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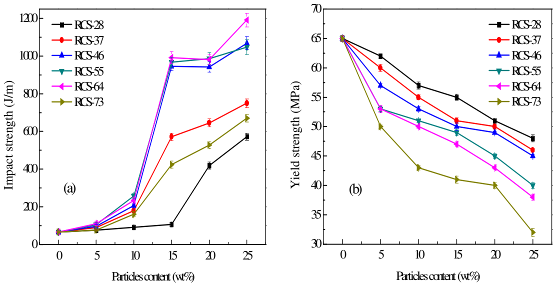
Modification of the core-shell ratio to prepare PB-g-(MMA-co-St-co-GMA) particles toughened poly(butylene terephthalate) and polycarbonate blends with balanced stiffness and toughness

Yang Guo[a], Shulin Sun *[a, b], Huixuan Zhang[a]

The particles with modified core-shell ratio provide an effective way to prepare polymer blends with superior toughness and stiffness balance.



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Modification of the core-shell ratio to prepare PB-g-(MMA-co-St-co-GMA) particles toughened poly(butylene terephthalate) and polycarbonate blends with balanced stiffness and toughness

Yang Guo[a], Shulin Sun *[a, b], Huixuan Zhang[a]

Abstract: Reactive polybutadiene-g-(methyl methacrylate-co-styrene-co-glycidyl methacrylate) particles with different core-shell ratio (RCS) were prepared by seeded emulsion polymerization method. The influence of RCS core-shell ratio on the toughness and stiffness of poly(butylene terephthalate) (PBT) and polycarbonate (PC) blends was investigated. Low core-shell ratio induced higher grafting degree and 'internal grafting' which were useful to keeping the blend stiffness. High core-shell ratio improved the soft rubber content and was beneficial to toughness improvement. The optimum grafting degree region was 56~187% for the RCS to achieve good dispersion. The RCS-28 and RCS-37 particles were efficient to keeping higher stiffness but lower toughening effect for PBT/PC blends due to their poor cavitation ability. RCS-73 toughened blends showed weak impact and yield strength due to its agglomeration morphology and high rubber phase content. In the present paper, PBT/PC/RCS-46 blends showed better toughness and stiffness balance. When the RCS-46 content was 15%, impact strength of 950J/m and yield strength of 50MPa could be achieved for the PBT/PC/RCS-46 blend.

Introduction

Polymer blends have attracted much attention for both industrial applications and academic purposes. Most polymer blends are designed to achieve improvement of the parent components, such as better processability, higher impact strength, better chemical resistance, and so forth[1, 2]. Among the blends studied, aromatic polyesters represent a major class of engineering plastics having excellent properties with a large variety of applications[3-8]. Poly(butylene terephthalate) (PBT) and polycarbonate (PC) are one important pair of polyester blends and have been investigated detailedly in recent years[9-15]. Most of the researches about PBT/PC blends were focused on the transesterification reactions, miscibility, crystallization

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property and phase morphology. The PBT/PC blends combine the excellent chemical resistance, easy processability of PBT phase and the good dimension stability, higher mechanical properties of PC phase.

However, the PBT/PC blends are notch sensitive and fracture in brittle way when standard notched specimens are tested. The poor notched impact toughness of PBT/PC blends limits their application, and suitable toughening measures should be applied to overcome this drawback. Zhang used ethylene-butyl acrylate-glycidyl methacrylate copolymer (PTW) to toughen PBT/PC blends[16, 17]. The notched impact strength increased up to 538J/m when the copolymer content approached 14wt%. Ethylene-co-glycidyl methacrylate (E-GMA) was used by Wu to improve the toughness of PBT/PC blends[18]. Core-shell impact modifier is another important toughener for PBT/PC blends. The modifiers used in the studies usually have a grafted poly(methyl methacrylate) shell and a polybutadiene or poly(n-butyl acrylate) rubber core. Fracture mechanisms showed that cavitation of rubber particles and massive shear yielding of the matrix were the major energy dissipation way[19, 20].

In order to obtain excellent impact strength of rubber toughened polymers, sufficient rubber content is necessary. However, due to the elastic nature of the rubber phase, higher rubber content will decrease the stiffness of the materials inevitably, such as the yielding strength and elastic modulus. So how to control the balance between the toughness and stiffness for the brittle polymer and rubber blends becomes very meaningful[21-25]. Fortunately, the core-shell rubber particles provide a possibility to modify the polymer blends with a superior toughness and stiffness balance. As we know, the typical core-shell particles include a rubber core phase (low modulus) and a plastic shell phase (high modulus). The rubber core can cavitate and induce the shear yielding of the matrix. The plastic shell can physically or chemically interact with the matrix to ensure dispersion and coupling. For the sake of keeping higher stiffness of rubber toughened polymers, much lower rubber addition is necessary. So according to the character of core-shell particles, we can modify the ratio of the core and shell phase to decrease the rubber content by decreasing the core phase percent.

In the present paper, the reactive core-shell particles (RCS) with different core and shell ratios were prepared to toughen PBT/PC blends in order to achieve the above purpose. The RCS particles were synthesized by the seeded emulsion polymerization method with the polybutadiene rubber (PB) as the soft core and the copolymer of methyl methacrylate (MMA), styrene (St) and glycidyl methacrylate (GMA) as hard shell. The PMMA components in the grafting shell have good miscibility with the PC phase and the epoxy groups of GMA can react with the carboxyl groups of PBT which is beneficial to the compatibility improvement [26-28]. The St can improve the grafting reaction rate of the RCS. So the RCS particles with the core/shell ratio changed from 20/80 to 70/30 were used to toughen PBT/PC blends and the detailed investigation will be discussed in the following part.

Experimental

Materials

The PBT was purchased from Engineering Plastics Plant of Yihua Group Corp., China. The PC used was a commercial product of Bayer Plastics designated as Makrolon 2805. The MFI of PBT and PC are 18g/10min and 3g/10min (240°C, 2.16Kg). To avoid hydrolysis of these polymers, all materials were dried at 105°C for at least 12h in a vacuum oven to remove absorbed water before melt-processing. The RCS particles with different core/shell ratio were prepared in our lab.

Preparation of RCS particles

RCS particles were synthesized by the seeded emulsion polymerization method. The PB seeded latex used in this study was supplied by Jilin Chemical Industry Group Synthetic Resin Factory (China). An oil-soluble initiator, cumene hydro-peroxide (CHP), was used in combination with a redox system. The redox initiator system, CHP, sodium pyrophosphate (SPP), dextrose (DX), KOH and $FeSO_4$ were used without further purification. The emulsion polymerization was performed in a 3L glass reactor under nitrogen at 70°C, and the reaction took place in an alkaline condition at PH10. First, the water, PB, initiator and KOH were added to the glass reactor and stirred 5min under nitrogen, then the mixture of St/MMA was added in a continuous feeding way to the glass reactor. After the addition of St/MMA, GMA was added to the reactor in the same way. The polymers were isolated from the emulsion by coagulation and dried in a vacuum oven at 60°C for 24h before being used. The properties of the RCS particles were list in Table 1.

Table 1 Composition of the RCS particles used in the paper

Designation used here[a]	Core content (wt%)	Shell Content (wt%)	St/MMA (wt/wt)	GMA content[b] (wt%)
RCS-28	20	80	3/1	1
RCS-37	30	70	3/1	1
RCS-46	40	60	3/1	1
RCS-55	50	50	3/1	1
RCS-64	60	40	3/1	1
RCS-73	70	30	3/1	1

[a] For the RCS-xy, x indicates the weight fraction of core phase and y indicates the weight fraction of shell phase for the different core-shell particles.

[b] Based on the whole core-shell particles weight

Particle size and grafting degree tests

Particle size was measured with a dynamic light scattering (DLS) on a Brookhaven 90 Plus laser particle analyzer (Brookhaven, USA).

The grafting degree was determined by extracting the ungrafted copolymers by acetone. The acetone solutions of the dried RCS impact modifiers were shaken for 8h at room temperature, and then the solutions were centrifuged at 15,000rpm in a GL-21M ultracentrifuge for 30min. The grafted particles were separated from the solution and the separation process was repeated three times. Then the separated particles were dried in a vacuum oven at 60°C for 12h and weighed for the grafting degree calculation. The grafting degree was calculated from the following equation:

$$\text{Grafting degree} = \frac{\text{weight of grafted polymers}}{\text{weight of PB particles}}$$

Blending and molding procedures

The blending was carried out in a Thermo Haake internal mixer. The content of PC in the blends was set at 30wt% and the contents of RCS particles were 5, 10, 15, 20 and 25wt% respectively. The temperature was set at 240°C with the rotation speed of 55rpm and a 5min mixing time. After blending, the samples with different compositions were obtained by hot press molding for 5min at 230°C and cold press molding for 3min at room temperature.

Mechanical tests

The notched Izod impact strength of the blends was measured by an XJU-22 Izod impact tester at 23^{o}C according to ASTM D256 (63.5mm×12.7mm×3.18mm). The notch was milled in having a depth of 2.54mm, an angle of 45° and a notch radius of 0.25mm. The tensile tests were carried out with an Instron-3365 tensile tester at a crosshead speed of 50mm/min at 23^{o}C according to ASTM D638.

Morphological observation

TEM micrographs were taken on a JEM-1011 transmission electron microscope (JEOL, Japan) operating at an accelerating voltage of 100kV. Ultrathin samples were obtained from the samples using a Leica ultra microtome at -100^{o}C (Leica, Germany). The PB phase of the RCS particles was stained using an aqueous solution of OsO_4 (2%) over a period of 2.5h. Polycarbonate was stained with an aqueous solution of RuO_4 for about 70min. SEM micrographs were obtained with a JSM6510 scanning electron microscope (JEOL, Japan) with the operation voltage of 10kV. Before the test, the samples were coated with a gold layer for SEM observation.

DMA test

The samples were compression molded in order to obtain bars that are suitable for DMA measurements. The dimension of the samples was 30mm×10mm×1mm and the dynamic mechanical analyzer used was the Diamond-DMA (Perkin Elmer, Japan) under single cantilever mode in a temperature range from -110^{o}C to 180^{o}C with a constant heating rate of 3^{o}C /min and a frequency of 1Hz.

Results and discussion

Properties analysis of the RCS

The properties of the RCS particles, such as particle size, grafting degree and morphology, have very important influence on the toughening behavior. The particle size of the PB used in the paper was 296nm. According to Bucknall's investigation, the particle size of the rubber can influence its caviation ability and for many high performance blends, the optimum particle size appears to be about 300nm[29, 30]. So in the present paper, the rubber core size of the RCS was very suitable to toughen PBT/PC blends. As seen from Fig. 1a, with the increase of core/shell from 20/80 to 70/30, the particle size of the RCS decreased from 489nm to 324nm. The decrease of the particle size for RCS can be explained by Fig. 1b, which shows the curves of theoretical and practical grafting degree of the shell phase of RCS particles. It can be found that the two curves are different and part of the shell monomers have not reacted with the PB rubber core. The grafting degree of the RCS decreased from 306% to 35% when the core-shell ratio changed from 20/80 to 70/30. So the higher shell monomer content can induce much grafted shell polymers on the PB phase and lead to bigger RCS particle size. On the other hand, the grafting degree of RCS can influence its dispersed phase morphology and the final mechanical properties of the blends, which will be discussed in the following part.

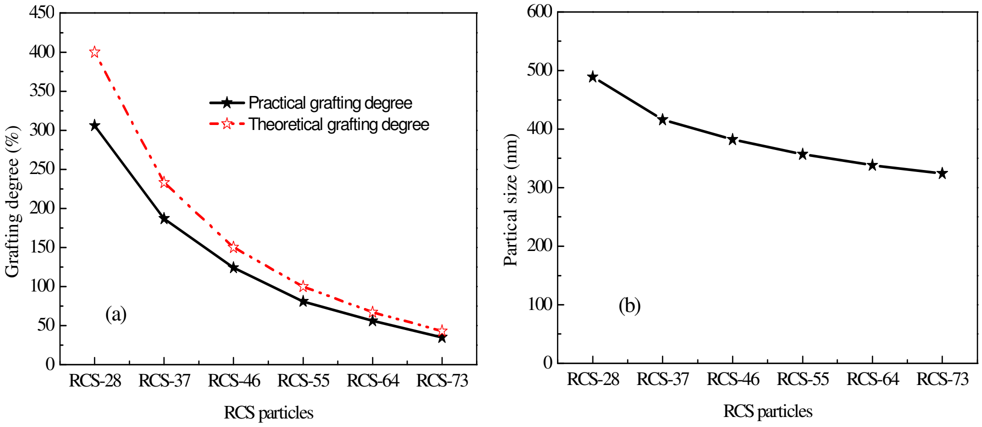
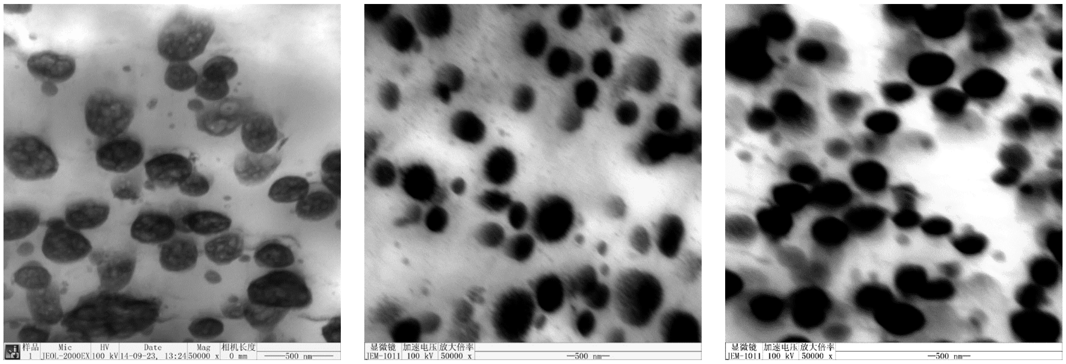


Fig. 1 Properties of RCS particles. (a) grafting degree, (b) particle size

The obvious difference of the core-shell ratio can also influence the micro morphology of the RCS. For the RCS particles, the shell is the MMA-co-St-co-GMA plastic phase which grafts onto the surface of PB particles and can be called 'external-grafting'. At the same time, because of the swelling of monomer into the PB rubber particles, the grafting polymerization can take place inside the rubber particles too, which can be called 'internal-grafting'. So the higher shell monomer content may result in much 'internal-grafting'. Fig. 2 shows the micro TEM morphology of the RCS particles. The PB particles have been stained black due to the chemical reaction between PB and OsO_4. It can be seen that, for the RCS-28, obvious 'internal-grafting' exists in the PB core since the white zone in the black PB particles. However, with the decrease of shell monomer content in the RCS, the 'internal-grafting' becomes not distinct, such as RCS-46 and RCS-64. The ‘external-grafting’ affects the dispersion of the rubber particles in the matrix, and the ‘internal-grafting’ can influence the elastic property of the particles. The change of the micro morphology of RCS will also influence the toughening ability of RCS particles.

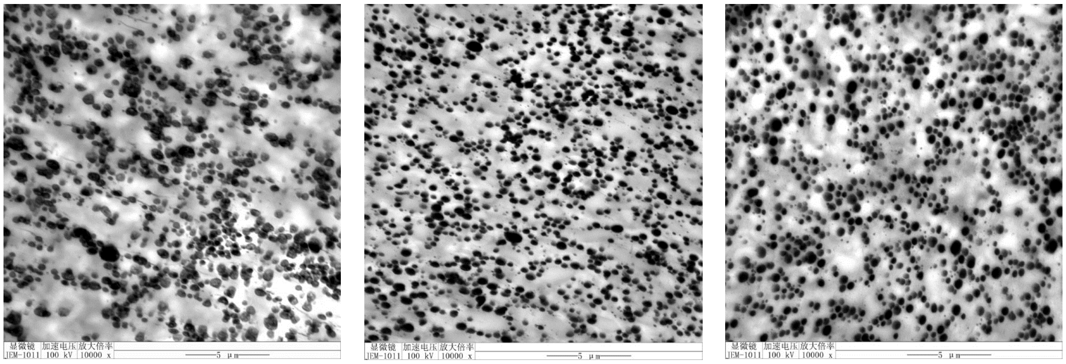


(a) RCS-28 (b) RCS-46 (c) RCS-64

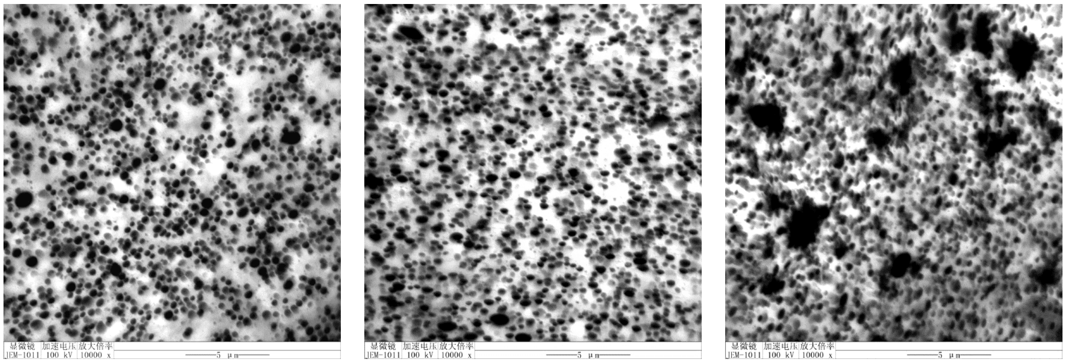
Fig. 2 The micro TEM morphology of the RCS with different core-shell ratios

Dispersed phase morphology

Dispersed phase morphology of the RCS particles is another important factor which can affect the mechanical properties of PBT/PC blends. Fig. 3 shows the TEM morphology of RCS blends. As for the core-shell particle, the grafting degree and the compatibility between the shell phase and the matrix will determine the dispersed phase morphology. In the present paper, the MMA-co-St-co-GMA copolymer shell has good compatibility with the PBT/PC matrix as recommended in the introduction part. The physical and chemical interactions between the MMA-co-St-co-GMA copolymer shell and PBT/PC are conductive to the dispersion. The influence of grafting degree on the dispersion of core-shell particles has been studied by Hasegawa et al. in detail[31]. They pointed out that, at low grafting degree, the polymer grafted particles could not form a stable colloid because the particles were not covered completely with grafted chains. On the other hand, the rubber particles also could not form a stable colloid at high grafting degree, as the matrix chains were expelled from the grafted chains. There was an optimum grafting degree for dispersing particles in polymer melts. Thus an agglomerated or a three-dimensional network structure of rubber particles formed when the grafting degree of the particles was not in the intermediate region. As can be seen from Fig. 3, RCS-28 forms some agglomeration phases which indicate the grafting degree of 306% is too high. As for the RCS-73, much larger agglomeration phases can be found so the grafting degree of 35% is too low for the particle. When the grafting degree is between 56% and 187%, the RCS particles show much better dispersed phase morphology.



(a) PBT/PC/RCS-28 (b) PBT/PC/RCS-37 (c) PBT/PC/RCS-46

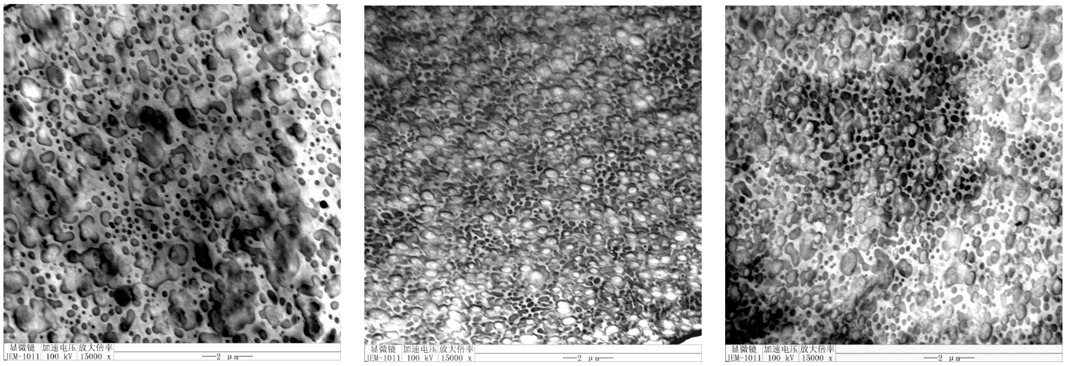


(d) PBT/PC/RCS-55 (e) PBT/PC/RCS-64 (f) PBT/PC/RCS-73

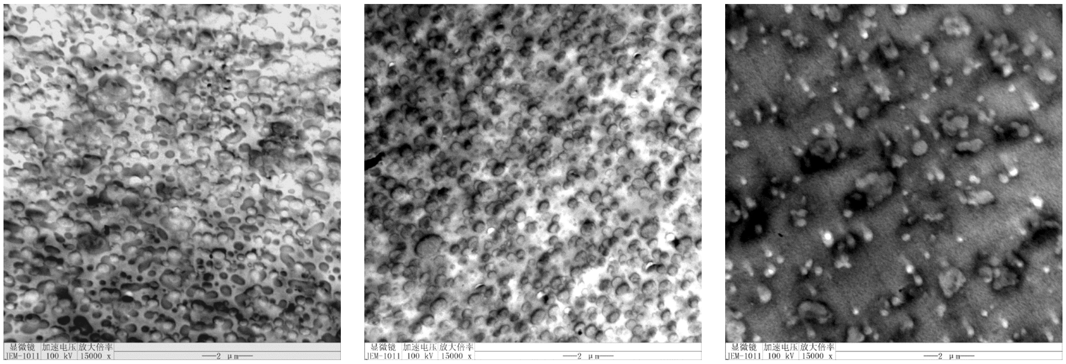
Fig. 3 Dispersed phase morphology of PBT/PC/RCS blends stained by OsO_4

In PBT/PC/RCS blends, the matrix includes PBT and PC phases. The miscibility between PBT and PC has been investigated widely[32-35]. Different conclusions on the miscibility behavior of PBT/PC blends have been reported, which ranged from complete immiscibility when casted from the common solvents to partial miscibility when melt blended. The complex behavior was due to liquid-liquid phase separation, crystallization of the PBT phase and the transesterification reactions. Now it is commonly accepted that PBT and PC are partially miscible for the melt blends due to the transesterification. Since PBT and PC are immiscible, it is necessary to show the position of RCS particles in the blends. In Fig. 4, samples were stained with ruthenium tetroxide to make the PC appear darker against a lighter PBT phase. Since the PMMA components in the grafting shell have good miscibility with the PC phase and the epoxy groups of GMA can react with the carboxyl groups of PBT, the RCS particles may locate in the PC phase, PBT phase or the interface between PBT and PC phases. As can be seen from Fig. 4, a small quantity of RCS-28 particles exists in the PC phase and most of the

RCS-28 particles disperse in the PBT phase and the interface. As for the RCS-37，RCS-46, RCS-55 and RCS-64 particles, most of the particles disperse in the dark PC phase and forms the PC encapsulated structure. In Fig. 4f, obvious agglomeration of RCS-73 takes place and the agglomerated particles are surrounded by the PC phase. So from Fig. 4, it can be concluded that PBT and PC are thermodynamically immiscible. The minor phase domain size of PC in the blends also proves the compatibilization effect of RCS particles for the PBT/PC blends.



(a) PBT/PC/RCS-28 (b) PBT/PC/RCS-37 (c) PBT/PC/RCS-46



(d) PBT/PC/RCS-55 (e) PBT/PC/RCS-64 (f) PBT/PC/RCS-73

Fig. 4 Dispersed phase morphology of PBT/PC/RCS blends stained by RuO_4

Mechanical properties

Fig. 5a shows the influence of RCS content on the Izod notched impact strength of PBT/PC/RCS blends. The RCS with different core/shell ratio displays different toughening ability. As for the PBT/PC/RCS-28 blends, the brittle-ductile transition takes place when the RCS-28 content is between 15~20wt%. The RCS-28 shows the worst toughening efficiency than other particles due to its lower rubber content, poor dispersion and bad cavitation ability. The RCS-37 has much better toughening ability than RCS-28 and when the RCS-37 content is

10~15wt%, the brittle-ductile transition occurs. With the increase of core-shell ratio, all the blends have the same brittle-ductile transition. The RCS-46, RCS-55 and RCS-64 show excellent toughening ability and the impact toughness of PBT/PC blends is improved more than 15 times. However, further increase of core/shell ratio induces the decrease of toughening ability such as RCS-73 due to the poor dispersed phase morphology. Fig. 5b shows the influence of RCS content on the yield strength of PBT/PC/RCS blends. The yield strength of the blends decreases significantly with the increase of RCS content. The decrease of the yield strength is due to the elastomeric nature of the PB rubber phase in RCS particles. From comparison it can be found that, at the same RCS content, the RCS particles with higher core/shell ratio reduce the stiffness of the PBT/PC blends much significantly due to the higher PB content. So according to the impact and tensile results, too high core/shell ratio is not necessary to achieve superior toughness and more important, which can decrease the stiffness of the materials. In the present paper, RCS particles with core/shell ratio of 4/6 show the optimum toughness and stiffness balance for the PBT/PC blends. Similar strategy can be applied into other core-shell particles toughened polymer blends.

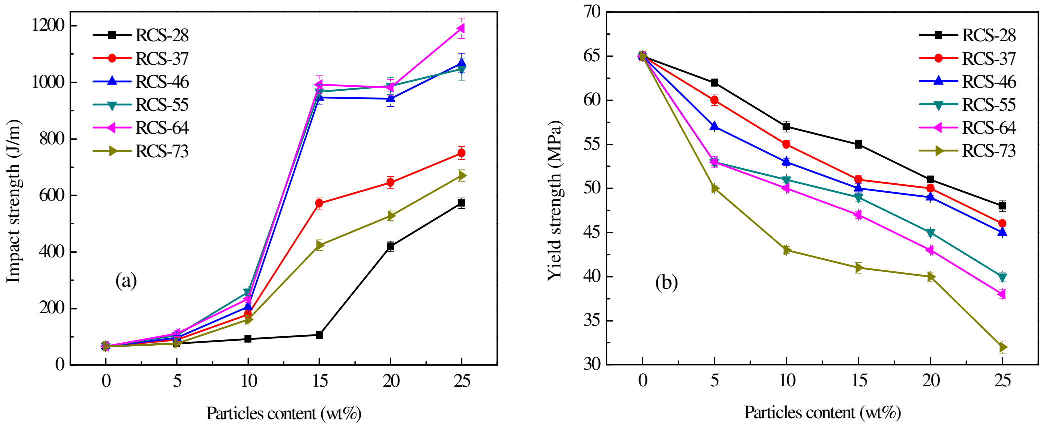
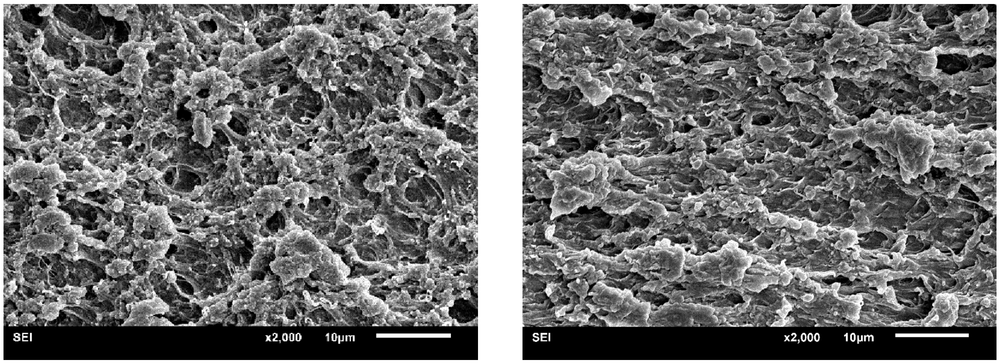


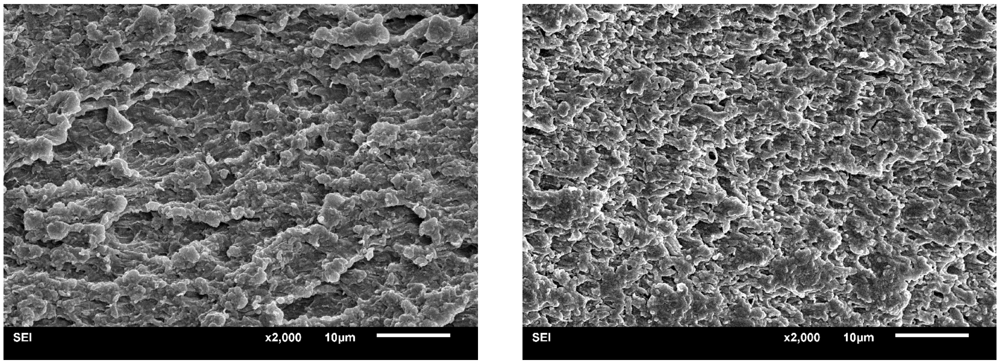
Fig. 5 Mechanical properties of PBT/PC/RCS blends. (a) Impact strength, (b) Yield strength

Toughening mechanisms

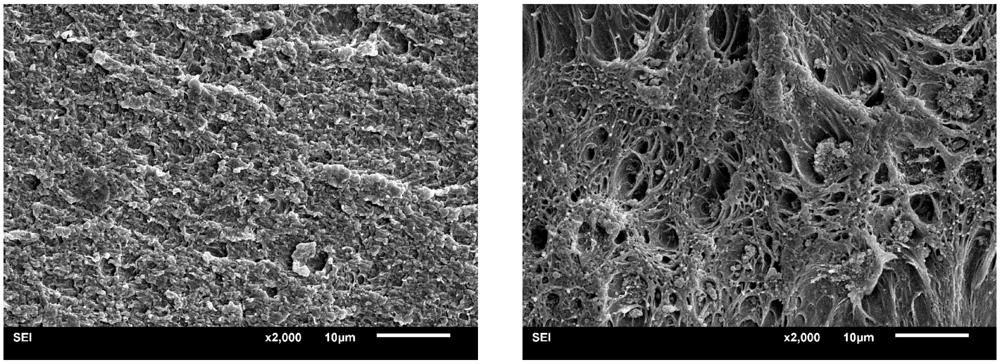
Fig. 6 displays the notched impact fracture SEM morphology of PBT/PC/RCS blends. The content of RCS particles in the samples was 20wt%. As expected, all the fracture surfaces of PBT/PC/RCS blends show the characteristics of ductile fracture. Obvious plastic deformation can be found on the fracture surface, which implies that shear yielding of the PBT/PC matrix has taken place. The shear yielding is the main energy absorption way and promotes the toughness improvement. In Fig. 6a~e, the interface between the RCS and the matrix is obscure, which testify the fine interfacial interaction between the matrix and the dispersed phase. However, Fig. 6f shows much clearer interface and aggregated RCS-73 particles, which further proves the poor interfacial properties between RCS-73 and PBT/PC blends.



(a) PBT/PC/RCS-28 (b) PBT/PC/RCS-37



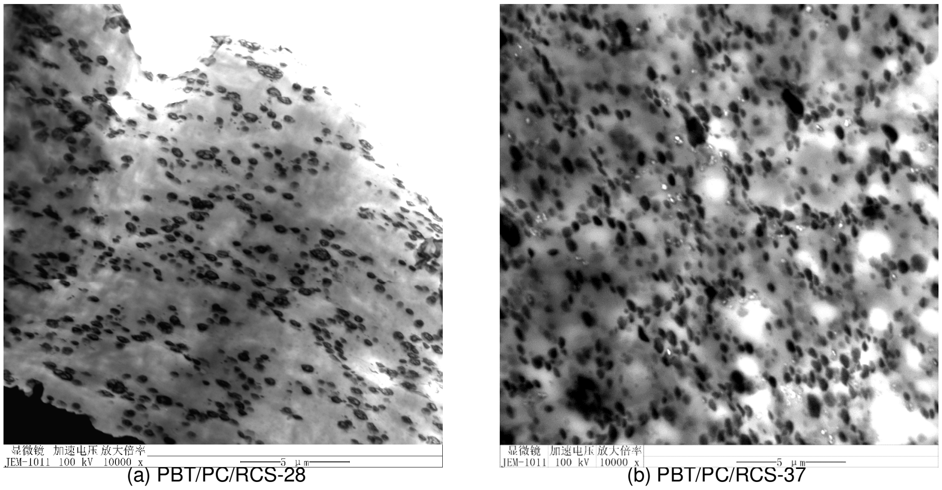
(c) PBT/PC/RCS-46 (d) PBT/PC/RCS-55



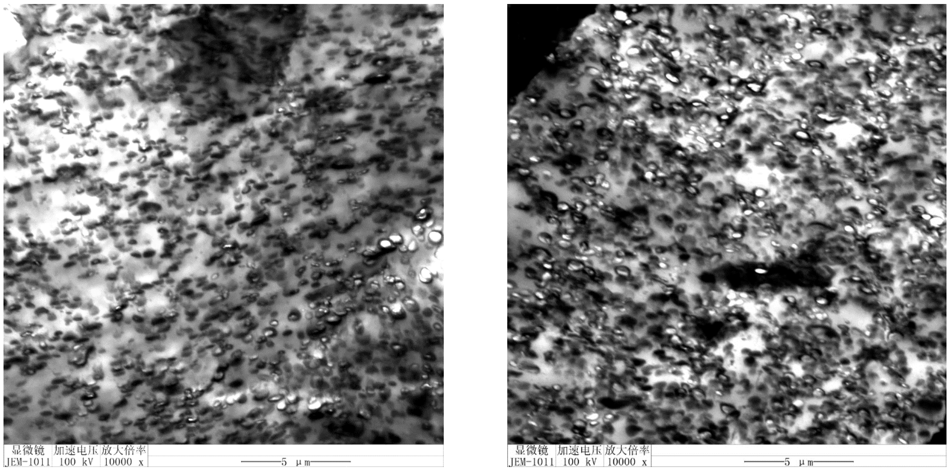
(e) PBT/PC/RCS-64 (f) PBT/PC/RCS-73

Fig. 6 SEM fracture surfaces of PBT/PC/RCS blends

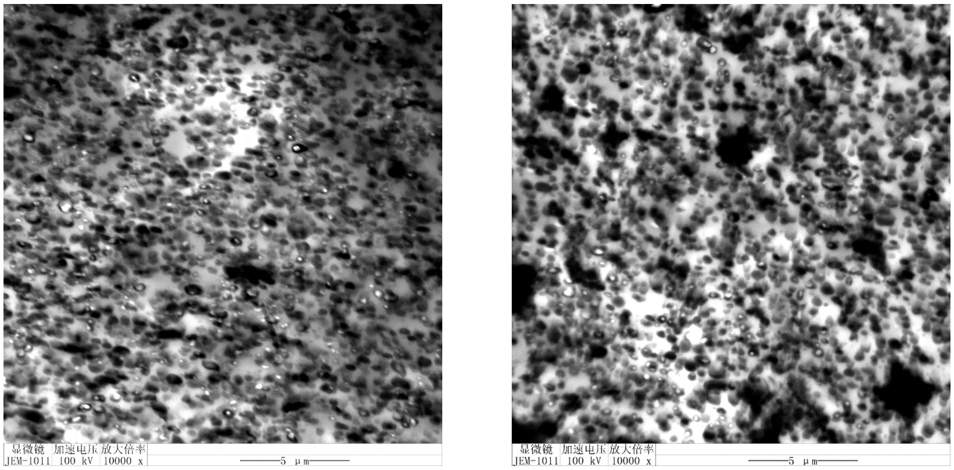
To correlate the different impact toughness of the blends with the internal deformation mechanisms, the TEM was used to observe the deformation zone under the impact fracture surface. Void formation plays a key role in rubber toughening. Until the rubber particles have cavitated, constraints on shear yielding remain very high in the plane strain region. To obtain enhanced levels of toughness, the blend must be capable of developing cavitation and producing shear yielding. Fig. 7 shows different deformation morphology of PBT/PC/RCS blends. The content of RCS particles in the samples was 20wt%. In Fig. 7a, no cavitation



(a) PBT/PC/RCS-28 (b) PBT/PC/RCS-37



(c) PBT/PC/RCS-46 (d) PBT/PC/RCS-55



(e) PBT/PC/RCS-64 (f) PBT/PC/RCS-73

Fig. 7 TEM micrographs in the deformed zone of the PBT/PC/RCS blends appears in the RCS-28 particles. The reason lies in the low core/shell ratio inducing the high grafting degree and ‘internal grafting’, which decease the elastic property and the cavitation ability of RCS-28 particles. So PBT/PC/RCS-28 blends display much higher brittle-ductile transition and lower impact toughness than the other blends. In Fig. 7b, some voids can be found which indicate that cavitation of the RCS-37 particles has taken place. However, due to the relatively low core/shell ratio, the ‘internal grafting’ also decreases the cavitation ability of RCS-37. So the number of cavitated particles is small and the impact toughness of the PBT/PC/RCS-37 is not very high. In Fig.7c~e, a lot of the RCS particles have cavitated which can promote the extensive shear yielding of the matrix and induce the superior impact toughness of the PBT/PC/RCS blends. As for the PBT/PC/RCS-73 blends cavitation also takes place, but the agglomeration of the RCS-73 particles limits the higher toughness. So the deformation mechanisms are cavitation of RCS rubber particles and shear yielding of PBT/PC matrix. The grafting degree, micro morphology and particles dispersion of the RCS can influence the cavitation and shear yielding, which lead to the different mechanical properties of the PBT/PC/RCS blends.

DMA analysis

The curves in Fig. 8 show the variation of Tanδ for PBT/PC/RCS blends as a function of temperature with different core/shell ratio for the RCS particles. The content of RCS particles in the samples was 20wt%. As can be seen, the peaks near -89°C, 57°C, 105°C and 150°C belong to the Tg of PB, PBT, MMA-co-St-co-GMA and PC respectively. DMA results also show that PBT and PC are thermodynamically immiscible due to the two separate T_g peaks. From

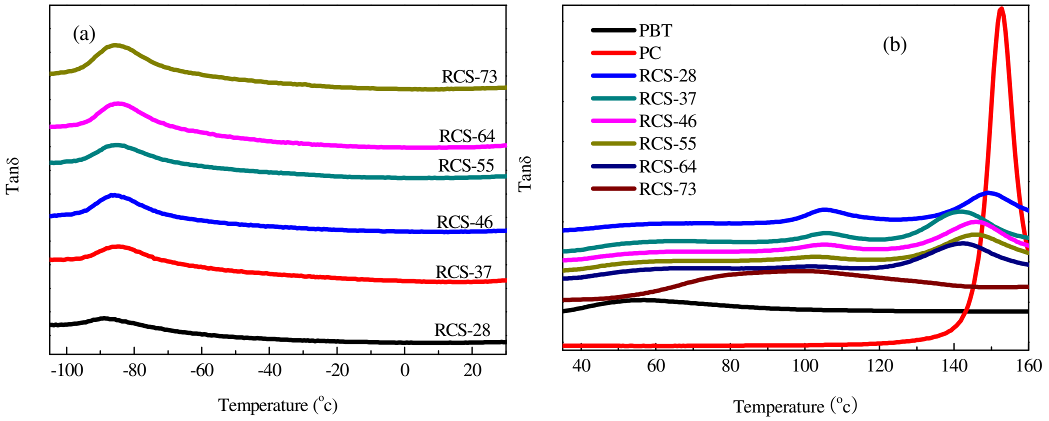


Fig. 8 The relationship between the temperature and Tanδ of PBT/PC/RCS blends

comparison it can be found the T_g of PB phase almost has no change though the variation of the core-shell ratio. However, the T_g of the PBT and PC phases close to each other and especially for the PBT/PC/RCS-73 blends, only a wide peak exists in the high temperature zone. So the change of RCS core/shell ratio not only affects the interaction between the shell phase and the matrix but also influence the interaction between the PBT and PC phases. Detailed explanation will be provided in another paper.

Fig. 9 shows the variation of storage modulus for PBT/PC/RCS blends as a function of temperature with different core/shell ratio for the RCS particles. As can be seen from Fig. 9, the lower core/shell ratio of RCS particles induces the higher storage modulus of PBT/PC/RCS blends. So DMA results also prove that low core/shell ratio of RCS is beneficial to the stiffness improvement of the PBT/PC blends.

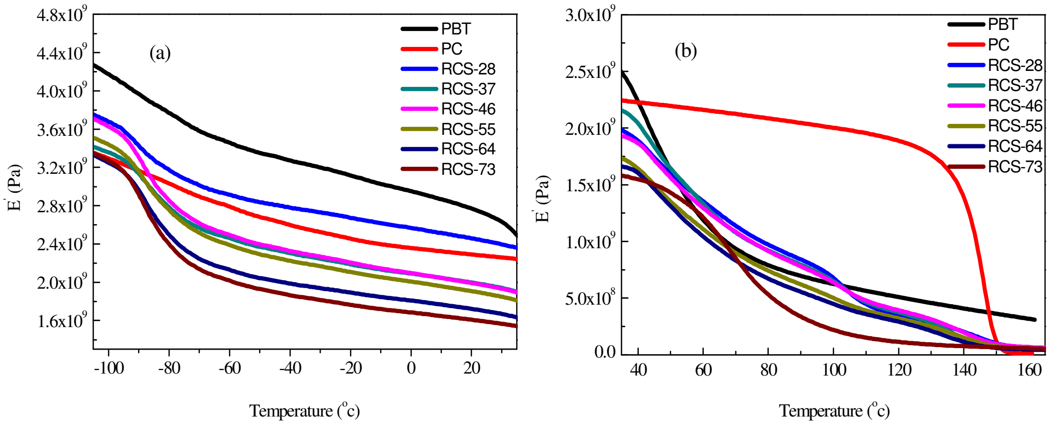


Fig. 9 The relationship between the temperature and storage modulus of PBT/PC/RCS blends

Conclusions

Modification of the core/shell ratio provides an effective way to prepare core-shell particles toughened polymer blends with superior toughness and stiffness balance. The change of core/shell ratio affected the grafting degree, micro morphology and dispersion of the RCS particles which influence the final mechanical properties of PBT/PC/RCS blends. Deformation results proved that cavitation of PB rubber particles and shear yielding of PBT/PC matrix were the major toughening mechanisms. The 'internal grafting' restrained the cavitation ability of PB and decreased the toughening efficiency of RCS which induced the higher brittle-ductile transition of the PBT/PC blends. The higher core-shell ratio induced lower grafting degree and could lead to agglomeration of RCS particles which also reduced the mechanical properties of the blends. DMA and TEM results showed PBT and PC were thermodynamically immiscible. The optimum toughness and stiffness balance for the blends was obtained by changing the core-shell ratio of RCS particles and the similar approach could be applied in other core-shell particles toughened polymer blends.

Acknowledgements

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