Macromol. Symp. ***176****, 167–180 (2001)*

Toughening of PBT by ABS, SBS and HIPS Systems and the Effects of Reactive Functionalised Copolymers

Gerson Luiz Mantovani, Leonardo Bresciani Canto, Elias Hage Junior, Luiz Antonio Pessan[*]

Universidade Federal de São Carlos, Department of Materials Engineering. 13565-905
São Carlos, SP – Brazil. pessan@power.ufscar.br

Summary: Poly(butylene terephthalate) (PBT) has been toughened by the addition of different impact modifiers such as acrylonitrile-butadiene-styrene (ABS), styrene-butadiene-styrene triblock copolymer (SBS), high impact polystyrene (HIPS) and HIPS/SBS systems with and without reactive compatibilising copolymer. PBT/ABS blends have been modified by methyl methacrylate-*co*-glycidil methacrylate copolymer (MMA-GMA) and the systems PBT/HIPS and PBT/SBS where modified by an *in situ* compatibiliser of styrene-*co*-glycidyl methacrylate copolymer (S-GMA). Addition of ABS A, ABS B, SBS and HIPS/SBS systems at high content of SBS, was very effective in increase the ability of PBT in absorb impact energy. Incorporation of HIPS to PBT at any level did not improve impact strength of the PBT matrix. By adding the acrylic copolymer to the PBT/ABS blends, the high impact strength behaviour of the blends observed at room temperature, has been extended to temperatures well below the room temperature. The effects of addition of reactive copolymer to the morphology of PBT/ABS blends have been studied. The results show the strong influence of the acrylic copolymer in controlling the phase morphology of the system studied. Addition of the styrene-*co*-glycidil methacrylate copolymer to the 50/25/25 PBT/HIPS/SBS system did not promote a significant decrease in the ductile-brittle transition behaviour for this blend. In fact, incorporation of the high glycidil methacrylate content styrenic compatibiliser has turned the system into brittle over the temperature range studied, i.e., the ductile-brittle transition has been suppressed.

Introduction

One of the major limitations of PBT, an engineering thermoplastic widely used in the industry, is its high impact strength sensitivity to small cracks or notch in the moulded part. Toughening of PBT can be achieved by melt blending it with appropriate elastomeric materials [1,2,3] where an adequate phase morphology obtained during the melt processing of the materials allow impact energy to be absorbed through toughening mechanisms not at play in neat PBT. Besides the generation of the optimised phase morphology for improvement of mechanical properties such as impact strength, stabilisation of the morphology obtained during melt processing and the brittle-ductile transition temperature of the system are also important issues for long term application of the material.

CCC 1022-1360/00/$ 17.50+.50/0

PBT has been successfully toughened by ABS materials using an MMA-GMA copolymer as the reactive compatibiliser [2,3]. However, previous work in the literature has shown that besides the *in situ* graft copolymer formation desired reaction in this system, undesired chemical crosslinking reactions also occur in the PBT/ABS/MMA-GMA systems. It appears that residual acid components in certain emulsion-made ABS materials catalyse ring opening polymerisation of the epoxy groups in GMA. In any case, the formation of a gel fraction leads to a reduction in the room temperature impact strength [3]. Other important issues in plastic toughening are the rubber content of the impact modifier, the chemical characteristics of the continuous phase and also the phase morphology of the impact modifier, in order to choose the appropriate potential reactive copolymer to improve compatibility and/or stabilise the morphology.

Several types of reactions may occur for the PBT/ABS/ MMA-GMA system when processed at high temperature. Fig. 1 illustrates three types of reactions that may occur between epoxy groups and carboxyl functionalities [3].

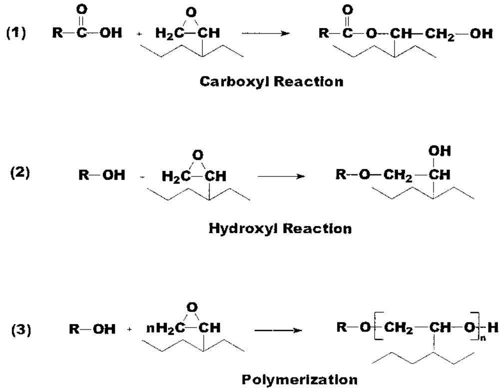
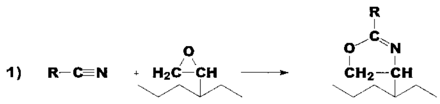


Fig. 1: Possible reactions between epoxy units and PBT hydroxyl and carboxyl end groups.

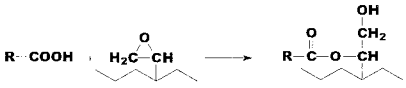
As shown by Hale, Keskkula and Paul [3] other reactions are also possible for the PBT/ABS/MMA-GMA systems. For instance, nitrile groups have been shown to react with epoxides in the presence of acid catalysts to form oxazoline linkages as follows:



Nitriles can also undergo hydrolysis to carboxyl groups, which in turn can react with the epoxides groups:

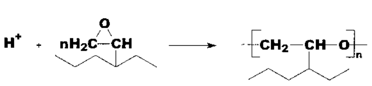
2) $R-C\equiv N + 2H_2O \xrightarrow{\text{acid or base}} R-COOH + NH_3$

3)



Strong acids may catalyze the above-mentioned nitrile/epoxide reaction or initiate ring opening polymerization of the oxirane functionality, i.e.

4)



In this work PBT toughening phenomena has been studied by using two types of ABS terpolymer with varying rubber content, chemical and physical characteristics, one type of SBS, one type of HIPS, and HIPS/SBS systems at different ratios. Comparison of the data obtained give some insights into the influence of rubber content, continuous phase chemical composition, and phase morphology of the impact modifiers on the toughening phenomena of PBT. These systems have also been studied regarding the effects of the addition of functionalised copolymers on its properties.

Experimental

Materials

The properties of the materials used in this work are shown in Table 1 and Table 2.

Methods

The copolymers MMA-GMA and S-GMA have been synthesised in our laboratories by mass polymerisation according to the procedures described in the literature [4,5].

The rheological behaviour of each material was characterised by torque rheometry using a HAAKE Rheomix 600p machine.

The mixtures were prepared in a twin screw extruder Baker Perkins 2019, at 220°C and 170 rpm and the specimens for the impact strength tests were prepared in an injection moulding machine ARBURG 270V at 240°C.

Notched Izod impact tests were conducted according to ASTM D256 as a function of temperature to determine the ductile-to-brittle transition, using a CEAST RESIL 25 equipment.

The morphology of selected blends was examined using a PHILIPS CM 120 transmission electron microscope (TEM) at an accelerating voltage of 100 KV. Ultrathin sections were obtained by cryo-microtoming samples from moulded IZOD bars, using a REICHERT ULTRACUT FC S microtome at – 40°C. Thin sections (30 – 100 nm) were stained with OsO_4 vapour for 15 hours. The rubbery phases of ABS, HIPS and SBS appear as dark domains in the TEM images.

Table 1. Characteristics of the materials used in this work.

Designation used here	Supplier designation	Haake Torque **Nm**	Rubber Content **Wt%**	Izod impact Strength[c] **J/m**	Source	Mol. Wt **g.mol^{-1}**
PBT[a]	Valox 315	2.0[b] 4.7[e]		51	GE	M_n= 35000 M_w= 100000
MMA-GMA[d]		1.0[b]		-		M_n= 60000 M_w= 115000
HIPS	Lustrex 4300	3.9[e]	8.9[g]	120	BASF	
SBS	Kraton D1102	7.6[e]	66.3[g]	-	Shell	
S-GMA2[f]						M_n= 18000 M_w= 137000
S-GMA5[f]		0.2[e]		-		M_n= 38000 M_w= 170000
S-GMA10[f]				-		M_n= 27000 M_w= 151000

[a] PBT carboxylic acid content is 80 eq/10^6 g (end-group titration method);
[b] 250°C and 60 rpm after 10 min;
[c] Room temperature/notched (ASTM D 256);
[d] Acrylic copolymer containing 10 %wt of GMA;
[e] 220°C and 50 rpm after 10 min;
[f] Styrenic copolymer containing 2, 5 and 10 %wt of GMA.
[g] FT-IR.

Table 2. Characteristics of the ABS used in this study.

Designation used here	Molecular and structural characteristics				surfactant residual %wt
	AN Content [c] %	Rubber Content [c] %	Graft ratio	SAN (free) MW $g.mole^{-1}$	
ABS A	14 (13)[a]	48 (50)[b]	0.3	$\overline{Mn} = 52000$ $\overline{Mw} = 114000$	3,6
ABS B	11 (12)[a]	56 (55)[b]	0.6	$\overline{Mn} = 28000$ $\overline{Mw} = 64000$	0,9

[a] Determined by elemental analysis method CHNS-O.
[b] Determined by iodine index.
[c] Determined by FT-IR.

Results and Discussion

PBT/HIPS, PBT/SBS and PBT/HIPS/SBS Systems

Fig. 2 shows the room-temperature notched Izod impact strength for PBT/HIPS and PBT/SBS blends. Toughening of PBT has been obtained by the addition of SBS. On the other hand, addition of up to 50 %wt of HIPS did not promote any toughening on the PBT matrix. HIPS is basically a blend of polystyrene (PS) and a graft copolymer of butadiene and styrene (PB-*g*-PS) that displays characteristic phase morphology constituted of substructured *salami* phase domains of the graft copolymer PB-*g*-PS embedded in a matrix of PS, whereas SBS is a triblock styrene-butadiene-styrene copolymer that exhibit a morphology depending of the styrene-butadiene ratio. The morphology of the SBS used in this work (66 %wt of butadiene) shows polystyrene microdomains dispersed in the elastomeric matrix. The low rubber content of HIPS (9 %wt), compared to SBS (66 %wt), is probably the determining factor for the low values of impact strength observed for the PBT/HIPS system.

Fig. 3 shows the impact strength as function of temperature for ternary blends of PBT/HIPS/SBS. A balance of mechanical properties can be obtained by varying the ratio of HIPS/SBS added into PBT due to the higher rubber content of SBS compared with HIPS. As can be observed in Fig. 3 the PBT/HIPS/SBS 50/10/40 blend presents a ductile behaviour similar to the PBT/SBS 50/50 blend, however, at a lower overall rubber content. Also, the combination of HIPS and SBS prevents an even more significant loss of modulus of the blend. The composition PBT/HIPS/SBS 50/10/40 shows similar impact strength and higher modulus compared to the PBT/SBS 50/50, as shown in Fig. 4.

The ternary blend PBT/HIPS/SBS 50/25/25 was chosen for the study on the effects of addition of reactive copolymer to the system due to its ductile-brittle transition behaviour. It has a ductile-brittle temperature of approximately 60 °C and the expectation was that compatibilisation could shift this transition temperature to lower values. It was expected that the addition of S-GMA into the ternary blend PBT/HIPS/SBS could promote a similar compatibilising effect as observed for PBT/PS and PET/PS systems in the literature [6,7]. The epoxy group of the S-GMA copolymer is expected to react with the acid end groups of PBT chains and the PBT-GMA-S chains should be located at the interface and act as *in situ* compatibilisers between PBT and PS phases. However, blends PBT/HIPS/SBS 50/25/25 with 5 %wt of S-GMA2 and S-GMA5 did not show a significant reduction in the ductile-brittle transition temperature compared to the non-reactive blend with the same composition, as show in Fig. 5. On the other hand, addition of the copolymer S-GMA10 to this blend produces an undesired effect on the impact strength. The incorporation of 5 %wt of the high GMA content compatibiliser S-GMA10 into the blend has turned the system into brittle over the whole temperature range studied, i.e., the ductile-brittle transition has been suppressed.

The morphologies of the PBT/HIPS/SBS 50/25/25 blends with and without the addition of reactive copolymer are shown in Fig. 6. The incorporation of S-GMA2 and S-GMA5 did not have a significant effect on the phase morphology of the blend, which correlates with the similar impact behaviour compared with the non-reactive blend. On the other hand, addition of S-GMA10 has caused a coarsening of the phase morphology of the system, which is in agreement with the poor impact properties of corresponding blends.

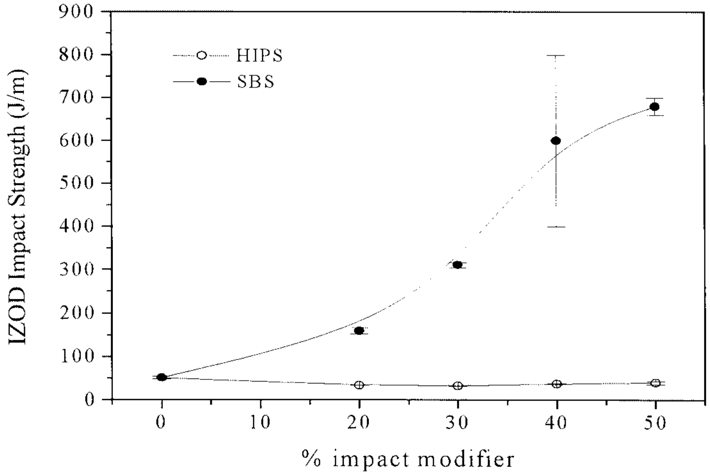


Fig. 2: Notched Izod impact strength PBT/HIPS and PBT/SBS blends at room temperature.

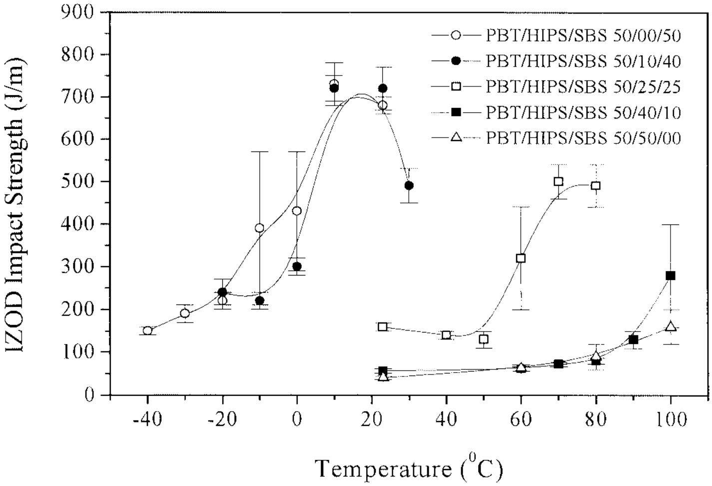


Fig. 3: Notched Izod impact strength *versus* temperature for blends PBT/HIPS/SBS.

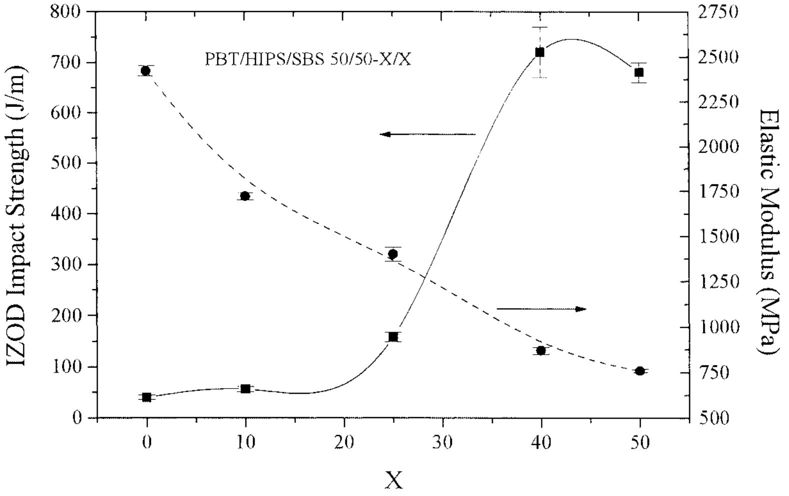


Fig. 4: Notched Izod impact strength and elastic modulus as function of SBS content for PBT/HIPS/SBS blends.

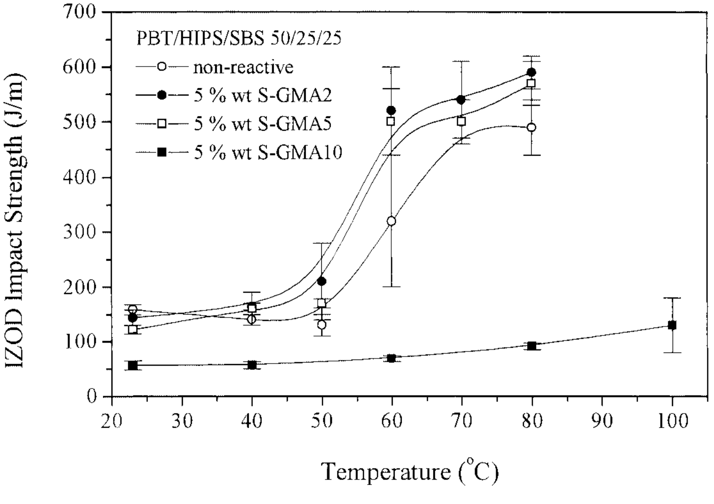
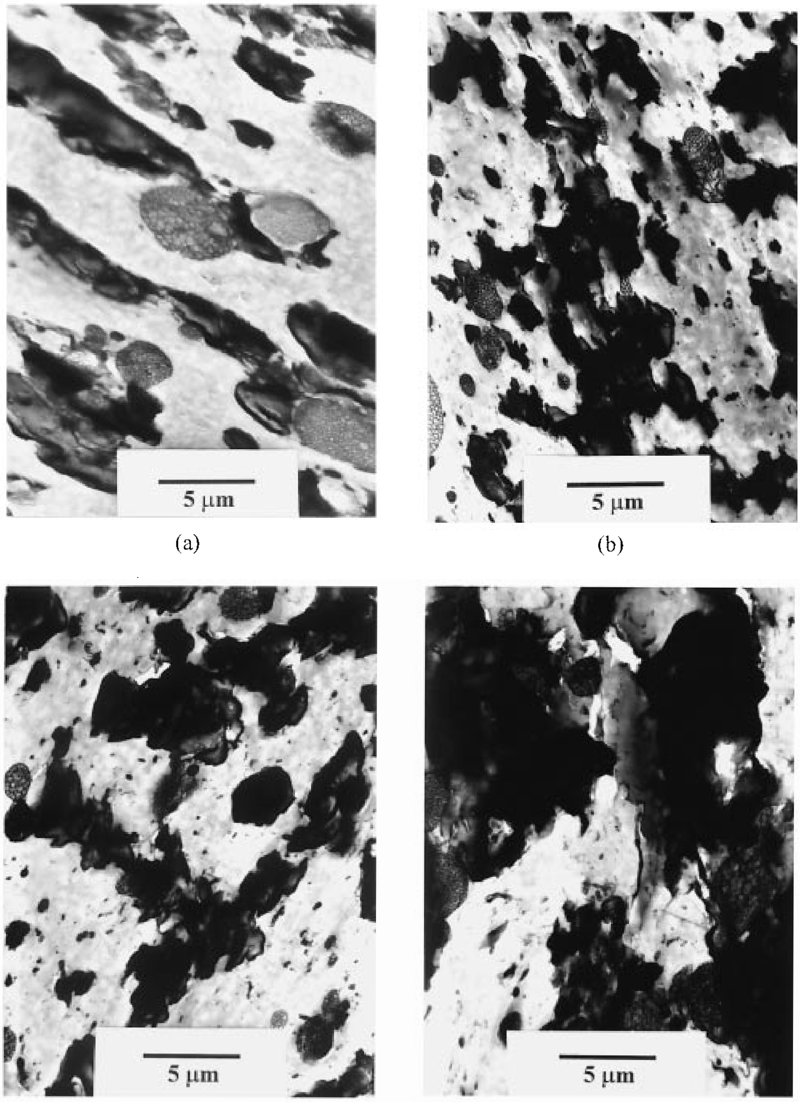


Fig. 5: Notched Izod impact strength *versus* temperature for reactive blends PBT/HIPS/SBS.



(a) (b)

(c) (d)

Fig. 6: Morphology of (a) PBT/HIPS/SBS 50/25/25 (b) PBT/HIPS/SBS/S-GMA2 50/25/25/5 (c) PBT/HIPS/SBS/S-GMA5 50/25/25/5 (d) PBT/HIPS/SBS/S-GMA10 50/25/25/5 observed by TEM. Samples prepared in a twin screw extruder at 220°C and moulded at 240°C. The rubbery phase of the HIPS and SBS is stained dark by OsO_4.

PBT/ABS Systems

PBT/ABS 60/40 and PBT/ABS/MMA-GMA 60-x/40/x=5 using two different grades of ABS, ABS A and ABS B, have been studied and the results are discussed in this paper. As shown in Table 2, ABS A and ABS B have similar rubber content but differ in structural characteristics and surfactant residue contents.

Figs. 7 and 8 show the notched Izod impact strength *vs* temperature for the blends of PBT/ABS A and PBT/ABS B, respectively. It can be observed that the ABS A-based blend without addition of reactive copolymer reach high values of impact strength (870 J/m) and show a ductile-brittle transition of approximately -10 °C. Addition of MMA-GMA copolymer to the PBT/ABS A blends shift the ductile-brittle temperature by 40 °C to approximately - 50 °C. However, the modified system shows lower impact strength (≅650 J/m) at room temperature and a maximum of 800 J/m at temperature closer to the ductile-brittle transition. On the other hand, a less significant change is observed when MMA-GMA is added to the PBT/ABS B blend, when compared to the changes observed for the PBT/ABS A system. ABS B-based blend shows high values of impact strength of 870 J/m with a ductile-brittle temperature transition of approximately -10 °C and these values are changed to 850 J/m and to -25 °C due to the addition of the acrylic copolymer. This behaviour has been attributed to the different level of surfactant residue in the emulsion made ABS terpolymer. Hale et all. [3] speculated recently that this reduction in impact strength at room temperature is due to chemical crosslinking reactions that take place in the PBT/ABS/MMA-GMA systems in addition to the desired reactions between the end groups of PBT molecules and the epoxy group of the acrylic copolymer. The acid residues of the surfactant catalyses the crosslinking reaction and leads to the formation of a gel fraction which causes a reduction in the impact strength of the system at room temperature. As shown in this work, the PBT blend based on ABS A terpolymer with 3.6 %wt of surfactant residue show a more significant reduction in the impact strength compared to the blend based on the ABS B which has 0.9 %wt of surfactant residue. When dealing with PBT/ABS/MMA-GMA systems at composition like 55/40/5, there is a high molar ratio between the ester groups of PBT (-COO-) and epoxy groups of MMA-GMA of about 130. This factor, together with the relatively high processing temperature suggest the possibility of acid-catalysed PBT chain breaking, due to the presence of the acid emulsifier in the ABS, as a competitive reaction to the acid-catalysed ring-opening polymerisation of epoxy groups. However, torque rheometry tests performed mixtures between PBT and acid residue extracted from ABS terpolymer and between the MMA-GMA copolymer and the acid residue extracted from the ABS terpolymer indicate that the reaction between the MMA-GMA and the acid residue are much faster than the reaction between the PBT molecules and acid residue of the ABS terpolymer. This behaviour and the molecular weight of the PBT after the extrusion and injection moulding process are under further investigation.

Another important issue to be considered in this discussion is the continuous phase in the impact modifier used in the system. The ABS A consists of polybutadiene rubber particles dispersed in an SAN matrix while ABS B may show either a phase morphology similar to ABS A or a phase morphology where the continuous phase is the rubbery phase polybutadiene, as observed in the literature [8]. We believe that the phase morphology observed for the ABS B is dependent on the how this material is processed. This characteristic can affects markedly the toughening phenomena of PBT and the effects of addition of reactive copolymer to the system. Depending on which is the continuous phase of the impact modifier an appropriate reactive copolymer could be chosen for compatibilisation between phases or stabilisation of phase morphology.

Figs. 9 and 10 show the significant effects of the addition of MMA-GMA copolymer on the phase morphology of the PBT/ABS blends studied. As can be observed, the effects are more pronounced in the ABS A-based system because in this impact modifier SAN is the material that constitute the continuous phase or matrix. Therefore, MMA-GMA is an appropriate *in situ* reactive copolymer for the PBT/ABS A blend for the epoxy group of GMA can react with the end groups of PBT molecules whereas the MMA can interact favourably with the SAN phase of the impact modifier [2]. For the PBT/ABS B blend, the SAN dispersed particles would not be available to interact with the MMA molecules of the functionalised copolymer MMA-GMA and also the MMA segments are not miscible with the polybutadiene matrix of the ABS B and therefore the reduction in interfacial tension between PBT and the impact modifier ABS would not be so effective.

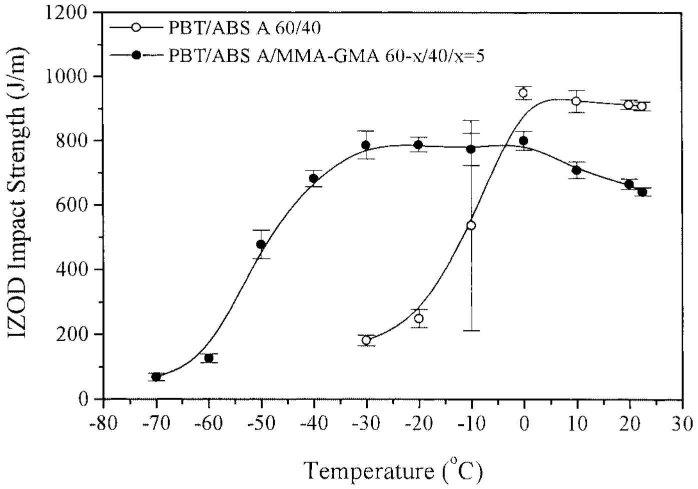


Fig. 7: Notched Izod impact strength *versus* temperature for blends containing 40 %wt ABS A.

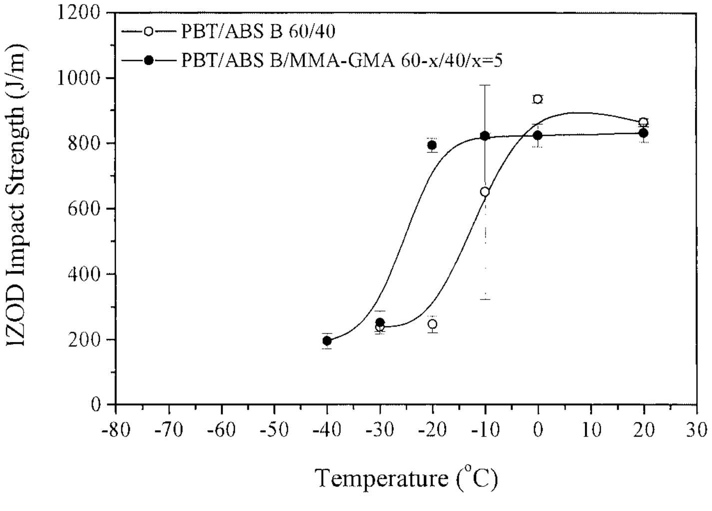
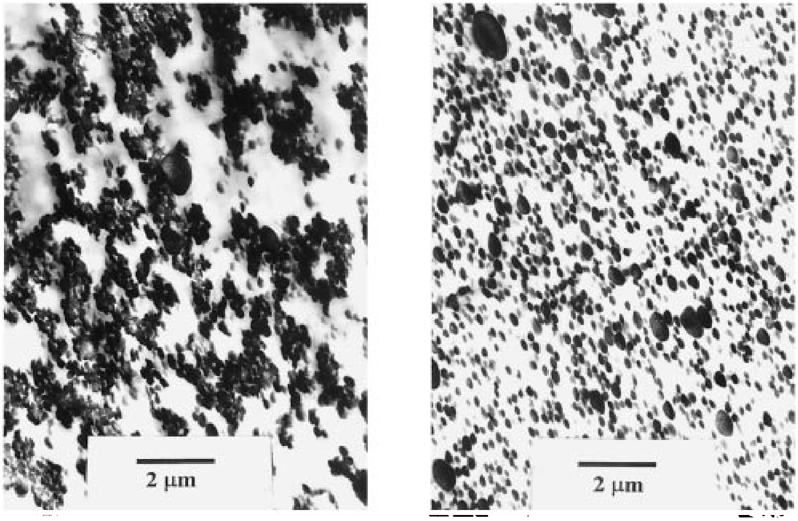
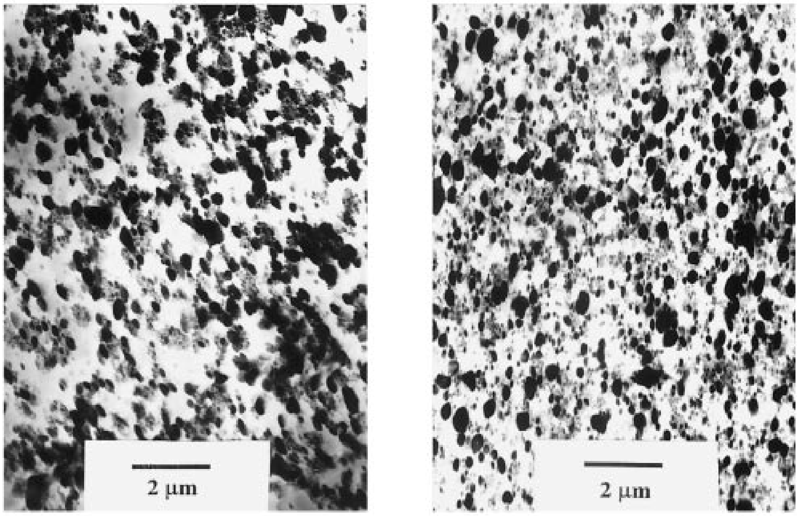


Fig. 8: Notched Izod impact strength *versus* temperature for blends containing 40 %wt ABS B.



(a) (b)

Fig. 9: Morphology of (a) PBT/ABS A (60/40) blends and (b) PBT/ABS A/MMA-GMA (60-x/40/x=5) observed by TEM. Samples prepared in a twin screw extruder at 220°C and moulded at 240°C. The rubbery phase of the ABS A is stained dark by OsO_4.



(a) (b)

Fig. 10: Morphology of (a) PBT/ABS B (60/40) blends and (b) PBT/ABS B/MMA-GMA (60-x/40/x=5) observed by TEM. Samples prepared in a twin screw extruder at 220°C and moulded at 240°C. The rubbery phase of the ABS B is stained dark by OsO_4.

Conclusions

Toughening of PBT by the addition of different impact modifiers additives has been studied and the results give insights into some important issues like rubber content, continuous phase chemical and structural characteristic, and phase morphology of the impact modifiers. The surfactant residue detected in the ABS materials used support speculations on the effects of chemical crosslinking reactions in PBT/ABS/MMA-GMA blends, however, it is also important to consider the phase morphology of the ABS terpolymer. In general, the MMA-GMA copolymer has significant effects on the phase morphology and is very effective in reducing the ductile-brittle transition temperature of PBT/ABS blends, mainly for ABS A. On the other hand, S-GMA copolymer was not very effective in extending the high impact strength behaviour of the PBT/HIPS/SBS system studied to lower temperatures.

Acknowledgement

This work was supported by FAPESP and FINEP/PRONEX-Brazil.
The authors would like to thank Nitriflex, GE Plastic South America, BASF, Shell Chemicals and Bayer for the materials.

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