ELSEVIER

Polymer 40 (1999) 365–377

polymer

Compatibilization of PBT/ABS blends by methyl methacrylate-glycidyl methacrylate-ethyl acrylate terpolymers

W. Hale, H. Keskkula, D.R. Paul*

Department of Chemical Engineering and Center for Polymer Research, University of Texas at Austin, Austin, TX 78712, USA

Received 26 September 1997; revised 23 February 1998

Abstract

Poly (butylene terephthalate), PBT, can be impact modified by blending with appropriate ABS materials within a limited range of processing conditions. The morphology of these uncompatibilized blends is unstable; the dispersed phase coarsens when the melt is subjected to low shear conditions, e.g. during certain moulding conditions, which has a deleterious effect on the final blend properties. Terpolymers of methyl methacrylate, glycidyl methacrylate (GMA), and ethyl acrylate have been synthesized and shown to be effective reactive compatibilizers for blends of PBT with styrene–acrylonitrile copolymers (SAN) or ABS materials as revealed by improvements in SAN or ABS dispersion and morphological stability. Evidence for reaction between the carboxyl endgroups of PBT and the epoxide groups of GMA during melt processing to form a graft copolymer is presented. The effect of terpolymer composition and content on morphology generation and stabilization of PBT–SAN blends has been examined in depth. Moderate amounts of GMA in the terpolymer (>5%) and small amounts of compatibilizer in the blend (<5%) were found to significantly improve SAN dispersion. Blends of PBT and SAN containing the compatibilizer did not show any coarsening of the dispersed phase particle size due to coalescence under certian conditions of low shear. A preliminary investigation into the effect of this compatibilizer on PBT–ABS morphology and impact properties revealed greatly improved rubber dispersion and low temperature toughness. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Methyl methacrylate–glycidyl methacrylate; Poly(butylene terephthalate); Styrene–acrylonitrile

1. Introduction

Blends of poly(butylene terephthalate) (PBT) and ABS (acrylonitrile–butadiene–styrene) materials are of commercial interest because of their potential combination of impact strength, modulus, heat and chemical resistance, and abrasion resistance [1–10]. With a proper choice of materials and process conditions, blends with excellent properties can be made without use of any compatibilizer; however, the useful processing window for these blends is quite narrow [1,4,6]. Furthermore, these materials have unstable morphologies since at low stress or quiescent conditions in the melt state the ABS domains can grow by coalescence resulting in a loss of mechanical properties. By proper compatibilization one may be able to achieve better properties, a more stable morphology, and a broader processing window.

A few studies on compatibilization of PBT blends have been reported recently. Polycarbonate (PC) has been successfully used as a dispersing agent for core–shell impact modifiers due to its near miscibility with PBT and the acrylic shell of these modifiers [11–17]. Rubbers containing various functionalities such as ester, hydroxyl, epoxide and maleic anhydride units have been used in attempts to toughen PBT [8,18–26] [27–33]. Thus far, one of the most effective reactive compatibilizers for polyesters have epoxide functionality generally obtained by incorporation of glycidyl methacrylate, GMA. Attempts to compatibilize PBT–ABS blends with S–AN–GMA terpolymers which are miscible with the styrene–acrylonitrile copolymer, or SAN, matrix of ABS have been reported [8]. Attempts to compatibilize blends of PBT with poly (2,6-dimethyl-1,4-phenylene oxide), PPO, and with polystyrene, PS, using styrene–GMA copolymers which are miscible with PPO and PS have been reported [34–36]. Likewise, efforts to compatibilize blends of PBT with polypropylene, PP, using PP–g–GMA polymers have been reported [20]. Several studies describe ternary blends of PBT, polyethylene, and ethylene–GMA copolymers (EGMA) [19,37–40].

To develop an effective compatibilization strategy for PBT–ABS blends, the analogy with nylon-6–ABS blends

---

* Corresponding author.

PII: S0032-3861(98)00189-X

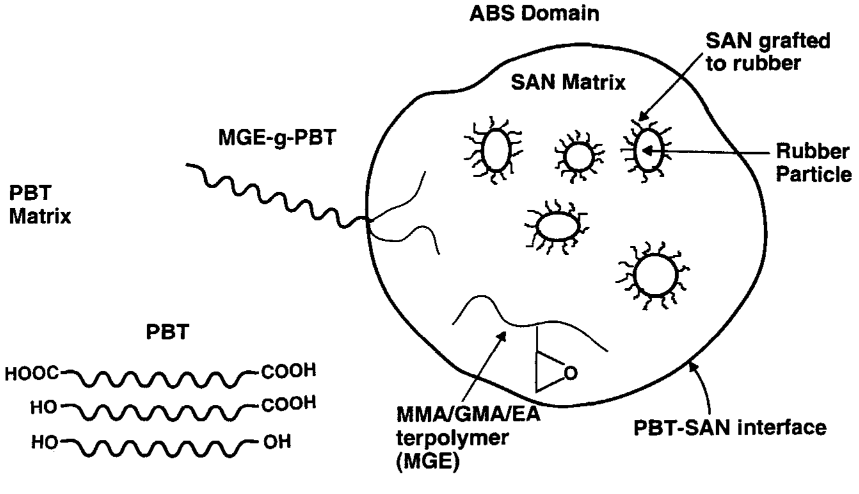


Fig. 1. Schematic representation of PBT–ABS morphology compatibilized by MMA–GMA–EA terpolymer.

might be followed where a polymer is added that is miscible with SAN and has anhydride functionality for reaction with the amine end groups of nylon-6 [41]. PBT has carboxyl and hydroxyl end groups which are potentially reactive, but these groups do not react rapidly enough with anhydrides so a more appropriate compatibilizer chemistry must be used [10,42–45]. The synthesis and characterization of epoxide containing copolymers that meet all of the requirements of an effective compatibilizer is described here. The chemical reactions that can potentially occur between epoxide units and the end groups of PBT are explored using a series of model compounds. The effects of this compatibilizer on the morphology of blends of PBT with SAN is examined since this is a simpler model system than blends with ABS. Finally, a preliminary examination of how this reactive compatibilizer affects the properties and morphology of PBT–ABS blends is presented; more detailed studies on the performance of compatibilized PBT–ABS blends will be reported later.

2. Compatibilization strategy

Fig. 1 illustrates the morphology of a PBT–ABS blend where the continuous phase is PBT. The ABS material, which consists of an SAN matrix containing cross-linked butadiene rubber particles to which a fraction of the SAN chains are grafted, forms the dispersed phase. The reactive compatibilizer should be miscible with the SAN phase and react at the interface with the carboxyl or hydroxyl end groups of PBT. Epoxide containing polymers seem to be a viable choice for rapid reaction with the PBT end groups. Poly(methyl methacrylate) (PMMA) as well as MMA–GMA copolymers are miscible with SAN copolymers having AN compositions in the range of typical ABS materials used here, as indicated by the experimental miscibility map summarized in Fig. 2 [46,47]. Methyl methacrylate (MMA) rich copolymers containing glycidyl methacrylate (GMA) and a small amount of ethyl acrylate (EA) to prevent the unzipping common for methacrylate polymers [48] have

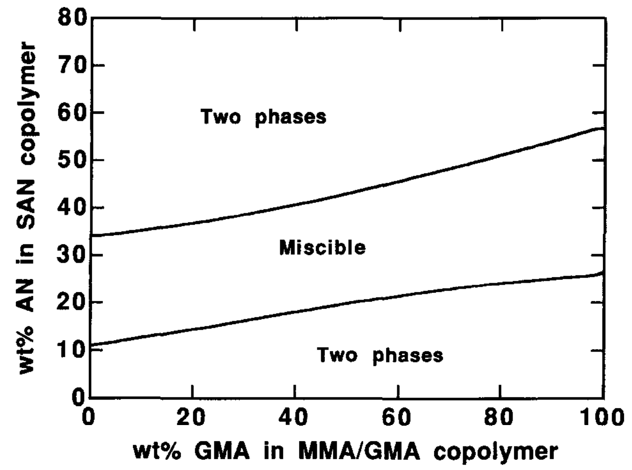


Fig. 2. Miscibility map for 50:50 blends of GMA–MMA copolymers with SAN copolymers [47].

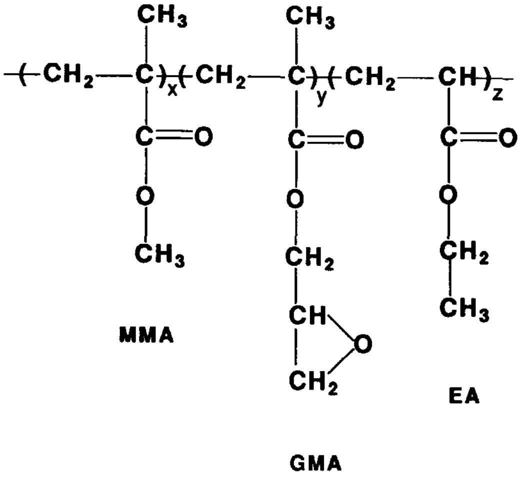


Fig. 3. Repeat units of methyl methacrylate–glycidyl methacrylate–ethyl acrylate terpolymers.

Table 1
Materials used

Designation used here	Supplier designation	Brabender torque (N m)	Temperature Izod-impact strength (J m^{-1})	Source
PBT	Valox 315	5.80[a]	50	General Electric
ABS	SAN-g	16.5[b]	550	Cheil Industries
SAN	Tyril 1000	6.5[a]	30	Dow Chemical
EGMA	Igetabond 2C	3.8[b]	—	Sumitomo
PMMA	Plexiglass V811 (100)	6.7[a]	—	Rohm and Haas

[a] Values taken after 10 min at 250°C, 50 RPM, using a 70 g sample
[b] Values taken after 10 min at 250°C, 50 RPM, using a 60 g sample

been synthesized and will be denoted by the acronym MGE, see Fig. 3. The presence of a small amount of EA in the copolymer does not affect miscibility with SAN [49].

Model compounds are used here to investigate the potential reactions of the hydroxyl and carboxyl end groups of PBT with epoxides that may create graft copolymers at the interface during melt processing conditions. Such graft copolymers strengthen the interface between domains, but perhaps more importantly they reduce interfacial tension and provide steric stabilization to reduce the rate of coalescence all of which shift the balance between drop break up and coalescence to give a finer dispersion and more stable morphology. Additionally, the grafting reactions increase the blend viscosity which can aid in ABS dispersion but may compromise some melt processing features of such blends.

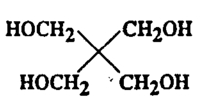
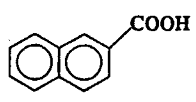
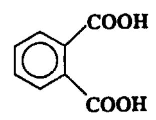
3. Experimental

3.1. Materials

Table 1 summarizes the materials used in this work. The PBT was obtained from General Electric Co. and according to the supplier it has $M_n = 35\,000$ and $M_w = 100\,000$. The ABS material used here is an emulsion-made SAN grafted rubber concentrate containing 45% rubber with an average particle size of 0.30 μm. The ungrafted SAN in this ABS material contains 25% AN and has $M_n = 35\,000$ and $M_w = 90\,000$. The graft to rubber ratio is 0.45 as determined by the manufacturer using procedures described elsewhere [1]. The SAN material used in this work, Tyril 1000 from Dow, contains 25% AN and has $M_n = 77\,000$ and $M_w = 152\,000$. The material designated as EGMA is a random ethylene–glycidyl methacrylate copolymer, containing 6 wt% GMA, from Sumitomo. The PMMA from Rohm and Haas was used as a control with 0% GMA in the MGE compatibilized series; the MGE materials synthesized here were designed to have similar melt rheological characteristics as this PMMA. A Brabender Plasticorder with a 50 ml mixing head operated at 50 rpm was used for rheological characterization of these materials.

Table 2 describes four low molecular weight compounds from Lancaster Synthesis used for simulating the reactions of the PBT carboxyl (2-naphthoic acid, phthalic acid) or hydroxyl (1-tetradecanol, pentaerythritol) end groups with epoxide rings.

Table 2 Low molecular weight model compounds

Chemical Name	Structure	Boiling Point (°C)(1)
1-Tetradecanol	$CH_3(CH_2)_{13}OH$	289
Pentaerythritol		260
2-Naphthoic acid		182 (at 0.1 mbar)
Phthalic Acid		N/A(2)

(1) At 1 atm unless otherwise noted.
(2) Melting point = 210 °C, boiling point not reported.

3.2. Compatibilizer synthesis

Terpolymers of MMA, GMA and EA were synthesized by various techniques. Emulsion and suspension techniques resulted in unusable cross-linked polymer. Bulk polymerization proved to be a simple and effective route for obtaining the desired materials. In batch copolymerization processes it is usual to limit conversion to low levels to minimize composition drift. However, in a laboratory process this entails a difficult purification and waste disposal problem when sizable quantities of polymer must be made. In view of the values of the reactivity ratios for the principal monomers, $r_{MMA} = 0.76$ and $r_{GMA} = 0.88$ [50] in the present case, composition heterogeneity should not be a serious problem so a high conversion process was adopted. Appropriate proportions of MMA, GMA and EA were premixed in 100 g batches. Both MMA and EA were used as received from the manufacturer; however, GMA was vacuum distilled to remove any difunctional monomer generated during its synthesis. The monomer solution and AIBN (1.5 g AIBN

Table 3
Characterization of MMA–GMA–EA terpolymers

Designation used here	Composition MMA–GMA–EA (weight ratio of monomer feed)	M_n (g mol^{-1})	M_w (g mol^{-1})	T_g (°C)
PMMA[a]	—	63 000	158 000	108
MGE-1	97:1:2	48 000	85 000	107
MGE-3	95:3:2	40 000	120 000	105
MGE-5	93:5:2	41 000	120 000	104
MGE-10	88:10:2	46 000	190 000	102
MGE-15	83:15:2	41 000	119 000	98
MGE-20	78:20:2	26 000	80 000	92

[a] Plexiglass V811 (100) from Rohm and Haas

Table 4
Processing conditions used to prepare PBT–SAN blends

Extrusion conditions			Injection moulding conditions[a]
Extruder	RPM	Temperature (°C)	Melt temperature (°C)
Twin screw[b]	170	220	240
		220	260
		260	240
Single screw[b]	30	230	240

[a] Arburg Allrounder injection moulding machine, mould temperature = 50°C, injection and holding pressure = 50 bar, injection time = 3 s
[b] Baker–Perkins co-rotating, fully intermeshing twin screw extruder (*D* = 15 mm)
[c] Killion single screw extruder (*L*/*D* = 30, *D* = 2.54 cm) outfitted with a high intensity mixing screw

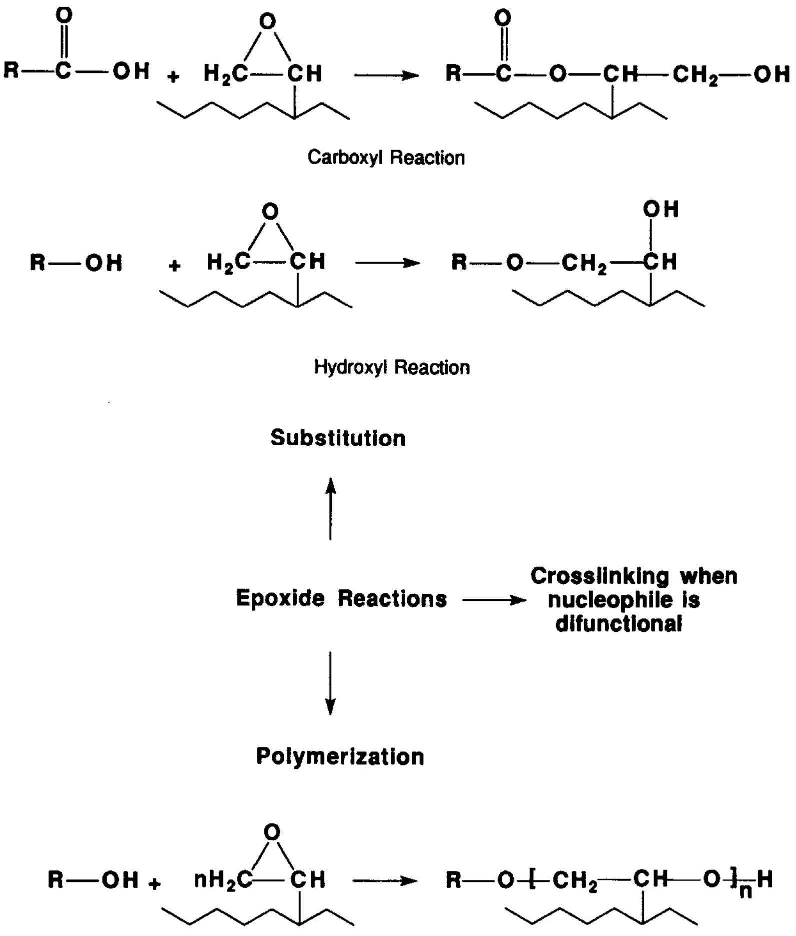


Fig. 4. Possible reactions between epoxide units with PBT hydroxyl and carboxyl end groups.

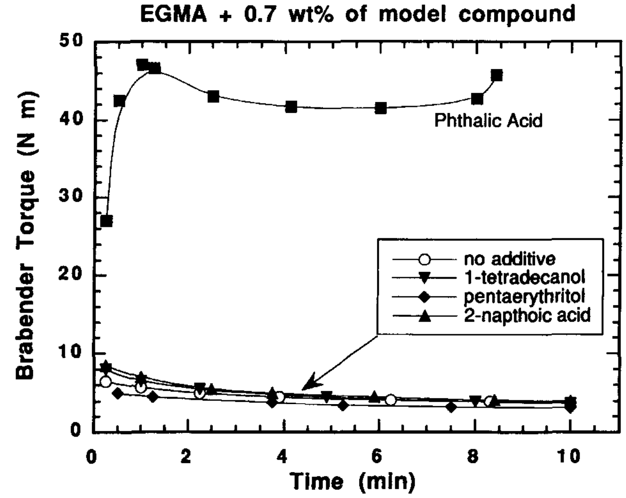


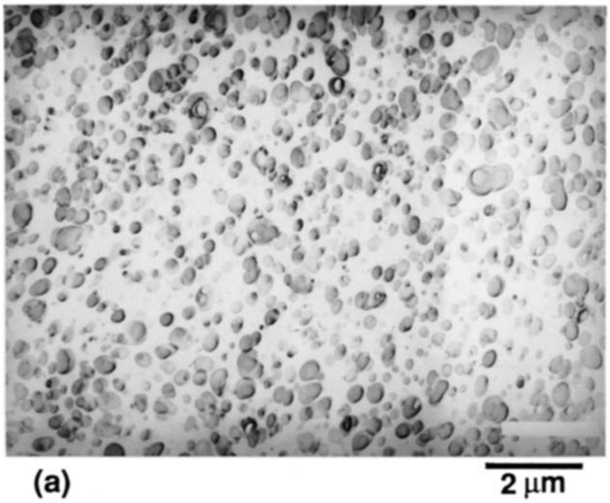
Fig. 5. Brabender torque response at 250°C of EGMA copolymer plus 0.7 wt% of various low molecular weight model compounds.

per 100 g monomer) were sealed in the reaction vessel. The AIBN quantity was set at a level to produce copolymers with molecular weights comparable to the commercial PMMA shown in Table 1. The reaction was carried out in a Kapak/Scotchpak heat sealable pouch with a polyester barrier film. The pouch containing monomer and initiator was submerged in a large water bath at 60°C and allowed to react essentially to completion (93%–97%). Considerable care must be exercised at high conversions where the viscous monomer–polymer solution undergoes auto-acceleration giving rise to a large exotherm [48]. If the temperature rises too high, the remaining monomer will vapourize and can rupture the pouch; to avoid this, the reaction mass was plunged into a large cold water bath just prior to the exotherm. The resulting polymer mass was crushed and cryogenically ground to a powder form, then vacuum dried at 65°C. Samples used for characterization were dissolved in chloroform and then precipitated by methanol to remove any remaining monomer. The compatibilizer was characterized by GPC and DCS techniques with the results shown in Table 3.

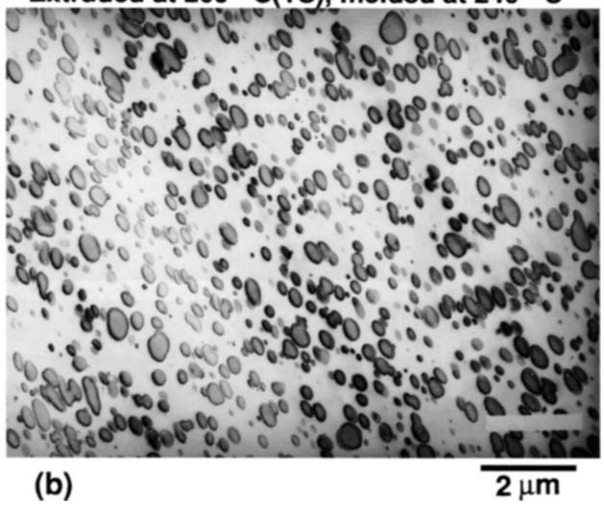
3.3. Blending protocol

Pellets of PBT were cryogenically ground to a powder form and, along with the reactive compatibilizer powder, dried for 16 h in a vacuum oven at 65°C. Cryogenically ground SAN powder and as-received ABS powder were dried for 16 h in a convection oven at 70°C. All components for each blend were thoroughly mixed prior to extrusion.

PBT/SAN (80/20)
Extruded at 220 °C(TS), molded at 240 °C



PBT/SAN (80/20)
Extruded at 260 °C(TS), molded at 240 °C



PBT/SAN (80/20)
Extruded at 220 °C(TS), molded at 260 °C

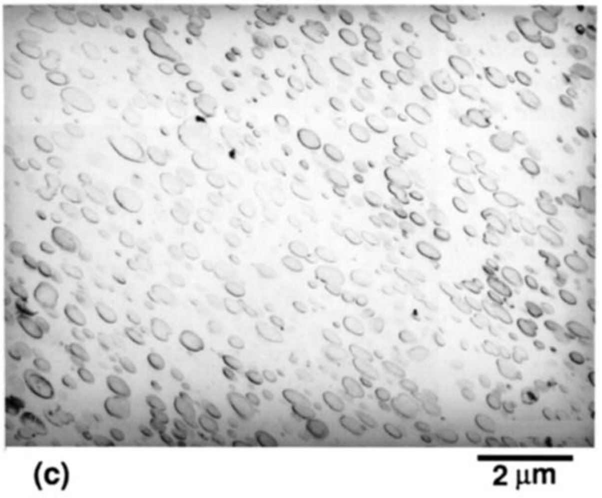


Fig. 6. TEM photomicrographs of binary PBT–SAN (80:20) blends prepared in a twin screw extruder and moulded at different temperatures: (a) extruded at 220°C, moulded at 240°C; (b) extruded at 260°C, moulded at 240°C; and (c) extruded at 220°C, moulded at 260°C. The SAN phase is stained dark by RuO_4.

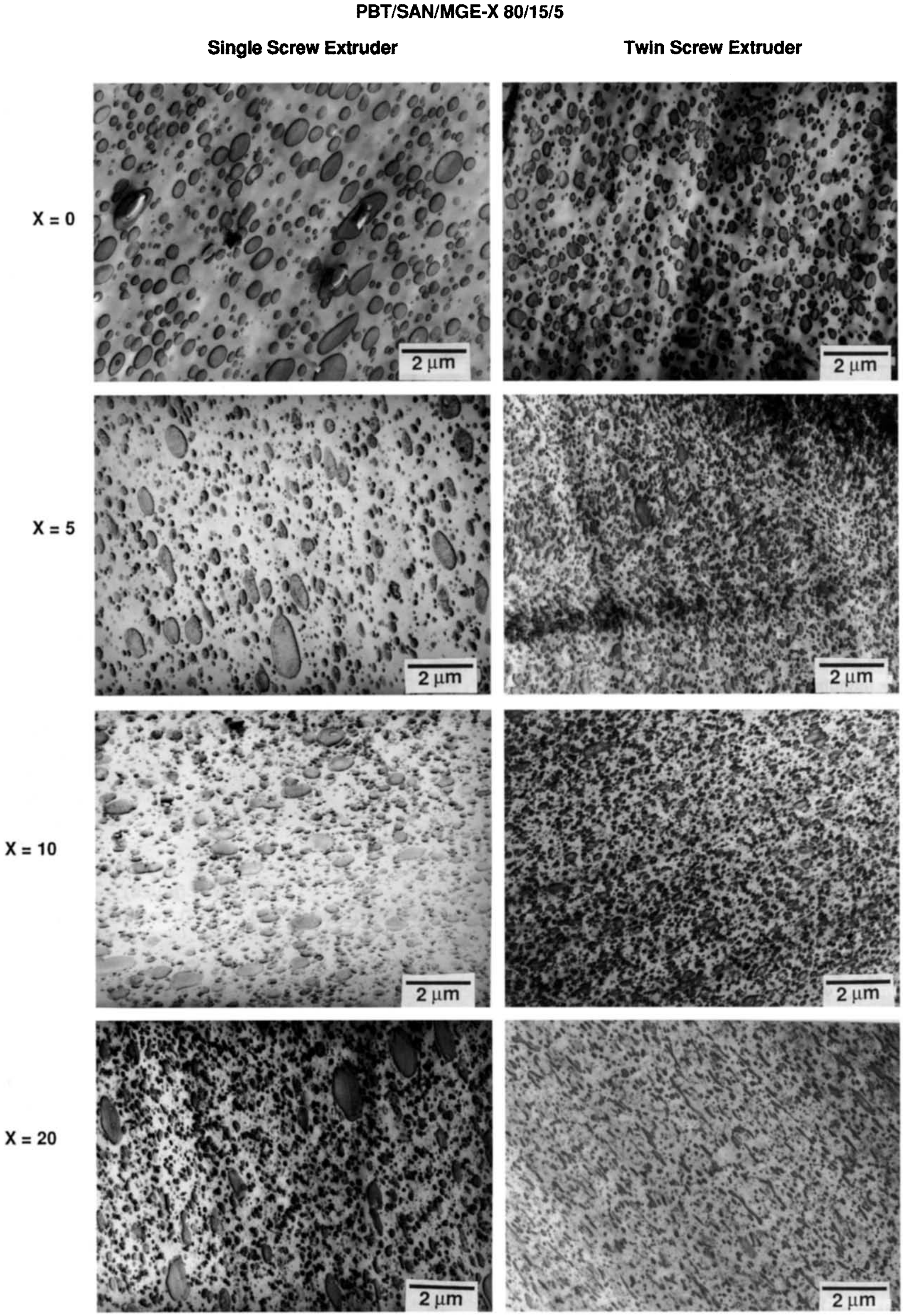

PBT/SAN/MGE-X 80/15/5
Single Screw Extruder
Twin Screw Extruder
X = 0
X = 5
X = 10
X = 20
2 μm

Table 4 provides information about the processing conditions and equipment used for the preparation of PBT blends. The single screw extruder used here is outfitted with an intensive mixing head but generally does not provide as effective mixing as the twin screw extruder does for the current blends. The range of processing temperatures is limited by the melting point (220°C) and the degradation temperature (>260°C) of PBT. The twin screw extruder could be used at a barrel set point of 220°C since the high shear generates heat that ensures the PBT is fully molten; however, the single screw extruder could not be operated at a set point below 230°C because it generates less heat. The temperature profiles for each extruder and the injection moulding machine were kept flat along the barrel.

3.4. Blend characterization

The morphology of the blends were examined by a JEOL JEM 200cx transmission electron microscope (TEM) at an accelerating voltage of 120 kV. Ultrathin sections taken from the centre of the gate end of injection moulded Izod bars (ASTM D256), perpendicular to the direction of flow, were obtained by cryomicrotoming at −45°C using a Riechert-Jung Ultracut E microtome. The sections were stained in RuO_4 vapour for 20 min or OsO_4 vapour for 24 h. RuO_4 stains the SAN phase while OsO_4 stains the rubber in the ABS. Effective weight and number average particle diameters of the dispersed phase were determined from TEM photomicrographs by digital image analysis using NIH Image software. The area of each particle is determined by the software and the equivalent diameter of a circle having the same area is calculated. No attempt was made to account for the fact that the microtome slice does not cut each particle at its equator.

Notched Izod impact tests were conducted according to ASTM D256 as a function of temperature to determine the location of the ductile to brittle transition. At least five samples each from the gate and far ends of the injection moulded Izod bars were tested at room temperature and in the temperature region of the ductile–brittle transition; at other temperatures fewer samples were tested, the exact number being dictated by the consistency observed. Only gate-end information is reported here, since differences between gate- and far-end specimens were typically insignificant.

Thermal analysis was performed on a Perkin–Elmer DSC-7 at a heating rate of 20°C min^{-1} in order to determine the glass transition temperature (T_g). Each sample was heated to 150°C then cooled to 25°C and reheated to 150°C. The T_g was determined using the onset method.

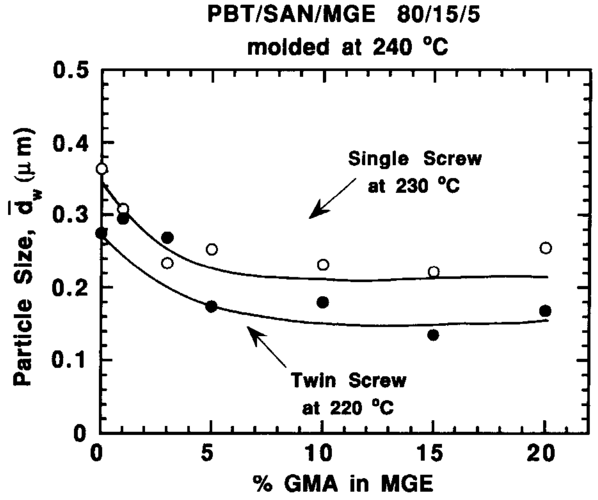


Fig. 8. Dispersed phase domain size of ternary PBT–SAN–MGE (80:15:5) blends as a function of the GMA content in the MGE compatibilizer. Blends were prepared in a twin screw extruder (220°C) or single screw extruder (230°C) and moulded at 240°C.

4. Reactions of epoxide groups

Fig. 4 illustrates three types of reactions that may occur between epoxide groups and hydroxyl and carboxyl functionalities. Both OH or COOH groups can act as nucleophiles that react with epoxides via nucleophilic substitution under appropriate conditions. There are two nucleophilic substitution reactions that can occur; generally, hydroxy groups are expected to attack the more substituted carbon of the epoxide while carboxyl groups should attack the less substituted carbon [51]. Note that these ring opening reactions generate a hydroxyl group which can potentially react with another epoxide ring to cause cross-linking; however, this was shown not to occur at the conditions of interest here. Cross-linking can occur when the attacking nucleophile is difunctional. Molecules of PBT can have reactive groups at either chain end; hence, various cross-linking type effects may occur [52]. Epoxides can also polymerize via ring opening reactions in the presence of an initiator [48]. The rate of these reactions can be altered considerably by the presence of catalysts [37]; indeed, residual catalyst from the synthesis of the PBT and possibly metal ions and other contaminants from the polymerization and recovery processes of emulsion-made ABS materials may influence the reactions with epoxides. Examination of such catalytic effects is beyond the scope of this investigation; however, a future paper will present evidence for epoxide reactions promoted by contaminants in emulsion-made ABS materials.

Fig. 7. TEM photomicrographs of ternary PBT–SAN–MGE (80:15:5) blends prepared in a twin screw extruder at 220°C or a single screw extruder at 230°C and moulded at 240°C for the following compatibilizers: (a) MGE-0 (PMMA); (b) MGE-5; (c) MGE-10; and (d) MGE-20. The SAN phase is stained dark by RuO_4.

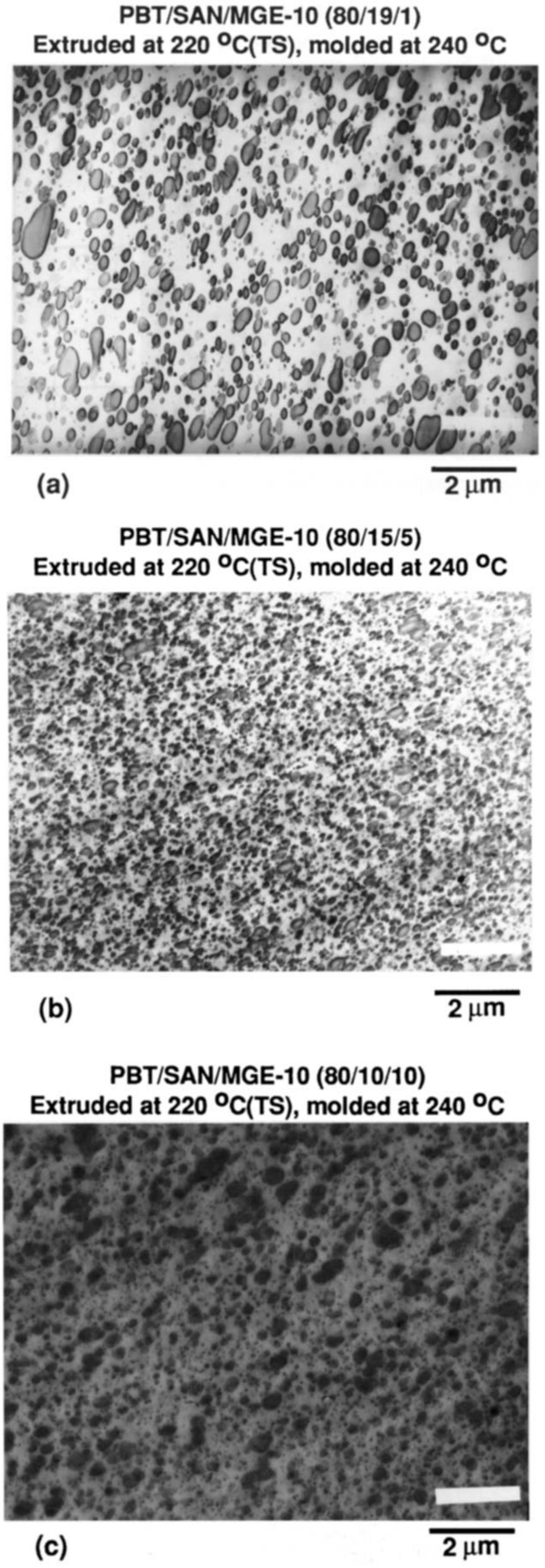


Fig. 9. TEM photomicrographs of ternary PBT–SAN–MGE-10 (80/20-X/X) blends prepared in a twin screw extruder at 220°C and moulded at 240°C: (a) X = 1% MGE-10; (b) X = 5% MGE-10; (c) X = 10% MGE-10. The SAN phase is stained dark by RuO_4.

The low molecular weight compounds shown in Table 2 which are monofunctional or multifunctional in terms of the hydroxyl or carboxyl group content can be used to distinguish among the possible reaction pathways shown in Fig. 4 that may occur during melt processing of PBT blends containing the MGE compatibilizer. This can be accomplished by observing the rheological response when the low molecular weight compounds are melt mixed with a polymer having numerous pendant epoxide units. These compounds were selected because of their low volatility at melt mixing temperatures and for their chemical similarity to the aliphatic hydroxyl and aromatic carboxyl end groups expected in PBT. A commercially available ethylene–glycidyl methacrylate copolymer, EGMA, was selected for these experiments since the MGE terpolymers used as the compatibilizer were available only in limited quantities. A Brabender torque rheometer was used to monitor the rheological response which can be used to distinguish among these reactions. The grafting of a low molecular weight monofunctional compound onto EGMA should cause little rheological change while reaction with a multifunctional compound which leads to cross-linking type effects should result in a large torque increase in the Brabender. A charge of EGMA with 0.7 wt% of the selected model compound was added to the Brabender and allowed to flux for 10 min; the resulting torque responses are shown in Fig. 5. None of the hydroxyl functional compounds used here have any effect on the torque nor does the monofunctional carboxyl compound. Only the addition of phthalic acid to EGMA produces a torque increase. For these experimental conditions, these results suggest that carboxyl groups react with the epoxide contained in the EGMA copolymer but hydroxyl groups do not. Therefore, we conclude that only the PBT carboxyl and not the hydroxyl endgroups have the potential to react with the epoxide functionality found in MGE terpolymers under the processing conditions used here.

5. Morphology of PBT–SAN blends

The effects of reactive compatibilization and processing conditions on the morphology of injection moulded PBT–SAN blends, a simplified model for the PBT–ABS system, are described here. The following section describes the stability of PBT–SAN blends with and without compatibilizer. TEM photomicrographs of uncompatibilized PBT–SAN blends containing 80% PBT prepared in the twin screw extruder at three different processing conditions are shown in Fig. 6. The blends shown in Fig. 6(a) and (b) were extruded at 220°C and 260°C, respectively, and then

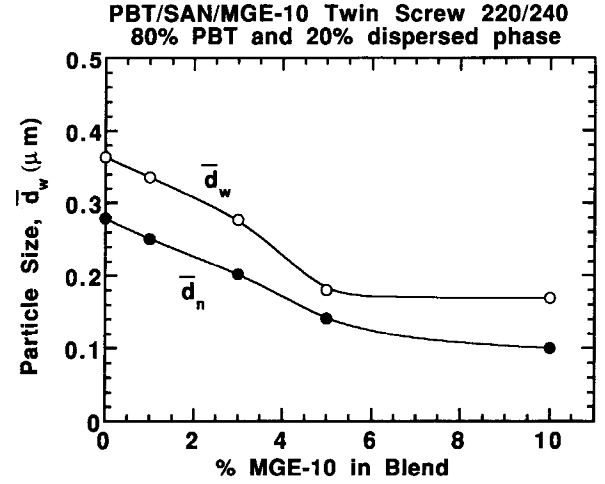


Fig. 10. Dispersed phase domain size of ternary blends (PBT–SAN–MGE-10, 80/20–X/X) as a function of MGE-10 content for blends prepared in a twin screw extruder at 220°C and moulded at 240°C.

injection moulded at 240°C. There is little difference between the two evidently because the twin screw extruder imparts sufficient stress on the blend, even at high temperatures, to obtain a fine dispersion of the SAN in the PBT matrix. However, when blends are injection moulded at 260°C, see Fig. 6(c), the morphology coarsens due to coalescence of SAN domains during the high temperature (low melt viscosity or stress) injection moulding.

Addition of the MGE terpolymer to PBT–SAN blends should produce a finer dispersion that is more stable against coalescence. This is illustrated by two series of experiments that vary the epoxide content in the blend. The first series involves a fixed SAN–compatibilizer ratio in the blend while the GMA content in the compatibilizer is varied. In the second series, the GMA content of the compatibilizer is fixed while the SAN–compatibilizer ratio is varied.

Fig. 7 shows TEM photomicrographs of blends containing PBT–SAN–compatibilizer in the fixed ratio 80:15:5 prepared in the twin and single screw extruders for cases where the compatibilizer contains 0%, 5%, 10% and 20% by weight of GMA. As the GMA content of the compatibilizer increases, the particle size decreases for blends prepared in either extruder; however, the SAN rich particles are larger and have a broader size distribution for blends prepared in the single screw extruder. Generally, fully intermeshing, co-rotating twin screw extruders provide better mixing than single screw extruders do. Fig. 8 shows the weight average particle diameter plotted as a function of the GMA content of the compatibilizer for this series of blends. The average SAN particle size for blends prepared in the twin screw extruder is typically lower than that prepared in the single screw extruder. At least 5% GMA in the MGE terpolymer (0.25% GMA total in blend) is required to achieve significant reduction in particle size; however, the particle size is not reduced much further as the GMA content is increased beyond this level.

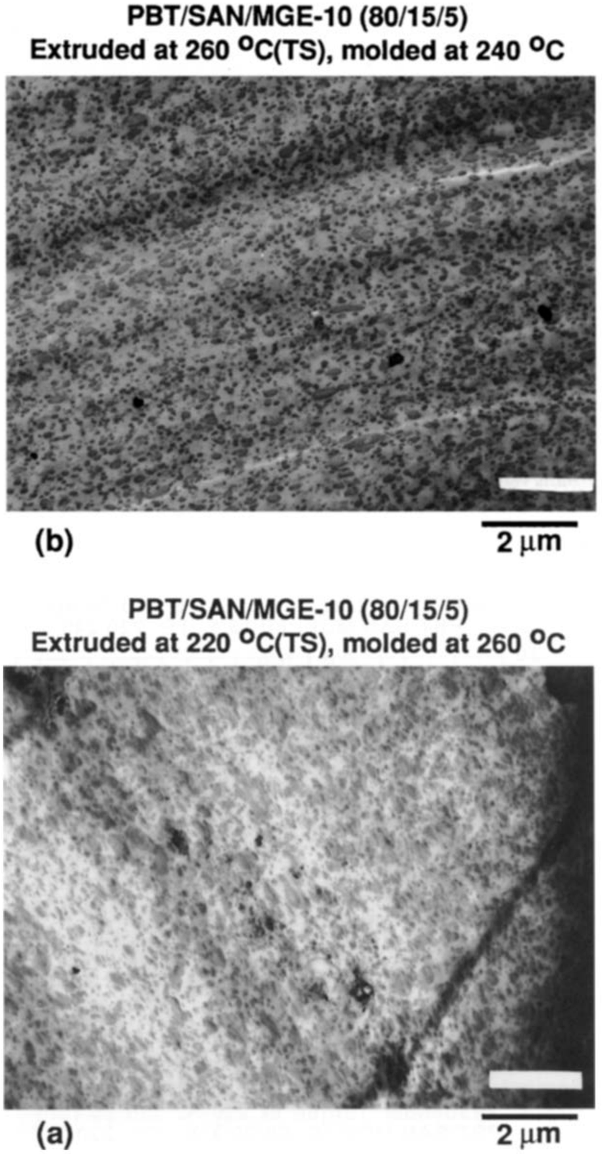


Fig. 11. TEM photomicrographs of ternary PBT–SAN–MGE-10 (80:15:5) blends prepared in a twin screw extruder and moulded at different temperatures: (a) extruded at 220°C and moulded at 260°C; and (b) extruded at 260°C and moulded at 240°C. The SAN phase is stained dark by RuO_4.

Fig. 9 shows the change in morphology within a series of blends (80% PBT) as the SAN–compatibilizer ratio is varied for the case where the MGE terpolymer contains 10% GMA (MGE-10). Fig. 10 shows the number average and weight average particle diameters for this blend series plotted as a function of the compatibilizer content. The dispersed phase particle size is significantly reduced by adding up to 5% compatibilizer while increasing the level to 10% does not lead to much further reduction in average particle size; the particle size distribution is broader at 10% than 5% of MGE-10.

For the uncompatibilized blends, the dispersed phase particle size coarsens at high moulding temperatures as shown in Fig. 6. However, for blends containing adequate amounts

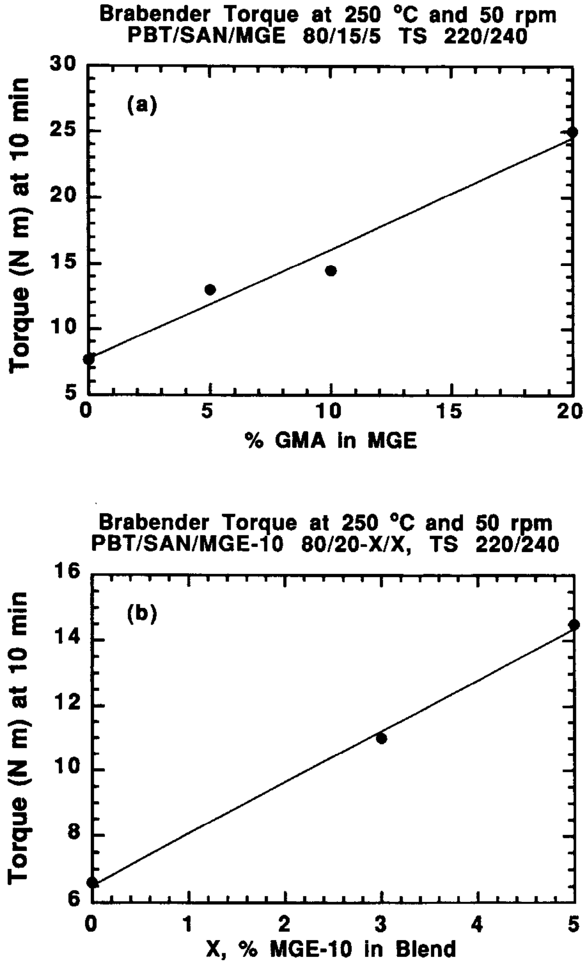


Fig. 12. Brabender torque (after 10 minutes at 250°C and 50 rpm) of ternary blend extrudates prepared in a twin screw extruder at 220°C: (a) PBT–SAN–MGE (80:15:5) blends where the GMA content in the MGE compatibilizer is varied; and (b) PBT–SAN–MGE-10 (80/20–X/X) blends where the MGE-10 content in the blend is varied.

of this compatibilizer coarsening during moulding does not seem to occur as seen in Fig. 11. Compared with extrusion compounding, the lower stress conditions during injection moulding involves minimal drop break up but coalescence continues when there is no compatibilizer. The graft copolymer formed at the interface in compatibilized blends sterically hinders particle collisions and suppresses coalescence.

Fig. 12 shows the effect of GMA content on the viscosity of compatibilized blends. Extrudate for select compositions from the two series of PBT–SAN–MGE blends discussed above, prepared in the twin screw extruder, were introduced into the Brabender and fluxed for 10 min at 250°C after which the torque was recorded. Incorporation of the MGE compatibilizer leads to graft copolymer formation which increases melt viscosity. To achieve good properties it is necessary to have a fine dispersion in the blend; however, the accompanying increase in melt viscosity is generally detrimental for processing of these materials. Significant SAN particle size reduction is achieved when the blend contains a total of 0.25–0.5 wt% GMA (GMA content of compatibilizer times content of compatibilizer in blend); however, increasing the GMA content beyond this point significantly increases blend viscosity while the SAN domain size does not change much. Thus, GMA levels in this range appear to be the practical upper limit for such compatibilized blends.

6. Stability of PBT–SAN morphology

Particle size growth in binary PBT–SAN blends was shown to occur during injection moulding, see Fig. 6(c). There is less shear or stress in the injection moulding step than experienced during extruder compounding; the resulting change in the balance between drop break up and coalescence is believed to be the reason for this growth in particle size. A Brabender experiment was used to further assess this effect and to document any difference in morphology stability between compatibilized and uncompatibilized PBT–SAN blends during low shear conditions in the melt state [53].

Appropriate amounts of PBT, SAN and compatibilizer (70 g total) were charged to a Brabender mixing chamber set at 250°C and fluxed at 50 rpm for 10 min; this thoroughly dispersed the SAN and compatibilizer throughout the PBT matrix and established a steady state particle size distribution in the melt mixture. After this, the Brabender rotor speed was reduced to 5 rpm to simulate a lower shear–stress state where drop break up is less effective but coalescence can still occur. Small samples of molten material were then removed as a function of time from the mixing chamber and quenched into water. The morphology of these samples was assessed by transmission electron microscopy. The TEM photomicrographs shown in Fig. 13 compare the dispersed phase particle size of PBT–SAN–MGE-10 (80:20:0 and 80:15:5) blends sampled at the time when the rotor speed was reduced ($t = 0$) and after 10 min at the lower speed. The dispersed domains in the uncompatibilized blend coarsen greatly over this time interval while the presence of 5 wt% MGE-10 stabilizes against coalescence and little change in particle size is observed. Fig. 14 shows quantitatively the particle size for these two blends as a function of time in the melt after the rotor speed was reduced. The weight average particle size for the uncompatibilized blend steadily increases while for the compatibilized blend particle size remains constant. Thus, addition of the compatibilizer stabilizes the morphology by suppressing coalesence. This is important for assuring uniform blend performance over a range of processing situations.

7. PBT–ABS blends

Addition of the MGE compatibilizer to PBT–ABS blends prepared in the twin screw extruder leads to significant improvement in mechanical performance as illustrated by

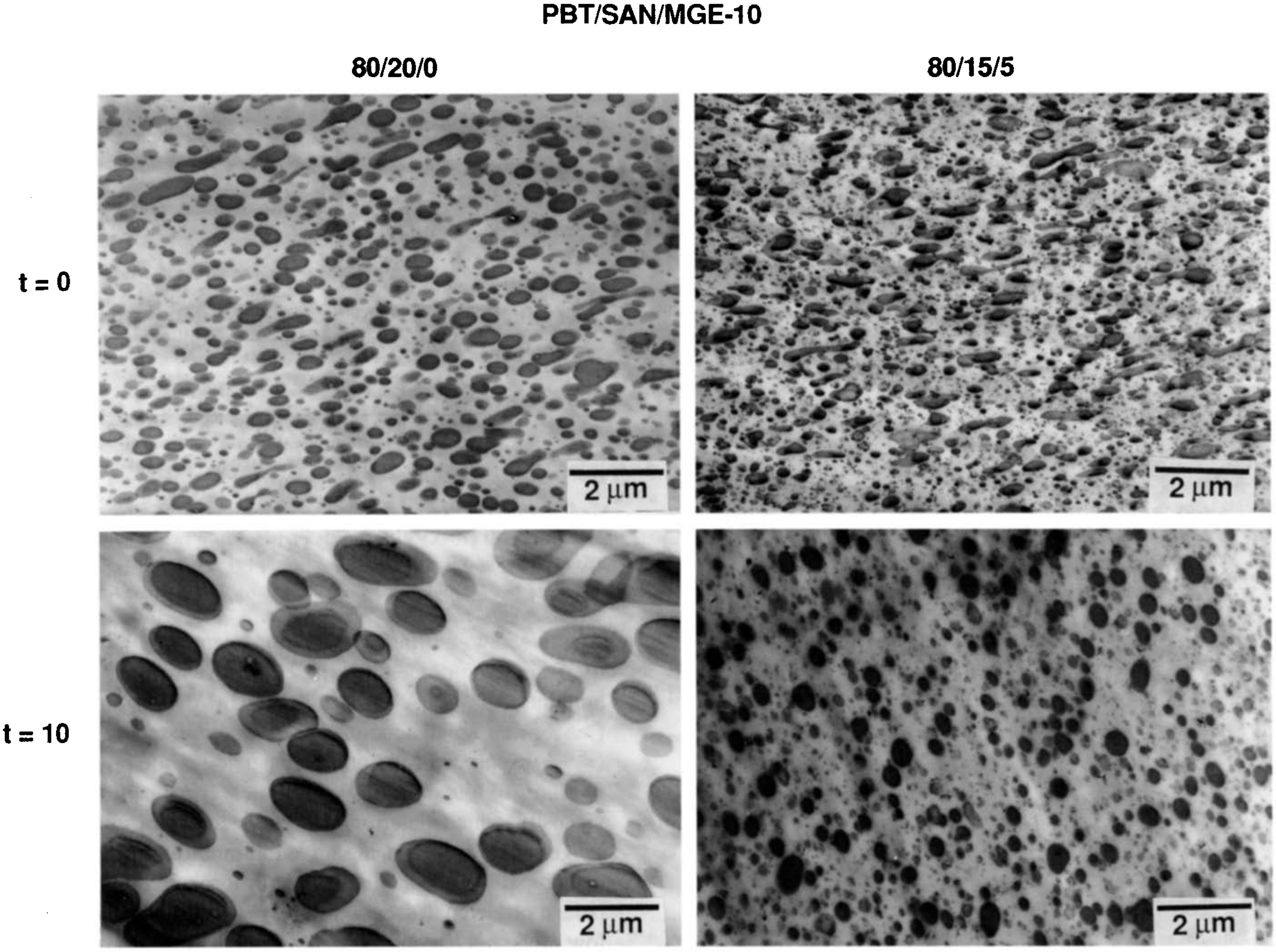


Fig. 13. TEM photomicrographs of compatibilized and uncompatibilized PBT–SAN blends prepared in the Brabender at 250°C before and after exposing the blends to low shear conditions (5 rpm) for 10 min.

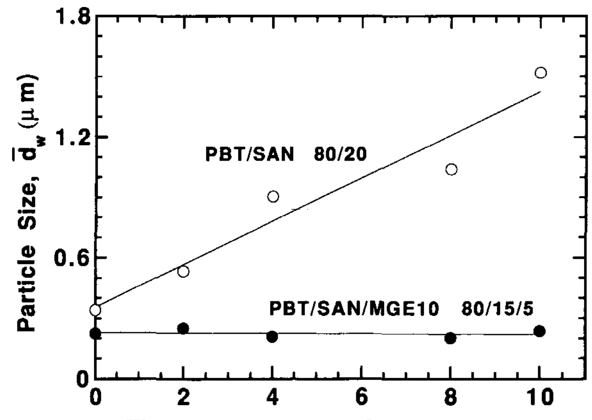


Fig. 14. Dispersed phase domain size of compatibilized and uncompatibilized PBT–SAN blends prepared in the Brabender at 250°C as a function of time at low rotor speed.

some preliminary results presented here. The TEM photomicrographs shown in Fig. 15 illustrate the change in morphology caused by adding the compatibilizer to blends containing 30% ABS. The spatial distribution of the ABS rubber particles, made visible in these photomicrographs by OsO_4 staining, reveals that the ABS domains are relatively large for uncompatibilized blends; i.e. the rubber particles are rather non-uniformly distributed in the PBT matrix. Addition of 5% of MGE-10 leads to a more uniform distribution of the rubber particles in the blend as a result of reducing the ABS domain size.

The Izod impact properties of these two blends are shown in Fig. 16 as a function of temperature. At room temperature, the blends with and without compatibilizer are super tough; however, the presence of the compatibilizer decreases the ductile–brittle transition temperature from −22°C to −50°C while reducing the room temperature toughness by 10%–15%. More detailed studies on mechanical properties of MGE compatibilized PBT–ABS blends will be reported in subsequent papers.

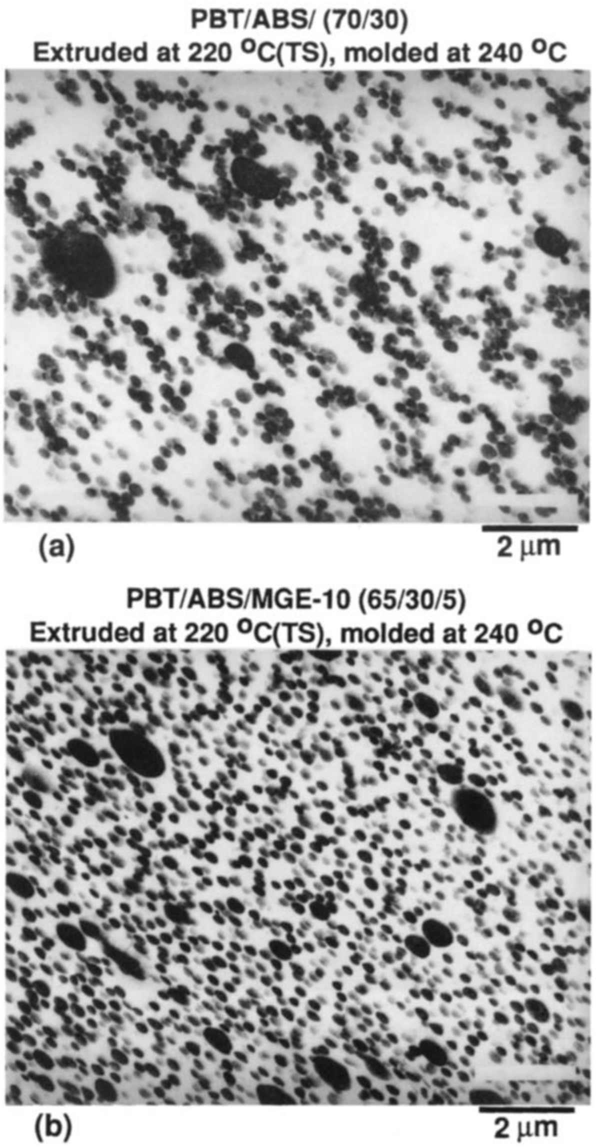


Fig. 15. TEM photomicrographs of PBT–ABS–MGE-10 (70-X)/30/X blends prepared in a twin screw extruder at 220°C and moulded at 240°C: (a) X = 0, uncompatibilized blend; and (b) X = 5, compatibilized blend. The rubber in the ABS phase is stained dark by OsO_4.

8. Conclusions

Uncompatibilized blends of PBT with SAN or ABS materials have an unstable morphology and, thus, in certain melt processing situations the level of dispersion may be inadequate for good properties. Terpolymers of methyl methacrylate, glycidyl methacrylate, and ethyl acrylate (MGE) were shown to be effective reactive compatibilizers for these blends as revealed by improvements in the degree of dispersion and morphology stability. These terpolymers are miscible with the SAN matrix of typical ABS materials. Evidence for graft copolymer formation by reaction of the epoxide units with PBT carboxyl end groups was presented. The twin screw extruder proved more effective than the single screw extruder (with an intensive mixing head) used here for processing these reactive blends. Moderate amounts of GMA functionality in the compatibilizer (>5%) and small amounts of compatibilizer in the blend (<5%) significantly improve dispersion while higher levels produce minimal improvement but continue to increase viscosity which deteriorates processing performance, e.g. longer cycle times during injection moulding. The addition of compatibilizer stabilizes blend morphology against dispersed phase coalescence when these blends are exposed to low stress melt conditions for prolonged periods of time. Compatibilized PBT–ABS blends show greatly improved low temperature toughness with a small loss in room temperature impact strength.

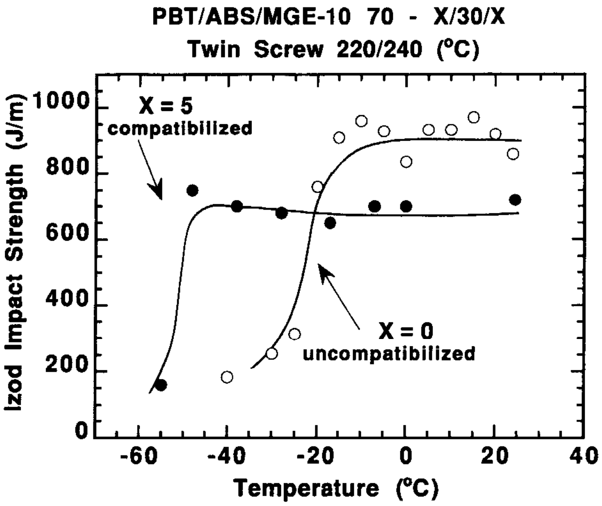


Fig. 16. Effect of temperature on notched Izod impact strength of PBT–ABS–MGE-10 (70-X)/30/X blends prepared in a twin screw extruder at 220°C and moulded at 240°C.

Acknowledgements

This work was supported by the U.S. Army Research Office. The authors would like to thank General Electric Co., Rohm and Haas, Cheil Industries, and Dow Chemical Co. for the materials and various technical communications.

References

[1] Hage E, Hale W, Keskkula H, Paul DR. Polymer 1997;38:3237.
[2] Hourston DJ, Lang S. In: Collyer AA, editor. Rubber toughened engineering plastics. London: Chapman and Hall, 1994:243.
[3] Utracki LA. Polym Eng Sci 1995;35:2.
[4] Binsack R, Rempel D, Humme G, Ott K-H (Bayer), US Patent No. 4 292 233,1981.
[5] Binsack R, Rempel D, Lindner C, Morbitzer L (Bayer), US Patent No. 4 535 124,1985.
[6] Wang I-CW (General Electric), US Patent No. 4 753 986, 1988.
[7] Benson CM, Burford RP. J Mater Sci 1995;30:573.
[8] Lee P-C, Kuo W-F, Chang F-C. Polymer 1994;35:5641.

[9] Van Berkel RWM, Van Hartingsveldt EAA, Van der Sluijs CL. In: Olabisi O, editor. Handbook of thermoplastics. New York: Marcel Dekker, 1997:465.
[10] Basu D, Banerjee A. J Appl Polym Sci 1997;64:1485.
[11] Okamoto M, Shimodu Y, Kojima T, Inoue T. Polymer 1993;34:4868.
[12] Hobbs SY, Dekkers MEJ, Watkins VH. J Mater Sci 1988;23:1219.
[13] Dekkers MEJ, Hobbs SY, Watkins VH. J Mater Sci 1988;23:1225.
[14] Brady AJ, Keskkula H, Paul DR. Polymer 1994;35:3665.
[15] Wu J, Yee AF, Mai Y-W. Polym Prepr 1992;33:626.
[16] Wu J, Mai Y-W, Cotterel B. J Mater Sci 1993;28:3373.
[17] Wu J, Mai Y-W. J Mater Sci 1993;28:6167.
[18] Deyrup EJ (Du Pont), US Patent No. 4 753 980, 1988.
[19] Hert M. Agnew. Makromol Chem 1992;196:89.
[20] Holsti-Miettinen RM, Heino MT, Seppala JV. J Appl Polym Sci 1995;57:573.
[21] Pratt CF, Phadke SV, Oliver E (General Electric), US Patent No. 4 965 111, 1990.
[22] Phadke SV (General Electric), US Patent No. 5 008 342, 1991.
[23] Greco R, Musto P, Rogosta G, Scarinzi G. Makromol Chem Rapid Comm 1988;9:129.
[24] Laurienzo P, Malinconico M, Martuscelli E, Volpe G. Polymer 1989;30:835.
[25] McCready RJ (Arco), US Patent No. 4 931 502, 1990.
[26] Cecere A, Greco R, Ragosta G, Scarinzi G. Polymer 1990;31:1239.
[27] Kanai H, Auerbach A, Sullivan V. Soc Plast Eng, ANTEC 1994;40:2817.
[28] Kanai H, Sullivan V, Auerbach A. J Appl Polym Sci 1994;53:527.
[29] Modic MJ (Shell Oil Co.), US Patent No. 5 300 567, 1994.
[30] Hourston DJ, Lane S, Zhang HX, Bootsma JPC, Koetsier DW. Polymer 1991;32:1140.
[31] Lane CA (Rhom. and Haas), US Patent No. 4 034 013, 1977.
[32] Cambell JR, Khouri FR, Hobbs SY, Shea TJ, Moffet AJ. Polym Prepr 1993;34:846.
[33] Wang X-H, Zhang H-X, Wang Z-G, Jiang B-Z. Polymer 1997;38:1569.
[34] Chung JYJ, Carter Jr. RP, Neuray D. (Mobay Chemical Co.), US Patent No. 4 554 315, 1985.
[35] Liu W-B, Kuo W-F, Chiang C-J, Chang R-C. Eur Polym J 1996;32:91.
[36] Kim JK, Lee H. Polymer 1996;37:305.
[37] Stewart ME, George SE, Miller RL, Paul DR. Polym Eng Sci 1993;33:675.
[38] Deyrup EJ (Du Pont), US Patent No. 4 753 980, 1988.
[39] Epstein BN (Du Pont), US Patent No. 4 172 859, 1979.
[40] Gallucci RR, Going RC. J Appl Polym Sci 1982;27:425.
[41] Majumdar B. Ph.D. dissertation, University of Texas at Austin, 1993.
[42] Khouri FF, Halley RJ, Yates III B (General Electric), US Patent No. 5 247 006, 1993.
[43] Khouri FF, Halley RJ, Yates III B. (General Electric), US Patent No. 5 212 255, 1993.
[44] Hwang C-FR, Scobbo Jr. JJ, Yates JB (General Electric), US Patent No. 5 583 179, 1996.
[45] Han CY, Gately WL (General Electric), US Patent No. 4 689 372, 1987.
[46] Nishimoto M, Keskkula H, Paul DR. Polymer 1989;30:1279.
[47] Gan PP, Paul DR, Padwa AR. Polymer 1994;35:3513.
[48] Odian G. Principles of polymerization, 2nd edn. New York: Wiley, 1981.
[49] Chu L, Paul DR, to be published.
[50] Iwakura Y, Kurosaki T, Asiga N, Ito T. Makromol Chem 1966;97:128.
[51] Bruice PY. Organic chemistry. Englewood Cliffs, NJ: Prentice-Hall, 1995.
[52] Kudva RA, Keskkula H, Paul DR. Polymer 1998;39:2447.
[53] Wildes G, Keskkula H, Paul DR, to be published.