulus and tensile strength decreased when the E-GMA content increased as a result of the elastomeric nature of E-GMA.



**Figure 3** Impact strength as a function of the content of E-GMA. The screw speed in the extrusion was 200 rpm.

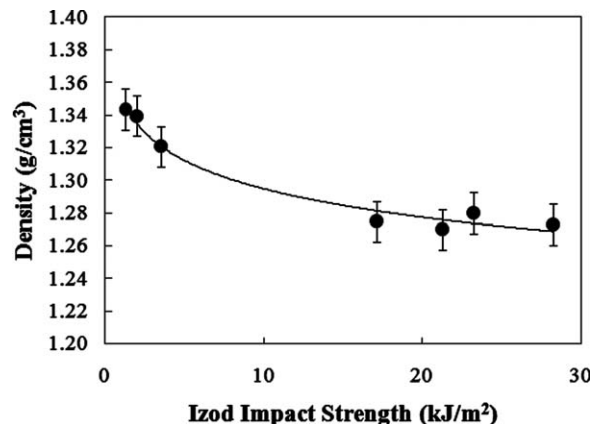


**Figure 4** Density as a function of the content of E-GMA. The screw speed in the extrusion was 200 rpm.

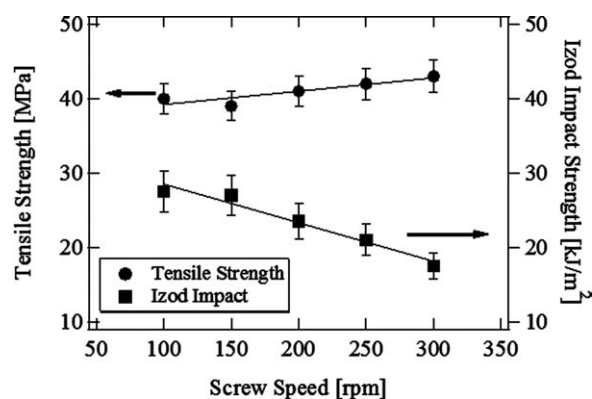
Figure 3 shows the impact strength of the RPET/E-GMA blends as a function of the E-GMA content. The impact strength increased slightly from roughly 1 to 4 kJ/m with the addition of 9 wt % E-GMA. The impact strength then drastically increased to 23.5 kJ/m as the E-GMA content approached 13.5 wt %. Further increases in the E-GMA content to 16 wt % led to only a slight additional increase in the impact strength. The highest impact strength achieved was typical of supertough blends because it was more than about 20 times that of neat RPET.

Figure 4 shows the density of the RPET/E-GMA blends as a function of the E-GMA content. The density was constant until the addition of 6 wt % E-GMA, where the density steadily decreased to 1.29 g/cm<sup>3</sup> at 13.5 wt % E-GMA. Further increases in the E-GMA content to 16 wt % led to only a slight change in the density to 1.28 g/cm<sup>3</sup>. We concluded that these density values corresponded well to the rule of mixtures, with the densities of RPET and E-GMA taken to be 1.35 and 0.95 g/cm<sup>3</sup>, respectively.

The correlation between the density of the RPET/E-GMA blends and the Izod impact strength is shown in Figure 5. As shown, the impact strength increased as the density of the blends decreased.



**Figure 5** Density for the Izod impact strength.

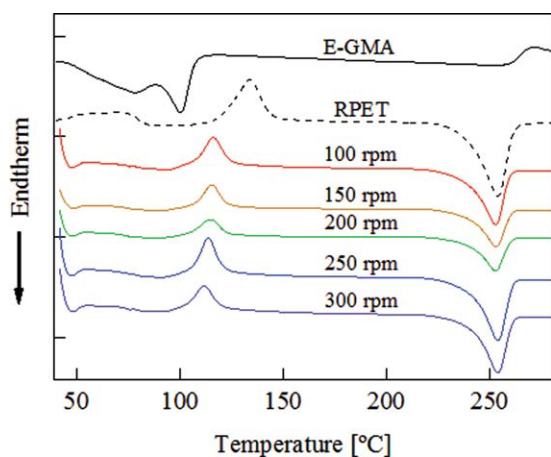


**Figure 6** Tensile strength and Izod impact strength as a function of the screw speed. The blend content was 86.5/13.5 RPET/E-GMA.

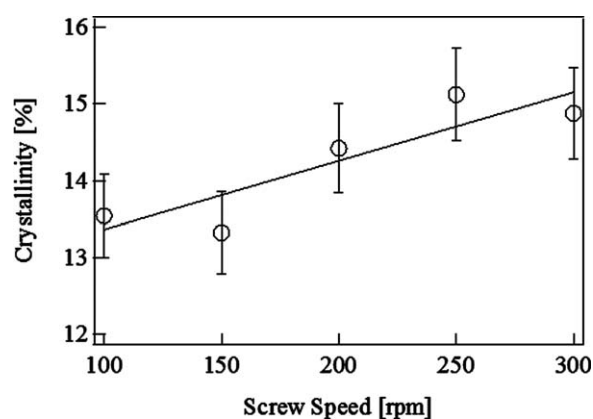
The density of the blends depended on its homogeneity; thus, the screw speed during compounding was varied to assess its effects on the density and, subsequently, the impact performance of the blends.

#### Effect of the screw speed

Figure 6 shows the tensile and Izod impact strengths as a function of the screw speed for the RPET/E-GMA (86.5/13.5 wt %) blends. The tensile strength depended on the screw speed and slightly increased from about 40 to 43 MPa with increasing screw speed. On the other hand, the Izod impact strength increased with decreasing screw speeds from 300 to 150 rpm. Therefore, we supposed that this increase in the impact strength was caused by changes in the crystallinity of RPET and/or a reaction between the RPET resin and the epoxy functional group in E-GMA.



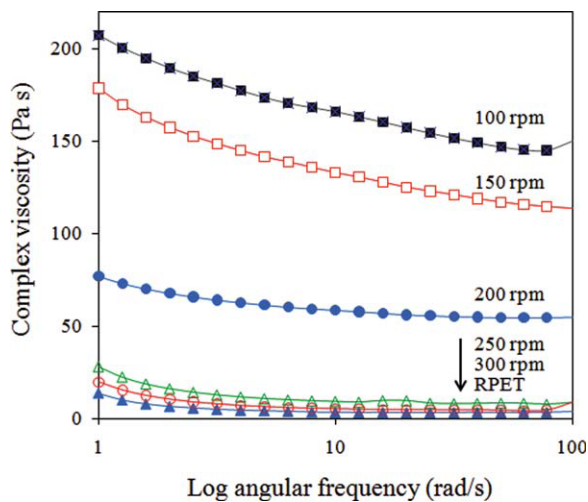
**Figure 7** DSC curve for the RPET/E-GMA blends. The blend content was 86.5/13.5 RPET/E-GMA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



**Figure 8** Crystallinity of the RPET/E-GMA (86.5/13.5) blends as a function of the screw speed.

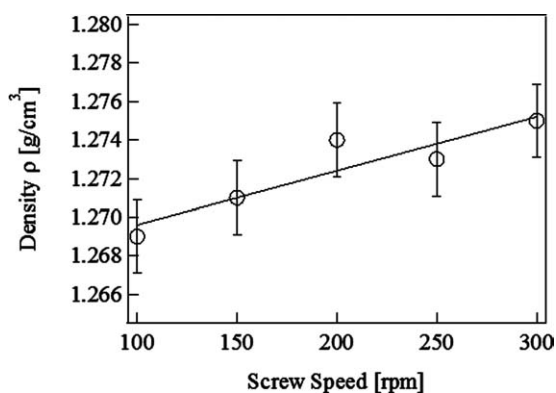
The crystallinity of the RPET/E-GMA blends was measured with DSC. Figure 7 shows the DSC thermograms of the first heating of neat E-GMA, neat RPET, and RPET/E-GMA (86.5/13.5 wt %). The RPET/E-GMA blends were prepared at various extruder screw speeds. As shown in Figure 7, a clear glass-transition temperature of neat RPET was recorded around 75°C, whereas a clear exothermic peak was observed around 140°C. This was caused by the crystallization of the residual amorphous regions formed as a result of rapid cooling of the samples during injection molding. However, similar exotherm peaks were shifted to the left in the RPET/E-GMA blends; furthermore, the peak temperature decreased with increasing screw speed. This could have been due to the presence of E-GMA,<sup>16</sup> and the crystallinity of the RPET/E-GMA specimens increased with increasing screw speed. On the other hand, the melting temperature of the RPET/E-GMA blends slightly decreased in all blends compared to neat RPET; this could have been caused by the branching of molecular chains as a result of reactions between the RPET and E-GMA phases. Figure 8 shows the crystallinity of the RPET/E-GMA specimens as a function of the screw speed. As shown, the crystallinity of the blends increased with increasing screw speed. Furthermore, this supporting well the results of the tensile test and Izod impact test, shown in Figure 6.

To estimate the effect of the processing conditions on the morphological changes in the RPET/E-GMA blends, the parallel-plate rheometer was used to measure the viscosities of the blends prepared at different screw speeds during compounding. The viscosities of the blends and monotonic RPET are shown in Figure 9. In the RPET/E-GMA blends, the E-GMA phase reacted with the hydroxyl groups from RPET to form a copolymer *in situ*, which was responsible for the uniform dispersion of E-GMA in RPET. Similarly, the carboxyl and hydroxyl groups

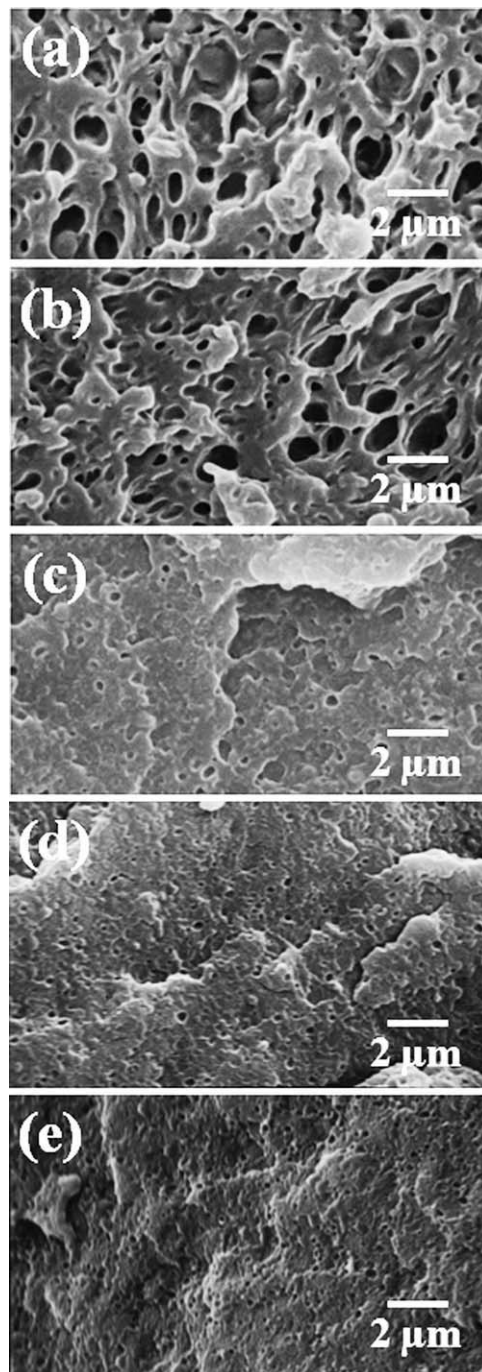


**Figure 9** Complex viscosity versus frequency for E-GMA-modified RPET. The blend content was 86.5/13.5 RPET/E-GMA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

in RPET reacted with the epoxy group from E-GMA in the melt state and, thus, increased the molecular weights of RPET, as confirmed by an increase in the viscosity. Furthermore, the dynamic viscosity of the RPET/E-GMA blends prepared at low screw speeds increased up to more than two times that of the blends prepared at high screw speeds. The viscosity of RPET was, however, much lower than that of the blends. Therefore, we suggest that the molecular weight of the blends increased because of the strong affinity between the RPET and E-GMA phases. However, the size of the E-GMA phase varied with screw speed; that is, a low screw speed generated lower shear rates, and therefore, the size of E-GMA was expected to be large. In this case, the friction generated between the E-GMA and RPET phases would have been higher, which contributed to the higher melt viscosity. The larger E-GMA particles would have also caused larger crazes during mechanical loading, hence, the appearance of large



**Figure 10** Density for the RPET/E-GMA blends. The blend content was 86.5/13.5 RPET/E-GMA.



**Figure 11** SEM images for the RPET/E-GMA blends at (a) 100, (b) 150, (c) 200, (d) 250, and (e) 300 rpm. The blend content was 86.5/13.5 RPET/E-GMA.

micropores on the surface of impact fractured surfaces, which are depicted and discussed in subsequent sections.

Figure 10 shows the density for RPET/E-GMA (86.5/13.5) prepared at screw speeds of 100, 150, 200, 250, and 300 rpm. The density of the blends indicated the extent of dispersion of the E-GMA phase in RPET. Higher blend densities were attributed to the better dispersion and/or stacking

between the RPET molecules and E-GMA molecules. Therefore, the blends prepared at a high screw speed (i.e., 300 rpm) were denser because this provided high shear rates that could efficiently break up and disperse E-GMA. In addition, as previously shown in Figure 8, the crystallinity of the blends showed a tendency to be the same with changing density. Hence, we believe that the density of the blends was dependent on the crystallinity and that the homogeneity that was affected by the screw speed. This is an interesting result when one considers that the mechanical performance of the blends could be significantly altered by just a variation in the compounding conditions.

### Morphology

Figure 11 shows SEM micrographs of the notch impact fractured surfaces of blends prepared at various screw speeds. In general, a brittle fracture surface could be expected from the unmodified RPET because it is known to be very notch-sensitive. However, as shown in Figure 11, the RPET/E-GMA blends fractured in a ductile manner. Many submicrometer pores were present on the fracture surface, and the average pore diameter became larger with decreasing screw speed. Inversely, the density of the blends decreased with increasing pore size. These pores did not originate from voids in the bulk; rather, the pores were formed because of crack propagation through the crazed regions as the material yielded during impact loading. Therefore, blends produced at low screw speeds contained larger E-GMA particles, which complicated crack propagation and caused the formation of larger micropores before fracture. As such, a higher energy was required to cause fracture, which explained the higher impact strength of the blends produced at low screw speeds.

### CONCLUSIONS

The effects of the reactive additive content and screw speed during extrusion of RPET/E-GMA blends

were investigated. With increasing E-GMA content, the blends became extremely tough, especially when the E-GMA content approached 13.5 wt %. On the other hand, the density of the blends decreased with increasing amount of E-GMA. Furthermore, the screw rotation speed during compounding also affected the density and impact performance of the blend, although the amount of E-GMA was kept constant. The fracture surface of the Izod impact test specimens showed ductile and microporous structures in the modified blends. The size of these micropores became smaller with increasing screw speed during the compounding process, which indicated a better dispersion of the E-GMA in RPET. Consequently, the density and mechanical properties of the RPET/E-GMA blends also changed with the variation of the crystallinity of RPET. Therefore, we suggest that the screw speed during compounding played an important role in determining the mechanical properties of the blends.

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