High-Impact Poly(ethylene terephthalate) Blends

M. PENCO,[1] M. A. PASTORINO,[2] E. OCCHIELLO,[2] F. GARBASSI,[2,*] R. BRAGLIA,[2] and G. GIANNOTTA[2]

[1]Università di Brescia, Dipartimento di Chimica e Fisica per i Materiali, Via Branze 38, Brescia I-25123 Italy, and [2]EniChem S.p.A., Istituto Guido Donegani, Via G. Fauser 4, Novara, I-28100, Italy

SYNOPSIS

Rubbers of different kind were tested as toughening agents of poly(ethylene terephthalate) (PET), noting significant morphological and mechanical differences. In particular, good results were obtained by using an ethylene–ethyl acrylate–glycidyl methacrylate copolymer. The resulting blend evidenced good particle distribution, and the latter was related to chemical interactions between the rubber epoxy groups and PET terminal groups, including the effect of low molecular weight and polymeric amine catalysts, and to extrusion conditions. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

In the last decade, a number of polymer blends and alloys have been introduced in the market, especially as engineering plastics.[1-4] In general, blend properties depend on compatibility. For instance, for fully compatible blends, mechanical and thermal properties are expected to be close to the average of blend components.[5-11]

A particularly important class of polymer blends includes high-impact materials obtained by the combination of thermoplastic crystalline polymers (e.g., polyesters and polyamides) with elastomers; the toughening effect is obtained by the dispersion of the rubber inside the thermoplastic matrix.[12-14] For this class of materials, the size and shape of the dispersed phase, along with its interactions with the matrix polymer, depend on the chemistry of components, on their melt viscosity, and on extrusion conditions and are important factors for determining mechanical performance.[15-20] In particular, while for plastics such as polystyrene and polymethylmethacrylate a matrix crazing mechanism is dominant, for polyesters and polyamides matrix yielding is most important; thus a sharp brittle–tough transition occurs when the interparticle distance is below a critical value.[19,20] Important characteristics, such

as interfacial tension (γ), matrix (η_m), and rubber (η_r) melt viscosities, average particle diameter (d), and shear rate in the extruder (G) are related by the following empirical equation, suggested by Wu (20):

$$G\eta_m d/\gamma = 4 (\eta_r/\eta_m)^\beta \qquad (1)$$

where β is a coefficient worth 0.84 if $\eta_r/\eta_m > 1$ and -0.84 if $\eta_r/\eta_m < 1$. In this article we studied the toughening of PET using a set of different elastomers, both reactive and unreactive toward PET terminal hydroxyl and carboxyl groups. The influence of type of elastomer was first assessed studying the blend morphology and mechanical properties. Then, for an elastomer reactive with PET end groups, the effect of the addition of compounds catalyzing the reaction of epoxide groups with carboxyls and/or hydroxyls was also studied.

EXPERIMENTAL SECTION

Bottle grade PET (IV = 0.74) from EniChem Fibre was used as the matrix phase. Before processing, the material was vacuum (> 1 mm Hg) dried at 110°C for 24 h. The typical formulation of nucleated PET used for toughening studies is reported in Table I. Commercial elastomers were used (Table II); all of them were vacuum dried at 50°C for 24 h before use. In the case of the elastomer-incorporating epoxide

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* To whom correspondence should be addressed.

Table I Typical Formulation of PET and Additives for Toughening Studies

Compound	Function	Producer	Amount
PET (bottle grade)		EniChem Fibre	45 kg
Talcum powder	Nucleant	Val Chisone S.p.A.	90 g
Sodium benzoate	Nucleant	Fluka, > 99.5% pure	135 g
Alkonox 240	Antioxidant	EniChem Synthesis	90 g
Anox 20	Antioxidant	EniChem Synthesis	135 g

Table II List of the Elastomers Used for Blending with PET

	Trade Name	Producer	Chemistry
R1	Kraton G 1652	Shell	Styrene–butadiene block copolymer
R2	Exxelor Va 1801	Exxon	Copolymer including ethylene, propylene, and maleic anhydride
R3	Lotril 3610 M	Orkem	Copolymer including ethylene and ethyl acrylate
R4	Lotader XX 8660	Orkem	Copolymer including ethylene, ethyl acrylate, and glycidyl methacrylate
R5	R4 with 0.3 w % N,N-dimethylstearylamine		

functions (Rubber 4), catalysts of the reaction of epoxide functions with PET end groups were also utilized, among them a commercial product (N,N-dimethylstearylamine, TCI, > 98%) and polymeric amine catalysts, prepared by reacting a reactive rubber with amines in a Brabender discontinuous mixer (Table III). Table IV provides a list of all PET–elastomer blends.

A Werner ZSK 40 co-rotating twin screw extruder was used, and the temperature of the various extruder regions was comprised between 260°C and 280°C. Nucleants, antioxidants, and catalyst were added to PET by dry blending before the extrusion, while the elastomer was added using a separate gravimetric feeder. The screw rotation rate was usually 100 rpm, unless stated otherwise, and the extruder throughput was 30 kg/h. Rheological testing was performed using a Goettfert Rheograph 2002 capillary rheometer, with an L/D ratio equal to 20.

Mechanical properties were determined on injection-molded specimens. The latter were prepared using a Sandretto injection molding machine and annealed at 120°C for 24 h in nitrogen atmosphere to equalize crystallinity. The thickness was 10.16 mm for notched Izod tests and 3 mm for tensile tests. In terms of characterization, mechanical testing was performed using an Instron dynamometer and a CEAST pendulus, according to ASTM D638, D790, and D256. The nominal strain rate at the start of tensile tests was 1 mm/min. The morphology of the samples was assessed using a Cambridge Stereoscan Scanning Electron Microscope (SEM).

RESULTS AND DISCUSSION

Effect of the Elastomer

In incompatible polymer blends, the morphology of the phase is strongly related to interfacial tension

Table III Components Used for the Preparation of Polymeric Amine Catalysts (PCAT 1–3)

	Compound	Producer
All catalysts	Lotader 4700 rubber	Orkem
PCAT 1	N,N-dimethylethylenediamine	Merck
PCAT 2	N,N-dimethyl-1,3-propandiamine	Merck
PCAT 3	4,4'-diaminodicyclohexylmethane	BASF

Table IV Composition of PET/Rubber Blends

| Formulation	Rubber	Catalyst	% Nucl. PET	% Rubber	% Catalyst
F1	R1		80	20	
F2	R2		80	20	
F3	R3		80	20	
F4	R4		80	20	
F5	R5		80	20	
F6*	R5		85	15	
F7*	R5		80	20	
F8*	R5		75	25	
F9*	R5		70	30	
F10**	R5		85	15	
F11**	R5		80	20	
F12**	R5		75	25	
F13**	R5		70	30	
F14	R4		70	30	
F15	R5		70	30	
F16	R4	PCAT 1	70	27	3
F17	R4	PCAT 2	70	27	3
F18	R4	PCAT 3	70	27	3
F19	R4	PCAT 3	70	28.5	1.5

All numbers are wt %.
* Extruder operated at 150 rpm.
** Extruder operated at 250 rpm.

and melt viscosity, which in turn are a function of temperature and extruder shear rate. As shown by Eq. (1), having similar melt viscosities helps in obtaining the finest particle size. The rheological curves of PET and of the rubbers quoted in Table II are reported in Figure 1. At the appropriate temperature and in the proximity of the effective shear rate of the extruder (100 s^{-1}), only R4 and R1 have a melt viscosity similar to the PET one. Extruder mixing was then performed, assessing the effect of the elastomer, followed by injection molding to obtain specimens for mechanical testing. No evident effect of the injection molding step was observed on the particle morphology, as observed by SEM; furthermore, prolonged annealing allowed us to perform characterization at a similar average crystallinity of PET.
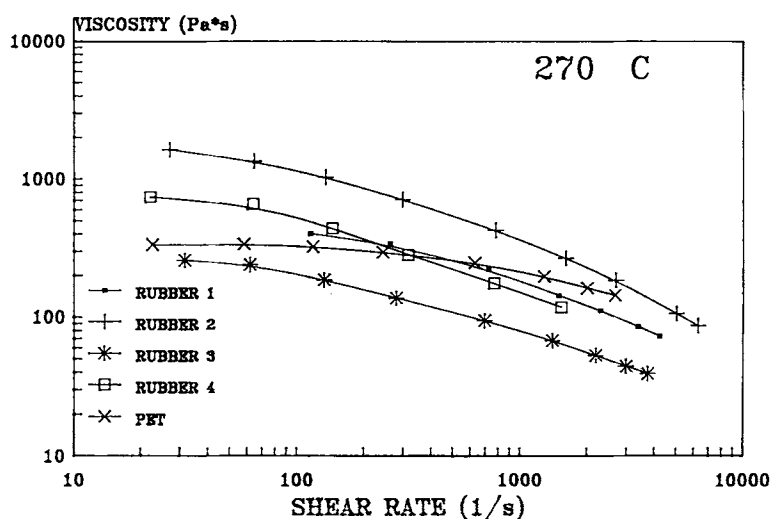

Figure 1 Rheological curves at 270°C of PET and of all rubbers utilized in this study.
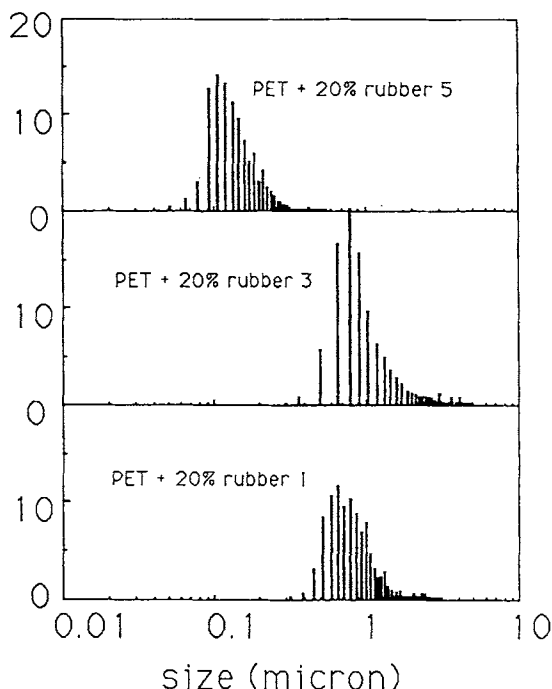
Figure 2 Distribution of rubber particle dimensions as a function of rubber type.

The results of mechanical testing of these mixtures are reported in Table V. This shows that the addition of elastomers to PET, as expected, leads to a reduction of properties such as tensile modulus. On the other hand, an astounding improvement of impact properties was observed, mainly in the case of the compositions F4 and F5 (see Table IV). Further evidence is provided in Figure 2 and Table VI; the former shows the distribution of particle sizes
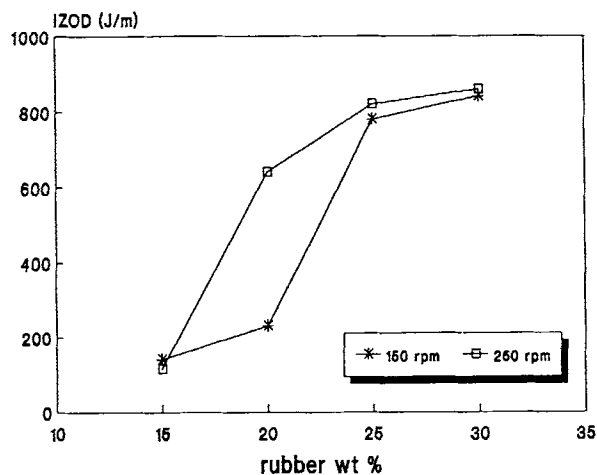
Figure 3 Effect on impact resistance of rubber amount and extruder parameters.

for some of the latter compositions, evidencing a much finer average size observed for F5. On the other hand, in Table VI, the results of rheological testing of components and morphological characterization of blends are utilized to calculate interfacial tensions, based on Eq. (1). It is evident that for F5 a particularly low interfacial tension is obtained, although of course this result is strongly affected by the reactivity of the rubber with PET, leading to the formation of graft co-polymers acting as compatibilizers.

It is also interesting to observe (Table V) that the addition of some catalyst to the composition further improves the impact resistance of the material and that the other composition with a rubber with a melt viscosity similar to that of PET does not improve as dramatically the impact resistance due to the absence of the compatibilizing effect of the formation of graft copolymers.

Effect of Rubber Amount and Extruder Parameters

We have shown that particularly good improvements in impact properties can be obtained by using a reactive rubber. We now comment on the effect of the amount of rubber and of extruder parameters, since it is known for these systems that impact properties are related to the interparticle distance, which is of course related to the rubber fraction, as reported by Wu.[19] Figure 3 shows the impact properties of compositions F6–F13. It is evident that a threshold minimum amount of rubber exists and that it depends on extruder parameters. In particular, it is clear that by increasing the mixing efficiency, better impact properties at low rubber amount can be obtained.

Effect of Catalyst Type and Amount

It is known that amine catalysts improve the reaction rate of epoxide moieties with carboxyls and

Table V   Effect of the Rubber on the Mechanical Properties of PET–Elastomer Blends

Formulation	Izod (J/m)	Tensile Modulus (GPa)
Virgin PET	42	2.4
F1	37	2.3
F2	103	1.4
F3	34	1.6
F4	490	1.5
F5	750	1.4

Table VI   Utilization of Eq. (1) for Calculating Interfacial Tensions

Formulation	Shear Rate (s^{-1})	Radius (μm)	Rubber Viscosity (Pa/s)	Viscosity Ratio	Interfacial Tension (mN/m^2)
F1	100	0.89	410	1.32	5.43
F3	100	1.19	214	0.69	6.77
F5	100	0.15	550	1.77	0.74

hydroxyls[21]; thus it is natural to utilize them for improving the grafting efficiency, as already shown. Yet the use of low-molecular-weight amine compounds in reactive blending experiments can be environmentally hazardous; thus the polymeric amine catalysts in Table III have been prepared.

Table VII shows the effect of varying the type and amount of catalyst on mechanical properties. It is clear that the tensile moduli are sensitive only to the relative percentage of PET and rubber, while impact properties depend effectively on the catalyst and show particularly good results for compositions F16 and F19. This is a particularly interesting result, since the use of a polymeric catalyst poses major compatibility and reactivity constraints as compared to a low-molecular-weight additive. Yet the combination of good performance with environmental friendliness appears most desirable.

CONCLUSIONS

Impact properties of PET can be improved by adding elastomeric phases. Particularly good results were obtained when using a reactive elastomer able to react with PET end groups. Considerations based on the master equation suggested by Wu have been presented, showing a drop of

Table VII   Effect of the Catalyst on the Mechanical Properties of PET–Elastomer Blends

Formulation	Izod (J/m)	Tensile Modulus (GPa)
Virgin PET	42	2.4
F14	236	1.3
F15	582	1.4
F16	555	1.4
F17	238	1.3
F18	363	1.4
F19	599	1.4

interfacial tension for a reactive system. We observed the existence of a threshold amount of rubber for having sizable improvements of impact properties. Furthermore, we noted a dependence of mechanical properties upon extruder parameters (namely, on the mixing efficiency). These effects may be related to the effect of the distance of rubber particles on impact properties. We also showed that the addition of catalysts of the reactions between rubber reactive groups (epoxides) and PET end groups (carboxyls and hydroxyls) is able to improve the grafting efficiency, thus acting on impact performance. The use of polymeric amine catalysts, which are able to reduce environmental hazards in reactive blending experiments, has also been shown to be effective.

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