

Structure–Properties Relationship in Toughening of Poly(butylene terephthalate) with Core–Shell Modifier

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ABSTRACT: The performance of acrylonitrile–butadiene–styrene (ABS) core–shell modifier with different grafting degree, acrylonitrile (AN) content, and core–shell ratio in toughening of poly(butylene terephthalate) (PBT) matrix was investigated. Results show PBT/ABS blends fracture in ductile mode when the grafting degree is high, and with the decrease of grafting degree PBT/ABS blends fracture in a brittle way. The surface of rubber particles cannot be covered perfectly for ABS with low grafting degree and agglomeration will take place; on the other hand, the entanglement density between SAN and PBT matrix decreases because of the low grafting degree, inducing poor interfacial adhesion. The compatibility between PBT and ABS results from the strong inter-

action between PBT and SAN copolymer and the interaction is influenced by AN content. Results show ABS cannot disperse in PBT matrix uniformly when AN content is zero and PBT/ABS fractures in a brittle way. With the addition of AN in ABS, PBT/ABS blends fracture in ductile mode. The core–shell ratio of ABS copolymers has important effect on PBT/ABS blends. When the core–shell ratio is higher than 60/40 or lower than 50/50, agglomeration or cocontinuous structure occurs and PBT/ABS blends display lower impact strength. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5363–5371, 2006

Key words: polyesters; blending; core–shell polymers; structure–property relations; emulsion polymerization

INTRODUCTION

Poly(butylene terephthalate) (PBT) is an important engineering thermoplastic, which combines the properties of rigidity, hardness, abrasion, solvent resistance, electric insulation, and short cycle times in injection molding.¹ However, PBT is highly notch sensitive; it is often ductile in unnotched Izod impact tests, but fails in a brittle manner when standard notched specimens are tested. The difference between unnotched and notched Izod impact strength indicates that PBT is fairly resistant to crack initiation but has only modest resistance to crack propagation.² The addition of impact modifiers can improve the notched impact strength and overcome the notch-sensitive property of PBT.^{3–8} Core–shell impact modifiers have been used to toughen polymer with improved notched impact strength successfully.^{9–13} Core–shell impact modifiers are generally made in emulsion that consist a crosslinking rubbery core and a rigid shell grafted on to the rubber. The shell aids in the isolation of the modifiers from the emulsion. The chemical composition of the shell

can be modified to impart compatibility or chemical reactivity with the matrix, which results in improved dispersion of the modifiers during melt processing and provides good adhesion with the matrix.

Acrylonitrile–butadiene–styrene (ABS) core–shell impact modifier has been used to toughen PBT successfully.^{2,14–20} With a proper choice of materials and processing conditions, PBT/ABS blends with excellent properties can be obtained without use of any compatibilizers. Hage et al.² studied the effect of ABS type, extrusion temperature, extrusion type, molding condition, and PBT type on the notched impact strength of PBT/ABS blends in detail, and PBT/ABS blends with high notched impact strength were obtained. A few studies on compatibilization of PBT/ABS blends have been reported recently.^{14–20} For PBT/ABS blends, compatibilizers were focused on the epoxy-functionalized copolymers. Lee et al.¹⁴ used styrene–acrylonitrile–glycidyl methacrylate (SAG) copolymer as a compatibilizer for PBT/ABS blends. This SAG copolymer contains reactive epoxy groups that are able to react with PBT end groups (–COOH or –OH) under melt condition to form PBT-co-SAN copolymer. Hale et al.^{15–19} used methyl methacrylate–glycidyl methacrylate–ethyl acrylate (MGE) copolymer as compatibilizer for PBT/ABS blends. MGE has been shown to be an effective compatibilizer for PBT/SAN and PBT/ABS blends as revealed by improvement in SAN or ABS dispersion, morphological stability,

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TABLE I
ABS Properties with Different TDDM Content

Designation used here	Rubber content (wt %)	Ratio of AN/St (wt/wt)	CHP content (mL)	TDDM content (mL)	ABS particle size (μm)
ABS-T0	60	25/75	0.6	0	0.359
ABS-T0.2	60	25/75	0.6	0.2	0.344
ABS-T0.5	60	25/75	0.6	0.5	0.355
ABS-T0.8	60	25/75	0.6	0.8	0.348
ABS-T1.2	60	25/75	0.6	1.2	0.365
ABS-T1.6	60	25/75	0.6	1.6	0.354

and low temperature toughness. In the previous study, epoxy-functionalized ABS was prepared in our lab to toughen PBT and supertough property was obtained.²⁰

Though PBT has been toughened by ABS impact modifier successfully, the influence of ABS core-shell modifier structure variety on the toughness of PBT/ABS blends had not been studied in detail, to our knowledge. The situation more often encountered in the use of core-shell particles as impact modifiers is their dispersion in matrices that are dissimilar to the grafted shell. The dispersed morphology of ABS core-shell impact modifier in the PBT matrix can be modified by the grafting properties such as grafting degree of SAN on PB particles, AN content in SAN shell and core-shell ratio of PB/SAN. These structure properties of ABS core-shell impact modifier can be modified separately during particle preparation by emulsion polymerization method. The purpose of this paper is to explore the effect of grafting degree, AN content and core-shell ratio of ABS on the morphology and impact strength of PBT/ABS blends, then the relationship between structure and properties in toughening of PBT with ABS core-shell modifiers can be studied in detail.

EXPERIMENTAL

Materials

The PBT used in this work is a commercial product of Yizheng Chemical Fiber Group, Jiangsu, China. The hydroxyl and carboxyl end group concentrations are 44 $\mu\text{eq/g}$ and 20 $\mu\text{eq/g}$, respectively. Prior to

each processing step, PBT was dried in a vacuum oven for 4 h at 120°C to remove absorbed water. ABS core-shell copolymers with different structure properties were obtained by emulsion polymerization method and their properties were listed in Tables I–IV.

Preparation of ABS core-shell modifier

In the preparation process a polybutadiene (PB) polymer had to be synthesized first, thereafter, AN and St were polymerized on PB particles. PB latex used in this study was supplied by Jilin Chemical Industry Group synthetic resin factory (Jilin, China). An oil-soluble initiator, cumene hydro-peroxide (CHP), was used in combination with a redox system. CHP, sodium pyrophosphate (SPP), dextrose (DX), and iron (II) sulfate (FeSO_4) used in the redox initiator system were not further purified. The emulsion polymerization was performed in a 2-L glass reactor under nitrogen at 63°C. The water, PB, initiator, and KOH were added to the glass reactor and stirred for 5 min under nitrogen, then the mixture of St, AN, and chain transfer agent, *tert*-dodecyl mercaptan (TDDM), was added in a continuous feeding way to the glass reactor. The polymers were isolated from the emulsion by coagulation and dried in a vacuum oven at 60°C for 24 h before being used.

Characterization of ABS core-shell modifier

The grafting degree and grafting efficiency were determined by extracting the ungrafted SAN by acetone (a solvent for SAN but not for PB). After the ace-

TABLE II
ABS Properties with Different CHP Content

Designation used here	Rubber content (wt %)	Ratio of AN/St (wt/wt)	TDDM content (%)	CHP content (mL)	ABS particle size (μm)
ABS-C0.2	60	25/75	0	0.2	0.365
ABS-C0.4	60	25/75	0	0.4	0.369
ABS-C0.6	60	25/75	0	0.6	0.359
ABS-C0.8	60	25/75	0	0.8	0.366
ABS-C1.0	60	25/75	0	1.0	0.364
ABS-C1.2	60	25/75	0	1.2	0.384
ABS-C1.4	60	25/75	0	1.4	0.368
ABS-C1.8	60	25/75	0	1.8	0.366
ABS-C2.2	60	25/75	0	2.2	0.352

TABLE III
ABS Properties with Different AN Content

Designation used here	Rubber content (wt %)	AN content in SAN (wt %)	TDDM content (%)	CHP content (mL)	ABS particle size (μm)
ABS-AN0	60	0	0	0.6	0.366
ABS-AN5	60	5	0	0.6	0.358
ABS-AN10	60	10	0	0.6	0.359
ABS-AN15	60	15	0	0.6	0.349
ABS-AN20	60	20	0	0.6	0.365
ABS-AN25	60	25	0	0.6	0.359
ABS-AN40	60	40	0	0.6	0.352

tone solutions of the dried ABS impact modifiers were shaken for 8 h at room temperature, the solutions were centrifuged at 15,000 rpm in a GL-21M ultracentrifuge for 30 min. The grafting degree and grafting efficiency were calculated from the following equation:

$$\text{grafting degree (\%)} = 100 \times \frac{\text{gel\%} - \text{PB\%}}{\text{PB\%}}$$

$$\text{grafting efficiency (\%)} = 100 \times \frac{\text{gel\%} - \text{PB\%}}{1 - \text{PB\%}}$$

where gel% is the weight fraction of the acetone insoluble part in the sample and PB% is the weight fraction of polybutadiene in the ABS sample.

Particle size of the ABS core-shell copolymer was measured with a Brookhaven 90 Plus Laser Particle analyzer.

Melt blending and molding procedures

The blending was carried out in a twin-screw extruder and constitutes of PBT/ABS blends were 70/30 (wt/wt) if no special explanation was given. The temperatures along the extruder were 220, 230, 240, 240, 240, 240°C and the rotation speed of the screw was 60 rpm. The straps of blends were cooled in a water bath and then palletized.

PBT/ABS blends were dried in a vacuum oven at 80°C for 24h then were injection molded to prepare Izod impact specimens for testing.

Morphological properties

The disperse morphology of ABS core-shell modifier in PBT matrix was characterized by scanning electron microscopy (SEM) (model Japan JSM-5600). The sample surface was cut at low temperature (−100°C) with a glass knife until a smooth surface was obtained, thereafter, the samples were etched in tetrahydrofuran at room temperature for 5 h to remove the dispersed phase and coated with a gold layer for SEM observation.

Mechanical properties

Notched Izod impact tests of PBT/ABS blends were performed at 23°C according to ASTM D256 on a XJU-22 apparatus. Samples with dimensions 63.5 mm × 12.7 mm × 6.35 mm were obtained from injection-molded specimens. The notch was milled in having a depth of 2.54 mm, an angle of 45° and a notch radius of 0.25 mm. At least five samples were tested and the data given represented the averaged results.

RESULTS AND DISCUSSION

Effect of grafting degree on the properties of PBT/ABS blends

Two methods were used to modify the grafting degree of ABS core-shell modifiers. One was to change the chain transfer agent (TDDM) content; the second was to change the initiator (CHP) content.

TABLE IV
ABS Properties with Different PB/SAN Core-Shell Ratio

Designation used here	PB/SAN ratio (wt/wt)	AN content in SAN (wt %)	TDDM content (%)	CHP content (mL)	ABS particle size (μm)	Grafting degree (%)
PB90	90/10	25	0	0.05	0.309	7.6
PB80	80/20	25	0	0.10	0.324	19.2
PB70	70/60	25	0	0.15	0.362	36.4
PB60	60/40	25	0	0.20	0.388	56.5
PB50	50/50	25	0	0.25	0.416	84.5
PB40	40/60	25	0	0.30	0.434	134.2

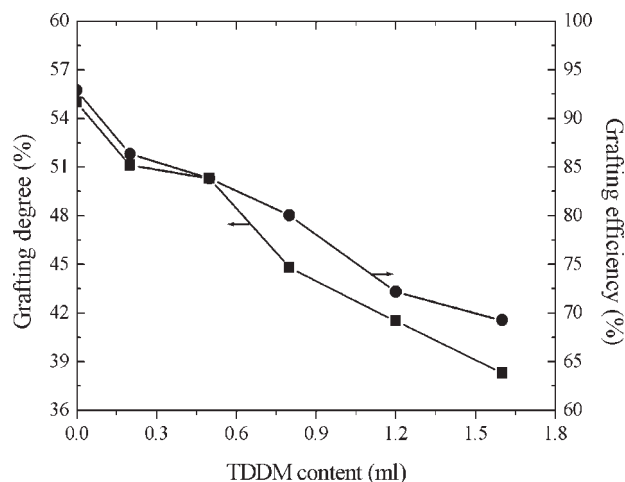


Figure 1 Effect of TDDM content on grafting degree and grafting efficiency of ABS impact modifier.

Effect of TDDM content on the properties of PBT/ABS blends

The effect of TDDM content on the properties of ABS core-shell modifiers can be seen from Table I and Figure 1. Figure 1 displays the influence of TDDM content on the grafting degree and grafting efficiency of ABS. As the amount of TDDM increases, the grafting degree

and grafting efficiency of SAN on PB rubber particles decrease. The increase of TDDM content in the reactive system improves the probability that propagating chain free radicals transfer to TDDM, which induces the decrease of grafting degree and grafting efficiency of SAN on PB particles. In the previous study,²¹ it was pointed out that TDDM could not change the number of grafting sites during emulsion polymerization process. So the decrease of grafting degree resulted in the decrease of molecular weight and grafting chain length of grafted SAN chains.

Figure 2 displays the influence of ABS grafting degree on the morphological properties of PBT/ABS blends. ABS with higher grafting degree dispersed uniformly in PBT matrix [Fig. 2(a)], however, with the decrease of grafting degree agglomeration of ABS in PBT matrix took place [Fig. 2(b,c)]. Two reasons may explain the formation of agglomeration structure of ABS phase. First, the surface of rubber particles cannot be covered perfectly by grafted SAN copolymers if ABS grafting degree is low and agglomeration of the rubber particles should be caused since the particles do not form a stable colloid. When the grafting degree becomes higher, the entropic repulsion between neighboring particles becomes stronger, resulting in the uniform dispersion of rubber particles in the ma-

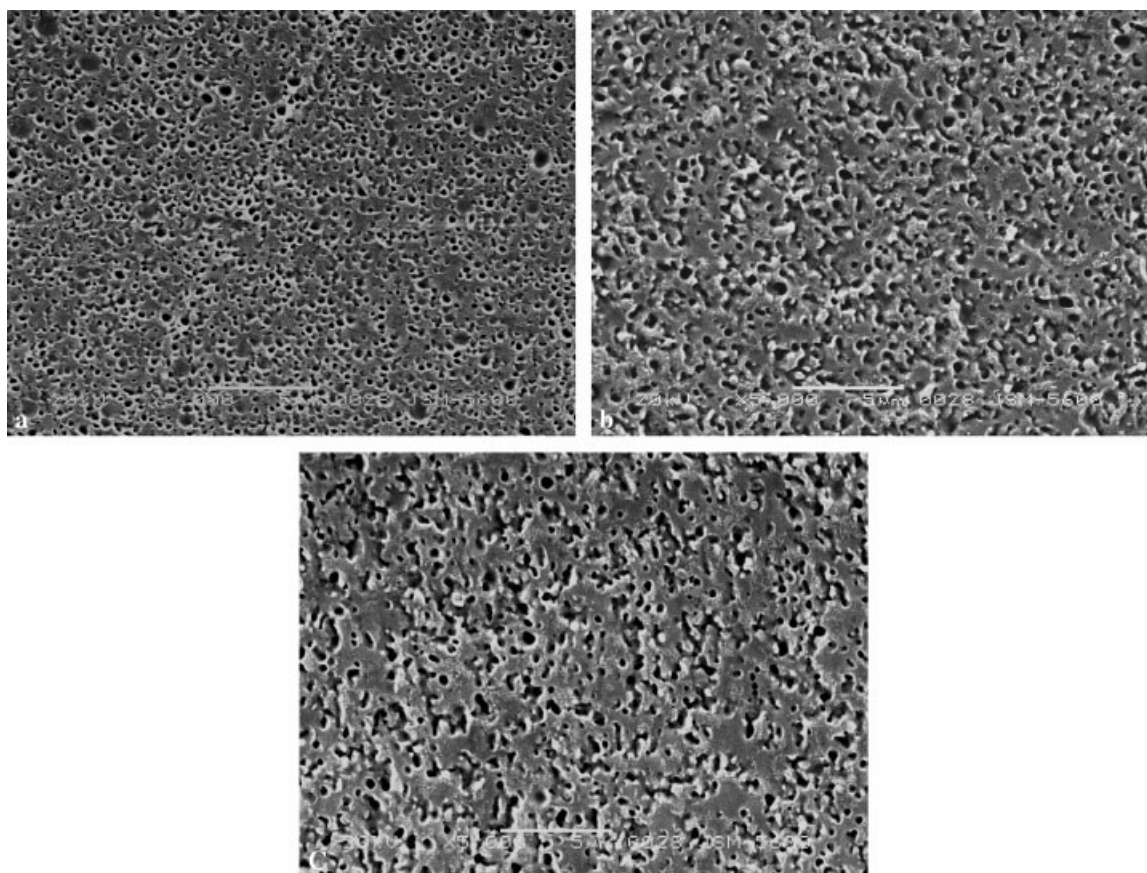


Figure 2 Effect of grafting degree of ABS on the morphology of PBT/ABS blends (TDDM series).

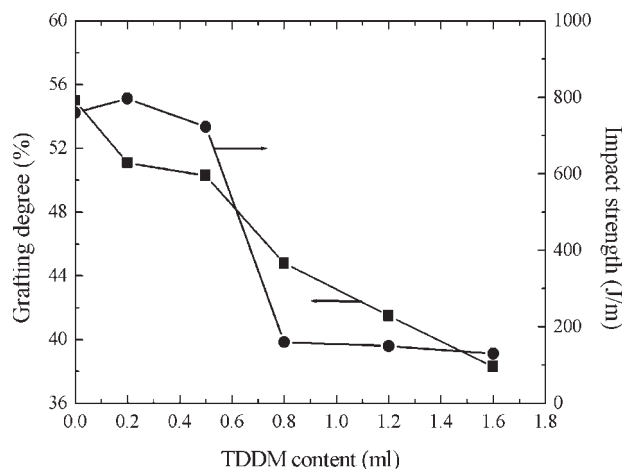


Figure 3 Effect of TDDM content on grafting degree and impact strength of PBT/ABS blends.

trix; second, the molecular weight of SAN chains on PB particles decreases with the decrease of grafting degree, which induces shorter grafting chain length, lower entanglement density between the SAN chains and PBT matrix, and poor interfacial adhesion strength. These reasons lead to the formation of agglomeration structure of ABS phase in PBT matrix. Similar result had been pointed out in other paper.²²

The relationship between grafting degree of ABS and notched Izod impact strength of PBT/ABS blends can be seen from Figure 3. PBT/ABS blends fracture in ductile mode when the grafting degree of ABS copolymers is more than 44.8%, otherwise, PBT/ABS blends fracture in brittle mode. The impact properties of PBT/ABS blends are consistent with the morphological properties.

Effect of CHP content on the properties of PBT/ABS blends

The effect of CHP content on the properties of ABS core-shell modifiers can be seen from Table II and Figure 4. With the increase of CHP content, more free radicals are produced; consequently, the number of grafting sites increases resulting in higher grafting degree and grafting efficiency. However, coupling reaction of free radicals may occur when too many free radicals are present, which decreases the grafting degree and grafting efficiency. From Figure 4 we can find the grafting degree and grafting efficiency increase with the CHP content, and then decrease when CHP content is beyond 0.4 mL.

The influence of grafting degree on the morphology of PBT/ABS blends for the CHP series is not very obvious (Fig. 5). In these blends, ABS particles can disperse in PBT matrix uniformly and no big agglomeration phase is observed. For ABS copolymers with

different CHP content, though grafting degree decreases when CHP content is high, the grafting sites increase with the CHP content. Then PB particles can still be covered well with SAN chain and agglomeration is not easy to occur.

Figure 6 displays the relationship between grafting degree and impact strength of PBT/ABS blends with different CHP content. PBT/ABS blends fracture in ductile mode when ABS copolymers have higher grafting degree and when the grafting degree is lower than 49.4%, the blends fracture in brittle mode. So we can conclude, though ABS can disperse in PBT matrix uniformly, the difference between grafting degrees can induce different mechanical properties of PBT/ABS blends. The essential reason lies in the different interfacial interaction. For this series, though the increase of CHP content increases grafting sites, the decrease of grafting degree will induce the decrease of grafting chain length and molecular weight of SAN chains, which induces poor entanglement between the SAN chains and PBT matrix. The decrease of chain entanglement with the CHP content leads to weak interfacial adhesion strength between PBT and ABS and induces PBT/ABS blends fracture in brittle mode.

Effect of AN content on the properties of PBT/ABS blends

The situation more often encountered in the use of core-shell particles as impact modifiers is their dispersion in matrices that are dissimilar to the grafted shell. The chemical composition of the shell can be chosen to impart compatibility with the matrix and which results in improved dispersion of the modifier in the matrix. ABS core-shell modifiers have been used to toughen poly(vinyl chloride) (PVC)^{23–25} and polycarbonate (PC)^{26–28} and results showed that the chemical composition of the shell, i.e., the AN content, had a very

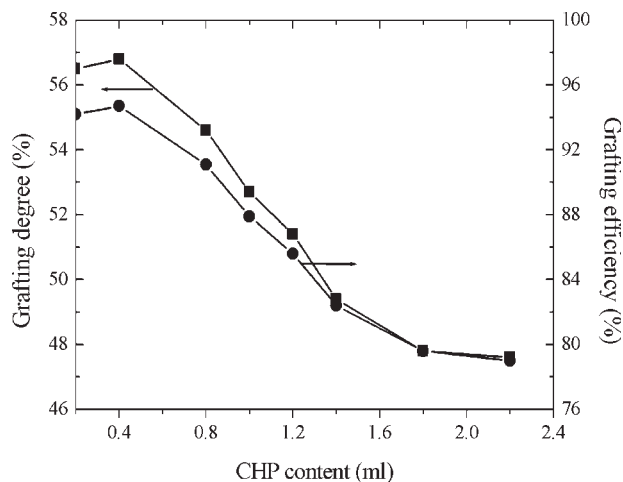


Figure 4 Effect of CHP content on grafting degree and grafting efficiency of ABS impact modifier.

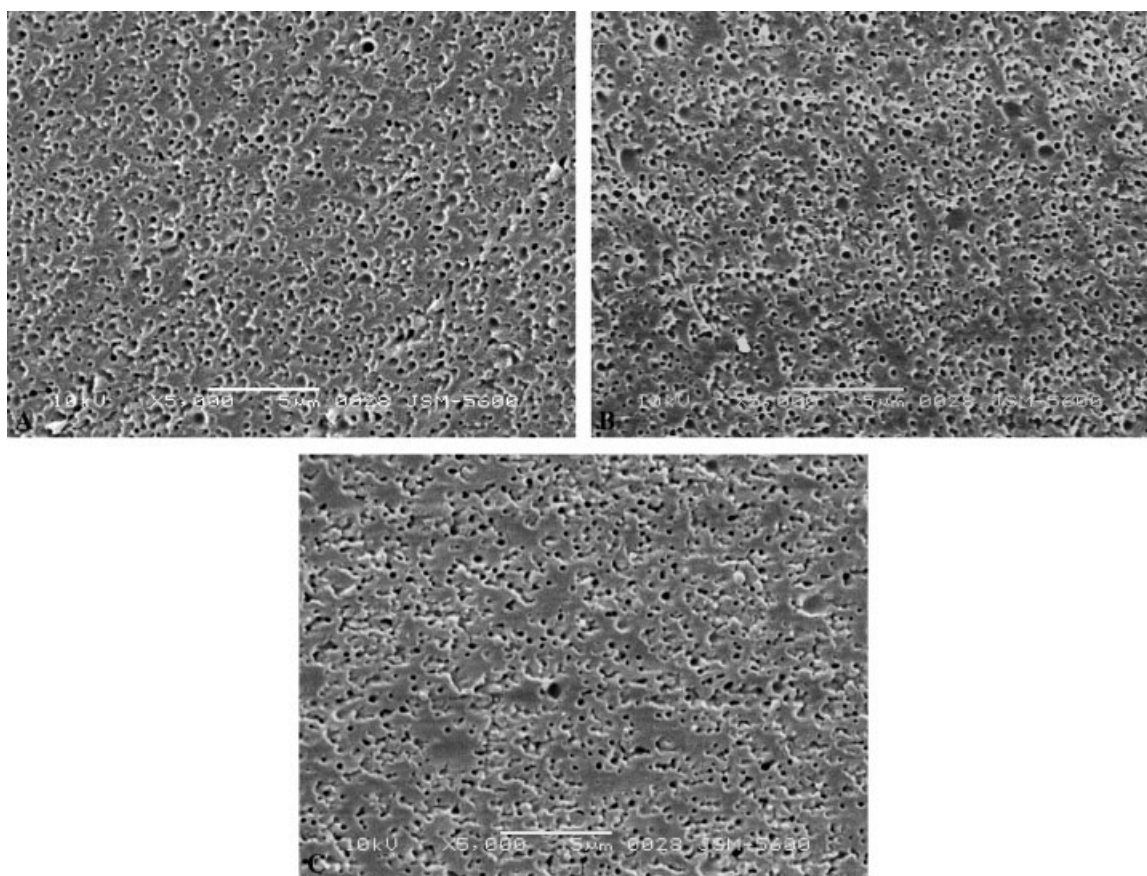


Figure 5 Effect of grafting degree of ABS on the morphology of PBT/ABS blends (CHP series).

important influence on the properties of these blends. For the PVC/ABS blends, it was found that PVC was miscible with SAN copolymer having AN compositions from 11.5 to 26%.²⁹ PC/ABS blend has been commercially available for many years and this blend showed excellent properties without any compatibilizer component. The useful properties of PC and ABS raised a considerable interest on the nature of the interaction between PC and SAN (the SAN represented the matrix of ABS). Results showed PC/SAN blend had optimum properties when the AN content was in the range of 25–27 wt %.³⁰

Similar with PC/ABS and PVC/ABS blends, it is believed that the favorable thermodynamic interaction between PBT and SAN is responsible for the excellent properties of the PBT/ABS blends without any compatibilization. So in this section, the influence of AN content in ABS on the properties of PBT/ABS blends was studied. Figure 7 displays the effect of AN content on the morphology of PBT/ABS blends. Agglomeration of core-shell modifiers takes place when only styrene is grafted [Fig. 7(a)]. With the introduction of AN in the shell, the dispersed morphology of the modifiers improves significantly and the content of AN does not influence the dispersed phase morphology obviously [Fig. 7(b–d)].

The influence of AN content on the notched impact strength of PBT/ABS blends can be seen from Figure 8. Consistent with the morphology character of the blends, when the AN content is zero, the blend has low impact strength and fracture in brittle mode, and with the increase of AN content the blends have high impact strength and all fracture in ductile mode. So

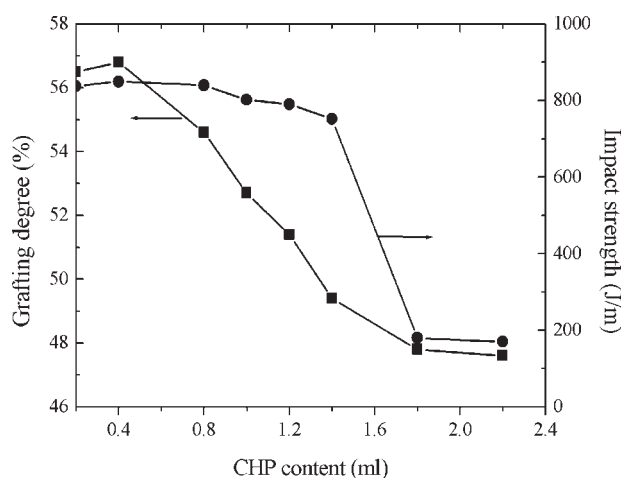


Figure 6 Effect of CHP content on grafting degree and impact strength of PBT/ABS blends.

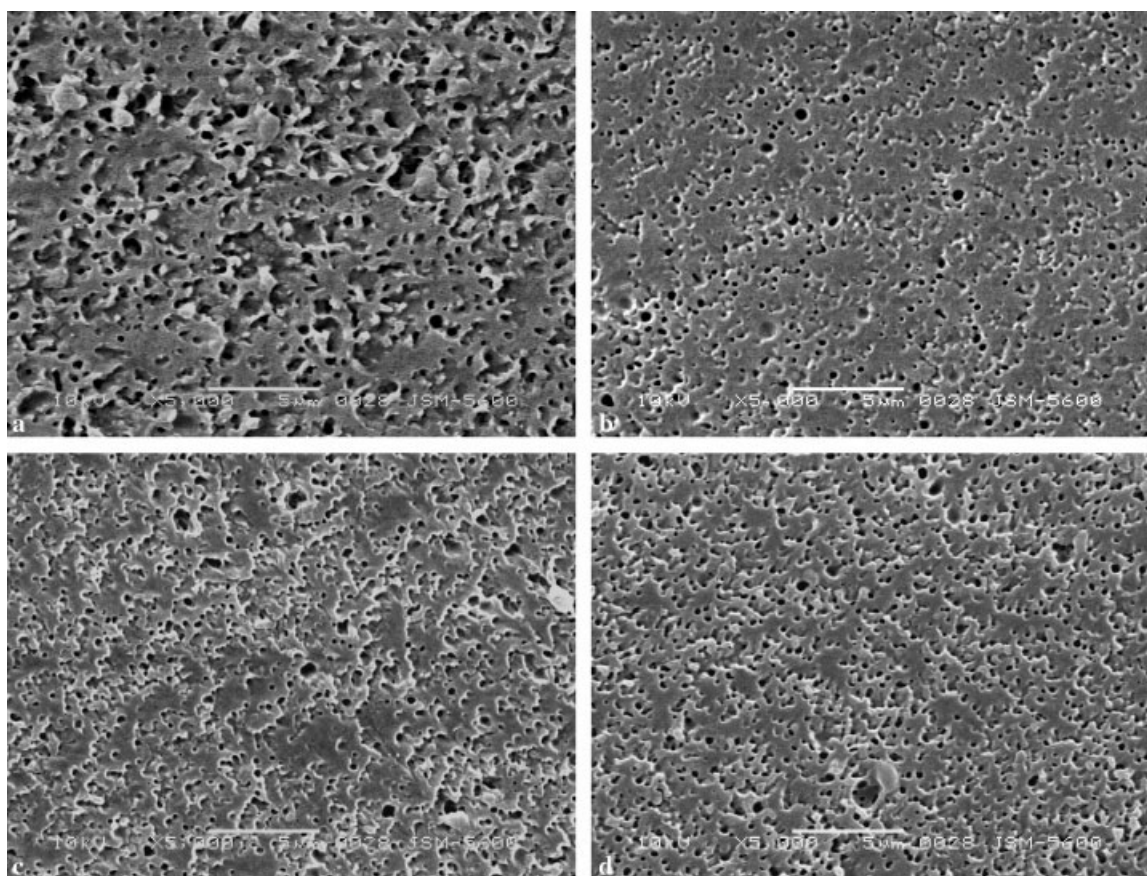


Figure 7 Effect of AN content in the shell of SAN copolymer on morphological properties of PBT/ABS blends.

dissimilar with PC/ABS and PVC/ABS blends, no optimum AN content in PBT/ABS blends was obtained. There is a wide AN range that can satisfy the fine morphological and mechanical properties of PBT/ABS blends.

Effect of core-shell ratio on the properties of PBT/ABS blends

A series of ABS impact modifiers with different PB/SAN ratio ranging from 90/10 to 40/60 were synthesized and blended with PBT. The PB concentration in PBT/ABS blends was kept at a constant value of 18 wt %. The influence of core-shell ratio of PB/SAN on the morphology of PBT/ABS blends was shown in Figure 9. Obvious agglomeration takes place and ABS particles display poor dispersed properties for the modifier with higher core-shell ratio, such as Figure 9(a). ABS particles with higher core-shell ratio have lower grafting degree (see from Table IV) and the surface of rubber particles cannot be covered perfectly with grafted SAN copolymer, which leads to agglomeration of the rubber particles by the van der Waals attraction. When the core-shell ratio of PB/SAN decreases, the grafting degree of SAN improves so PB particles can be covered well and the entropic repulsion between neighboring particles becomes stronger

resulting in uniform dispersion of impact modifiers in PBT matrix, such as Figure 9(b). With the further decrease of PB/SAN ratio, the grafting degree of SAN increases and PB particles can be fully covered. However, since the PB content in ABS copolymer decreases with the increase of shell content, much ABS have to be added into the PBT matrix to keep

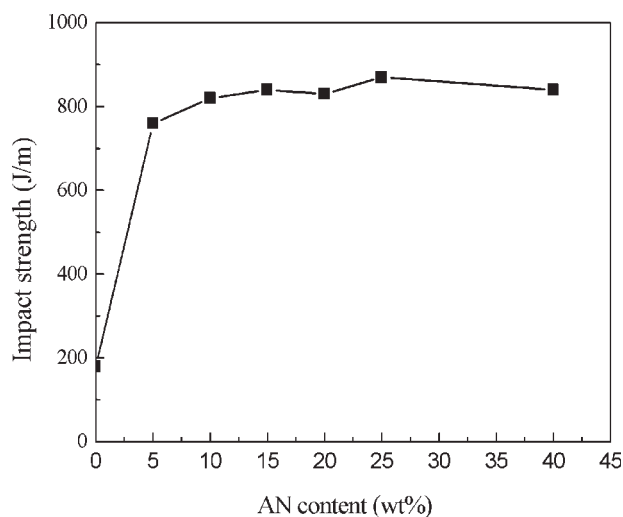


Figure 8 Effect of AN content in the shell of SAN copolymer on impact strength of PBT/ABS blends.

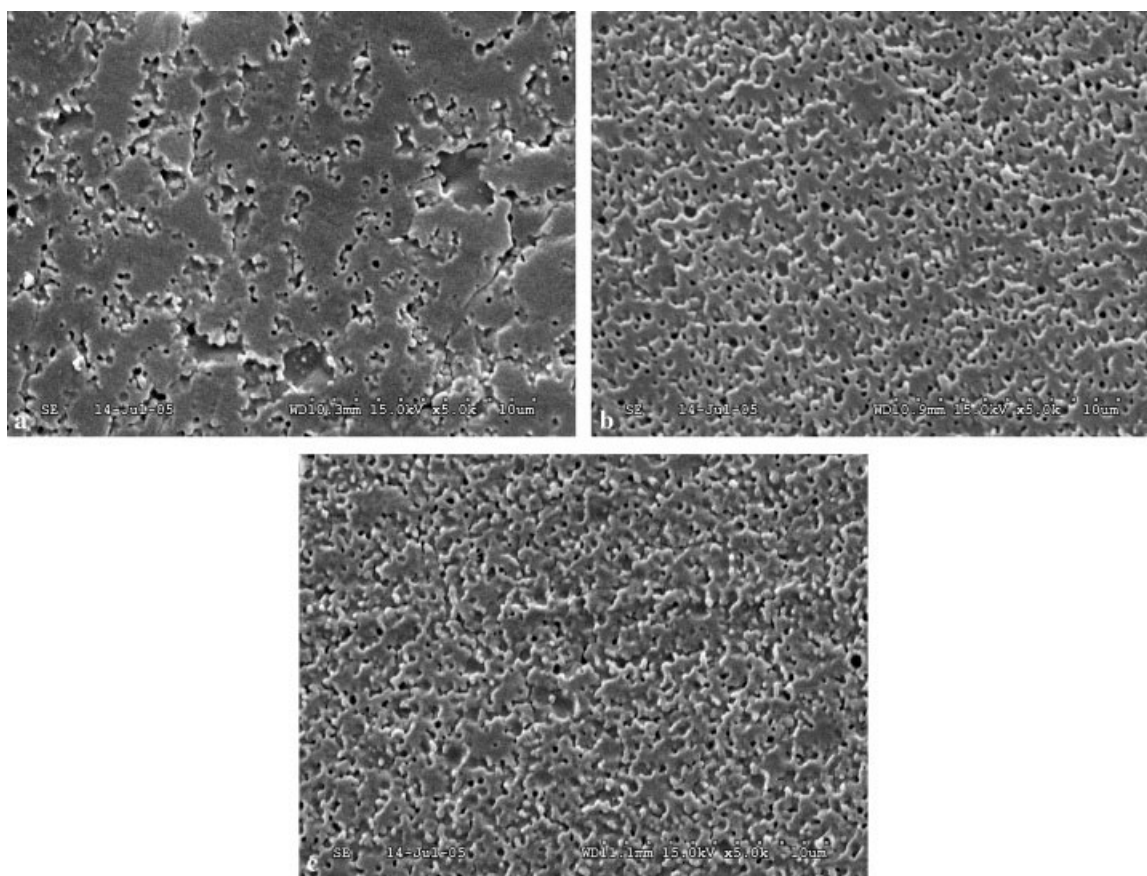


Figure 9 Effect of PB/SAN ratio in ABS copolymer on morphological properties of PBT/ABS blends.

a constant PB content and the blend tends to form cocontinuous structure, such as Figure 9(c).

Figure 10 displays the influence of core-shell ratio of PB/SAN on the impact strength of PBT/ABS blends. PBT/ABS blends show maximum impact strength value when the PB/SAN ratio is 60/40 and PBT can be toughened when the core-shell ratio of PB/SAN ranges from 70/30 to 50/50 and PBT/ABS blends fracture in ductile way in this region. For ABS with higher PB/SAN ($\geq 70/30$) ratio, ABS cannot disperse in PBT matrix uniformly and form big agglomeration phase, which is not beneficial to the toughening of PBT. On the other hand, for ABS with lower PB/SAN ratio ($< 50/50$), PBT/ABS blends tend to form cocontinuous phase structure and which still induces brittle fracture of the blends.

CONCLUSIONS

In this paper, ABS core-shell impact modifiers with different grafting degree, AN content, and PB/SAN core-shell ratio were prepared through emulsion polymerization method and these ABS copolymers were used to toughen PBT.

Two methods were used to modify the grafting degree of ABS core-shell modifiers. One was to

change the chain transfer agent (TDDM) content; the second was to change the initiator (CHP) content. Results showed the grafting degree of ABS decreased with the TDDM content. Morphology and impact tests showed agglomeration took place and PBT/ABS

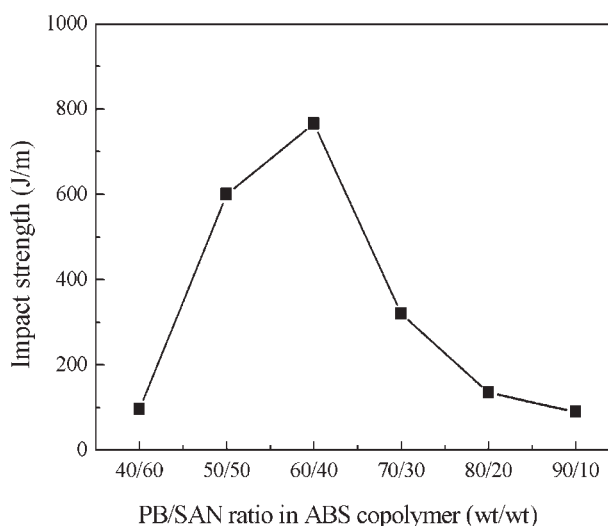


Figure 10 Effect of PB/SAN ratio in ABS copolymer on impact strength of PBT/ABS blends (the content of PB was set as 18 wt %).

fractured in brittle mode when grafting degree was low ($\leq 44.8\%$), otherwise, ABS dispersed uniformly in PBT matrix and the blends fractured in ductile mode. The grafting degree of ABS increased with CHP content, however, when the CHP content was too high, the grafting degree decreased again. The effect of grafting degree on the morphology of PBT/ABS blends for the CHP series was not obvious and ABS had a good dispersed morphology, however, when the grafting degree was lower than 49.4% the blends fractured in brittle way.

The interaction between SAN and PBT was influenced by AN content. Results showed ABS could not disperse in PBT matrix uniformly when AN content was zero and PBT/ABS fractured in brittle way. With the addition of AN in ABS, PBT/ABS blends fractured in ductile mode. There was a wide AN range that can satisfy the fine morphological and mechanical properties of PBT/ABS blends.

The core-shell ratio of ABS copolymers had important effect on PBT/ABS blends. When the core-shell ratio was higher than 60/40, agglomeration occurred in PBT/ABS blends; on the other hand, when the core-shell ratio was lower than 50/50, the blends tended to form cocontinuous phase structure. So core-shell ratio 50/50 to 60/40 was optimum constitution.

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