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Morphology and Properties of Poly(ethylene terephthalate)/Polycarbonate Alloy Toughened with Different Kinds of Elastomers

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Summary

Recycled Poly (ethylene terephthalate) (PET) was blended with Polycarbonate (PC) together with elastomers. Three kinds of elastomer: POE (ethylene-octene copolymer), SEBS(styrene-ethylene/butylenes-styrene triblock copolymer) and SEBS-g-MA (maleic anhydride grafted SEBS) were selected. Scanning electron microscope (SEM) results showed the alloy blended with SEBS exhibiting smallest particle size distribution and it had better mechanical properties than the others, especially in broken-elongation and impact strength. The alloy blended with SEBS-MA didn't reach high performance was due to the existence of small amount of active monomer: MDI (methylenediphenyl diisocyanate). The preferential reaction by SEBS-MA with MDI not only resisted the chain-extending progress induced by MDI but also resulted in coalescence of SEBS-MA. In addition, though SEBS was the best selection to this system, experimental results showed that the weight ratio of SEBS must also be limited in a certain degree. Over much contents of SEBS resulted in coalescence together affect compatibility between components.

Introduction

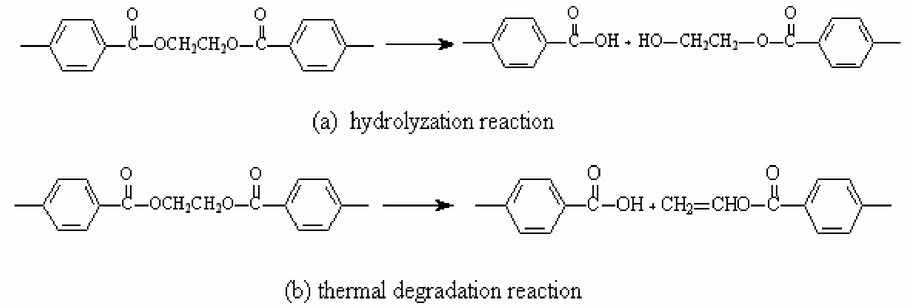
Soft drink bottles are preferentially produced of Poly (ethylene terephthalate) (PET). This market success is mainly caused by the excellent properties in transparency, chemical resistance, and beneficial barrier properties. Rapidly increasing use of PET bottles results in a large amount of waste PET, which should be recycled in a cost-efficient manner. Successful development of the value-added recycling technique will not only solve the existing environmental problem, but also convert the post-consumer plastic wastes into valuable resources.

Blending of PET with various polymers [1-8] offers a good opportunity to convert the recycled PET into high performance engineering plastic. Recently, attentions had been put on the PET/ Polycarbonate (PC) blending system [9-19], which could make the alloy with property combination of good dimensional stability from the PC and excellent solvent resistance from PET. However, to improve toughness, especially notched impact toughness, toughening by incorporation of rubber or other elastomers is required. Typical impact modifiers include poly(methyl methacrylate)-grafted -

butadiene-styrene rubber (MBS), ABS(with high polybutadiene content ≥50%), ASA rubber(≥50% acrylate rubber) and bastyrene-ethylene/butylenes-styrene triblock copolymer (SEBS)[20]. The phase separation between the polymer and the rubber is an important requirement, and the mechanical resistance increases if the rubber has low elastic modulus in relation to the matrix, good adhesion to the matrix, optimized average particle size distribution and separating distance between the elastomeric zone.

Some researcher focused on functionalized elastomers (such as maleic anhydride grafted SEBS (SEBS-g-MA) [21-24] and ethylene-methacrylate-glycidyl methacrylate copolymer (E-MA-GMA)[25]). The in situ formation of a graft copolymer by reaction of PET hydroxyl end groups with functional group was confirmed. The graft copolymer acted as a compatibilizer to lower the interfacial tension and suppress the tendency of coalescence, thus improving the dispersion of elastomers and enhanced interfacial adhesion between the components.

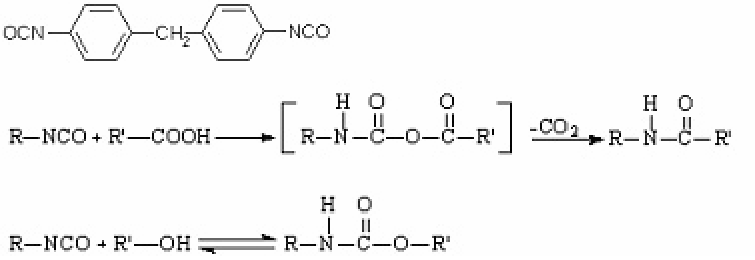
Another key issue in the processing is the decrease of molecular weights of PET caused by hydrolytic (a) and thermal degradation (b) as presence of retained moisture or contaminants.



Scheme 1. Hydrolytic and thermal degradation reaction of PET in the processing

Adding chain extender is an effective way to increase the molecular weights (or melt viscosity) of PET. Some popular chain extender are dianhydrides, bis(oxazolines), bis(dihydrooxazine), carbodiimides, diepoxides, and diisocyanates[26].

In this research, MDI (methylenediphenyl diisocyanate) was added as chain extender during the reactive blending, as its isocyano group (-NCO) can react with hydroxy and carboxyl end group of PET and PC.



Scheme 2. The molecular formula of MDI and its chain-extending reaction with PET and PC

Three elastomers (POE, SEBS, SEBS-MA) were selected and respectively blended with PET/PC blends. The effectiveness of toughening by various elastomers and the influence of the chain extender were investigated in this research.

Experimental

Materials and Sample Preparation

Recycled PET bottle flakes was provided by Zijang Bottle Co.(Shanghai, China), IV = 0.65dL/g; PC (polycarbonate) was supplied by Teijin Co. (Japan), Intrinsic viscosity(IV) = 0.70 dL/g. MDI(methylenediphenyl diisocyanate) was supplied by the Japan Polyamide Incorporation. Three kinds of elastomers used in this study were: POE (ethylene-octene copolymer), SEBS(styrene-ethylene/butylenes-styrene triblock copolymer) and SEBS-g-MA(maleic anhydride grafted SEBS). Table 1 shows the detail information of the three elastomers.

Table 1. Elastomer characteristic

Elastomer	Trademark	M_w (g/mol)	M_n (g/mol)	S/EB	Grafed Anhydride(wt%)
POE	Engage 8150	74000	79000	-	-
SEBS	Kraton G1652	77000	75000	28/72	-
SEBS-MA	Kraton 1921X	77000	75000	28/72	0.1

Supplied by Shell Chemical Co. (USA)

Before blending, PC and PET were dried at 120°C in vacuum for 6h, other components were vacuum dried for 6h at 70°C. Blends were prepared in a TSE-35A twin-screw extruder (L/D=45, Nanjin Ruiya Polymer Machine Co) at a temperature range of 100-240°C under a screw speed of 100rpm. These processing parameters were selected after preliminary studies to determine the effect of processing temperature on PET molecular weight. The extrudates were pelletized at die exit, dried, and injection molded into standard dumbbell tensile specimens (150 mm gauge length, 10 mm width, and 4 mm thickness) and rectangular bars (80 mm length, 10 mm width, and 4 mm thickness) by a QS-100T injection molding machine produced by Shanghai Quansheng Polymer Machine Co. The barrel temperature of injection molding machine kept at 240°C, and the mold temperature was at 40°C. The rectangular bars were subsequently used to izod notched impact testing. A 45° V-notch (depth =0.8 mm) was machined midway on one side of the bar with a slow speed to avoid plastic deformation.

Characterization

For particle size determination, izod bars were immersed in liquid nitrogen for 30 min and freeze fractured. Blend samples were etched with dimethylbenzene for 4h at ambient temperature to remove elastomers. After drying in vacuum, the fracture surface were coated with gold and examined in Jeol JSM-35CF scanning electron microscope (SEM), and the accelerating voltage was15 kV. Images analysis was carried out to measure the apparent diameter (a_i) of the dispersed phase, which was then concerted into true particle diameter (d_i). Typically, over 200 paticles from different photographs of a specimen surface were analyzed to calculate the number-average diameter d_n from following relationship:

$$\overline{d_n} = \frac{\sum n_i d_i}{\sum n_i}$$

Where n_i is the number of particles having the true particle diameter d_i.

The melt flow rate (MFR) was tested by SRZ-400C made by Changchun Mechanical Properties Testing Machine Ltd. (R.P.R.), according to Chinese standard GB/T3682-2000, at 260°C.

Viscosity measurements were carried out in a mixture of phenol and dichloroethane (60:40 by volume) using an Ubbelohde dilution viscometer. The intrinsic viscosity(IV), [η], was determined by extrapolation using the Huggins equation.

Mechanical properties tests were conducted by WSM-20KN Mechanical properties testing machine produced by Changchun Mechanical Properties Testing Machine Ltd according to the Chinese standard (GB/T1040-1992) for tensile strength and elongation at break; GB/T9341-2000 for the flexural strength and flexural modulus; GB/T1043-1993 for izod impact strength.

Results and discussion

Blends Morphology

Etched frozen-fractured surfaces of the specimens with the same composition (PET/PC/elastomer/MDI=60/30/10/0.9) were shown in Figure 1. All elatomers were nearly dispersed as spherical particles, but they were obviously different in sizes and distribution. Their particle size distributions calculated from SEM images were given in Figure 2. POE had the largest average particle sizes with a broad distribution (1.48±0.53 μm), SEBS showed smaller particle size distribution (0.35±0.13 μm), but surprisingly, SEBS-MA had not dispersed more uniformly than SEBS (0.98±0.24 μm).

Differences in size and shape of elastomer particles in the blend mainly derive from the interfacial tension among the components, in other words, the compatibility of the system. POE used in this research was ethylene-octene copolymer, which is immiscible with PET and PC. The interfacial adhesion between POE and other components was poor, and it dispersed in random as described above. SEBS, as styrene copolymer, has considerable phenyl group proportion in the molecular chain (28%, as shown in Table 1). For some extent of similarity to the chemical structure of PET and PC, the compatibility of SEBS with other components in this blending system could be improved comparing that with POE. When SEBS were grafted with maleic anhydride end group(SEBS-MA), it would normally be considered to disperse homogeneously as its interfacial adhesion with the matrix strengthened by reaction of maleic anhydride with the hydroxyl end group of PET and PC. But in fact, SEBS-MA was not dispersed perfectly as expected, this abnormal phenomenon was due to the effect of chain extender, whose isocyano group also has extraordinary reaction activity with SEBS-MA.

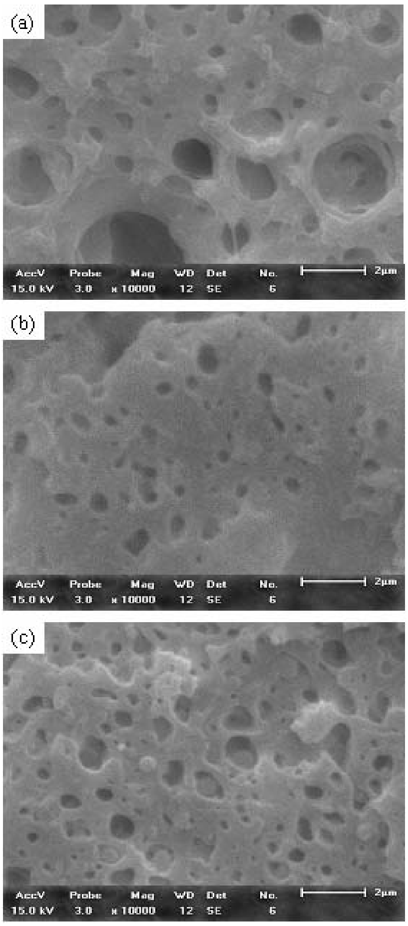


Figure 1. SEM images of frozen-fractured PET/PC/elastomers blends (elastomers were etched before examined). (a)-POE, (b)-SEBS, (c)-SEBS-MA

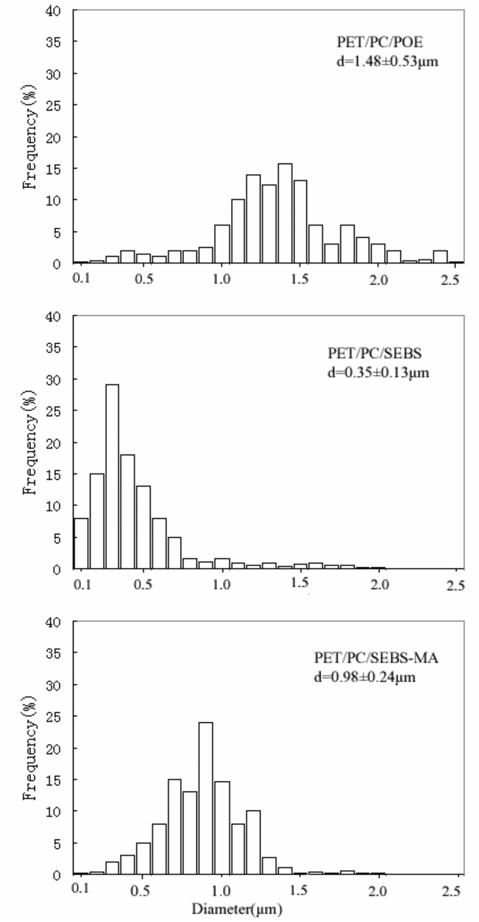
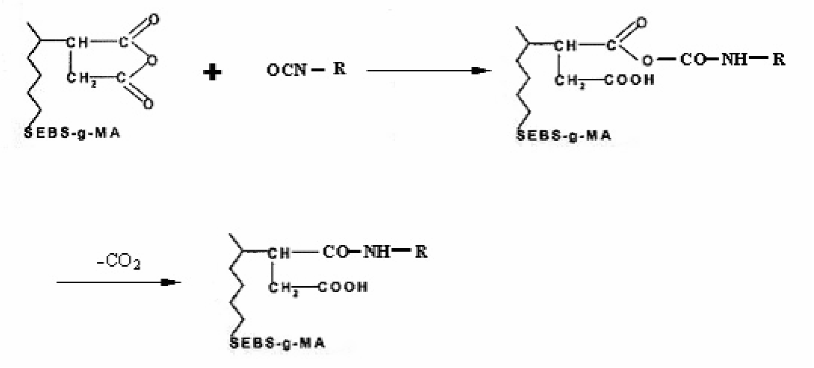


Figure 2. Particle size distribution of the Elastomers (a)-POE, (b)-SEBS, (c)-SEBS-MA

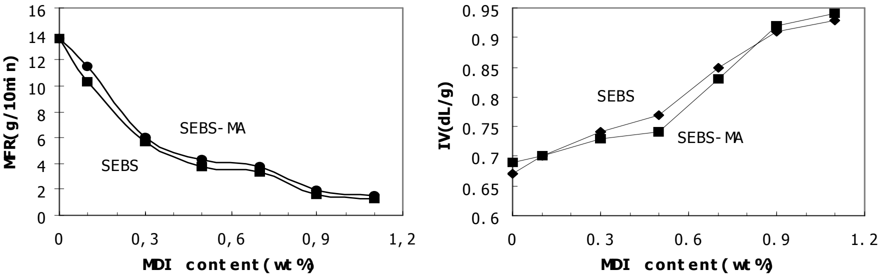


Scheme 3. The reaction between SEBS-MA and MDI

The negative effect of the chain extender on dispersion of SEBS-MA can be explained by considering the competitive reactions among SEBS-MA, PET and MDI. Because the reactivity between isocyano group and anhydride is higher than that between hydroxyl and anhydride groups, MDI preferentially reacted with maleic anhydride group of the SEBS-MA than with the groups of PET and PC. The preferential reaction consumed most of maleic anhydride groups to react with the matrix, so SEBS-MA dispersed with larger particle size than that of SEBS.

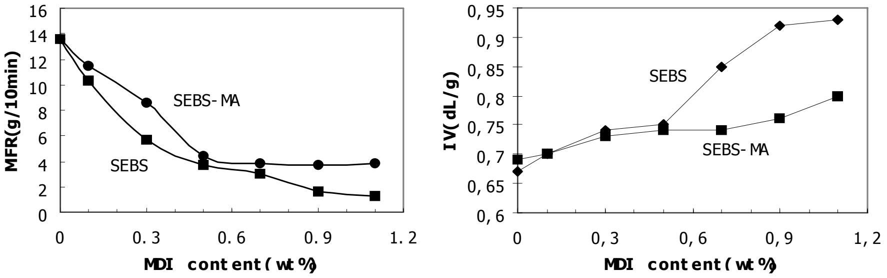
Effects of MDI contents on the MFR and IV of the blends with SEBS or SEBS-MA (with the same composition described above) are shown in Figure 3. Both of the two blends' melt and intrinsic viscosity increased with increasing content of MDI, and proved the molecular weights of alloy were increased by the presence of the chain extender.

When these blends were etched with dimethylbenzene and elastomers were taken out (Figure 4), the viscosity of the residual phase with SEBS-MA etched decreased remarkably compared with the sample with SEBS etched. It was reasonable to suppose that the increased viscosity of PET/PC/SEBS-MA was caused mainly by the viscosity increase of SEBS-MA phase. That was in accord with the explanation by competitive reaction, some MDI, which could increase the matrix's molecular weights, were consumed by SEBS-MA.



(a) (b)

Figure 3. Plots of MFR (a) and IV (b) against contents of MDI for the blends with SEBS or SEBS-MA



(a) (b)

Figure 4. Plots of MFR (a) and IV (b) against contents of MDI for the blends with SEBS or SEBS-MA (elastomers were etched before examined)

Mechanical Properties

The mechanical properties of PET/PC alloy and the ones with different elastermers (PET/PC/elastomer/MDI : 60/30/10/0.9) were shown in Table 2. The alloy with SEBS exhibited the best mechanical properties, especially tensile and impact strength.

In Figure 5, tensile deformation of all blends was characterized by formation of a macroshear band at the yield point and a neck then propagated from one side of the macroshear band. The primary difference of these blends was in the stability of propagating neck, which attributed to their ductility. The necked region of alloy with SEBS propagated all the way to the end of the gauge section (with the largest elongation, 192.2%), and it uniformly strain hardened with a small increase in stress until the neck started propagate again from the other side of the macroshear band. It was the second region of cold drawing. When the entire gauge section had necked, there was a region of uniform strain hardening that terminated when the specimen fractured at one end of the neck.

SEM images of different alloys impact-fractured at ambient temperature were shown in Figure 6. Brittle-ductile (B-D) transition of the PET/PC alloy can be observed. The fracture of alloy with POE was clearly showed separated phase (Figure6, a) and displayed a brittle surface; the one of the alloy with SEBS-MA began to display cavitation and matrix shear yielding (Figure 6., c); but the alloy with SEBS show full extend of matrix yielding (even its fracture surface display certain extend of orientation), and its impact strength value was 78.3kJ/m^2 which was the largest one among all the alloys (Table 2).

Table 2. Mechanical properties of blends with different elastomers

Mechanical Properties	Blending System			
	PET/PC	PET/PC/POE	PET/PC/SEBS	PET/PC/SEBS-MA
Tensile Strength (MPa)	36.6	39.9	46.7	47.1
Elongation at Break (%)	19.5	20.2	192.2	106.5
Flexural Strength (MPa)	75.3	69.0	73.5	71.2
Flexural Modulus (GPa)	2.15	2.01	2.12	2.05
Unnotched Impact Strength(kJ/m^2)	48.6	38.7	Not broken	62.3
Notched Impact Strength(kJ/m^2)	15.3	14.5	78.3	32.3

Usually said, the toughness of the polymers will be improved by maleic anhydride grafted elastormer, because the functional group (-MA) reacts with end group (-OH) of matrix, which attribute to strengthen interfacial adhesion and improve the compatibility between components. But in our experiment results, it was opposite to the above theory that the mechanical properties of the alloy with SEBS were better than the one with SEBS-MA. This phenomenon was caused by the existence of another active ingredient: chain-extender (MDI). The preferential reaction between

MDI and maleic anhydride group would not only resist the chain-extending progress induced by MDI but also result in coalescence of SEBS-MA.

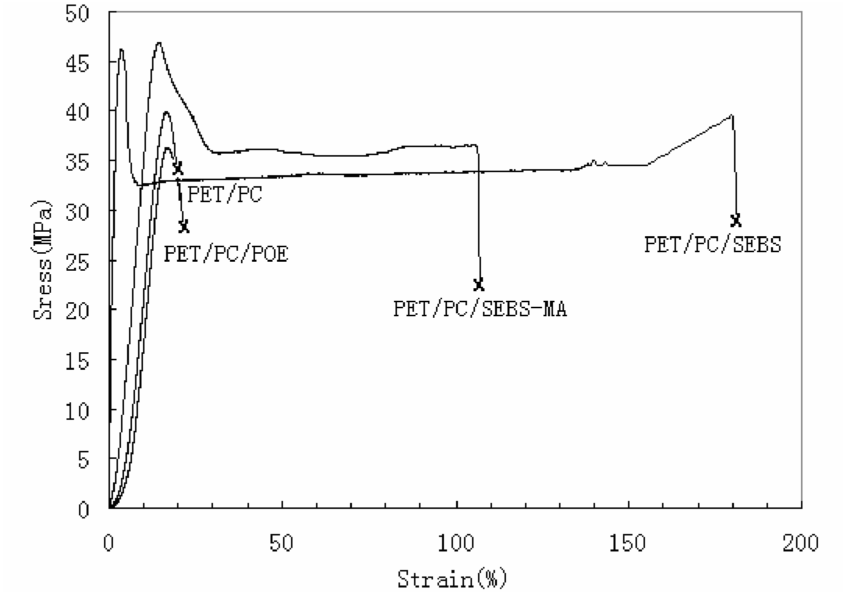


Figure 5. Stress-stain curves of PET/PC alloy blended without or with different elastomers

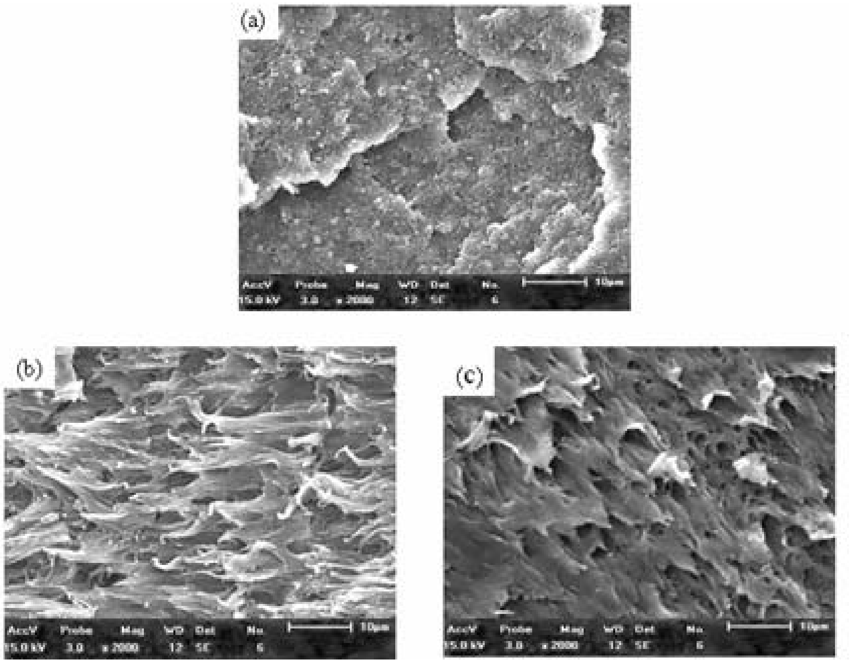


Figure 6. SEM images of blends with different elastomers fractured at ambient temperature (a)-POE, (b)-SEBS, (c)-SEBS-MA

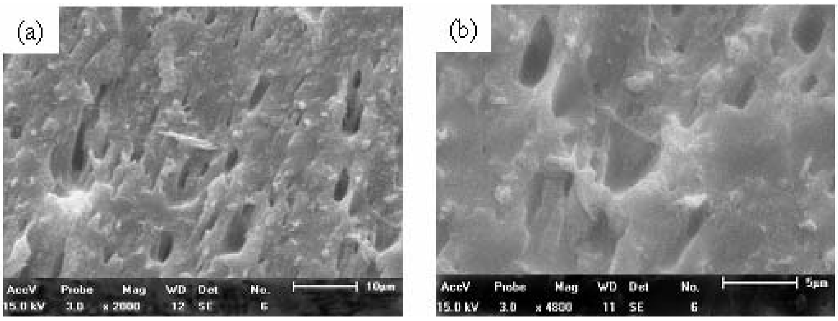


Figure 7. SEM images of freeze-fractured PET/PC/SEBS blends (SEBS weight ratio was 20%,(a)×2000; (b)×4000)

Though SEBS was relatively suitable to this blending system, the weight ratio of SEBS must be in a limited content. Table 3 is the mechanical properties of PET/PC alloy with different SEBS contents, and it can be concluded that over contents of SEBS would also result in the decrease in stiffness and toughness of the alloy.

Figure 7 are the frozen-fractured images of the alloy with SEBS weight ratio of 20% (SEBS was etched before testing). In Figure 7, the particle shape of SEBS was irregular and the average particle size (above 4μm) was much larger than the ones tested before with 10% elastomers (below 1.54μm). In addition, phase separating phenomena could also be found. That was because SEBS was partially miscible with PET and PC, too much SEBS not only resulted in the coalescence, but also affected the compatibility between other components.

Table 3. Effect of SEBS content on mechanical properties of PET/PC/SEBS alloy

Mechanical Properties	SEBS content			
	5%	10%	15%	20%
Tensile Strength (MPa)	47.2	46.7	42.1	31.5
Elongation at Break (%)	150.3	192.2	142.3	35.0
Flexural Strength (MPa)	74.3	73.5	68.2	65.6
Flexural Modulus (GPa)	2.10	2.12	1.98	1.86
Unnotched Impact Strength(kJ/m^2)	Not broken	Not broken	65.3	48.4
Notched Impact Strength (kJ/m^2)	56.2	78.3	43.2	20.5

Conclusion

PET/PC alloy toughened with three kinds of elastomers were prepared by the twin-screw extruder, And MDI was added simultaneously as chain-extender so as to increase the molecular weight of recycled PET phase. The alloy with POE showed poor mechanical properties due to the immiscible with PET and PC. In PET/PC/SEBS-MA blending system, the competitive reactions (among SEBS-MA, PET and MDI) resulted in coalescence of SEBS-MA and its toughness didn’t raise much. The alloy with SEBS exhibited highest performance among them, but its content should also be limited in a certain degree.

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