

Preparation of Core-Shell Structured Polyacrylic Modifiers and Effects of the Core-Shell Weight Ratio on Toughening of Poly(butylene terephthalate)*

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Abstract Core-shell structured polyacrylic (named CSSP) impact modifiers consisting of a rubbery poly(*n*-butyl acrylate) core and a rigid poly(methyl methacrylate) shell with a size of about 353 nm were prepared by seed emulsion polymerization. The CSSP modifiers with different core-shell weight ratios (90/10, 85/15, 80/20, 75/25, 70/30, 65/35 and 60/40) were used to modify the toughness of poly(butylene terephthalate) (PBT) by melt blending. It was found that the polymerization had a very high instantaneous conversion (> 95.7%) and overall conversion (99.7%). The morphology of the core-shell structure was confirmed by means of transmission electron microscopy. Scanning electron microscopy was used to observe the morphology of the fractured surfaces. Differential scanning calorimeter was used to study the crystallization behaviors of PBT/CSSP blends. The dynamic mechanical analyses of PBT/CSSP blends showed two merged transition peaks of PBT matrix, with the presence of CSSP core-shell structured modifier, that were responsible for the improvement of PBT toughness. The results indicated that the notch impact strength of PBT/CSSP blends with a core-shell weight ratio of 75/25 was almost 8.64 times greater than that of pure PBT, and the mechanical properties agreed well with the SEM observation.

Keywords: Poly(butylene terephthalate) (PBT); Core-shell structured polyacrylic (CSSP); Emulsion polymerization; Toughness; Structure-property relations.

INTRODUCTION

Poly(butylene terephthalate) (PBT) is an important engineering thermoplastic with superior properties, such as high rigidity, solvent resistance, high rates of crystallization, fine insulation and short cycle times in injection molding. It can be used in automotive interior, electronics and electrical instrumentations, household appliances and communications^[1–7]. However, the remarkable disadvantages of PBT, namely, the high notch sensitivity and low impact strength, greatly limit its wide application. Hence, PBT toughening raises great interests of researchers in recent years. In order to overcome this drawback, elastomeric particles have been utilized to toughen PBT resulting in blends with high toughness; however the domain sizes of the rubbers are hard to be controlled for their process-dependence^[5, 8, 9]. The role of the elastomeric particles in the matrix depends on the stress state in the blend. In a high triaxial stress state around the notch tips during impact, the rubbery particles are able to withstand the dynamic load together with the matrix, and the matrix stress concentration becomes low. Many reports have shown that one of the main sources of toughening in the blends under high triaxial stress

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state comes from the ability of these particles in promoting dilatational deformation by rubber cavitations and interface debonding. As the dilatational deformation takes place, the triaxial stress plane-strain condition is relieved, initiating extensive plastic deformation in the matrix and significantly promoting energy absorption mainly when the matrix yields by shear yielding like PBT^[10, 11].

Among rubbery impact modifiers, the core-shell structured polyacrylic (CSSP) fillers are commonly used for polymer toughening because of their predetermined size and high toughening effects^[12]. In order to minimize the strain, the core has to be made of a suitably elastomeric material. The role of the shell is to ensure compatibility with the matrix. Core-shell structured polyacrylics, like poly(butyl acrylate)/poly(methyl methacrylate) (PBA/PMMA) have been generally used to toughen poly(vinyl chloride) (PVC)^[13] and polycarbonate^[14]. Clearly these properties are much dependent on the relative composition of the core and shell layers as well as on the structure of the core-shell particles, such as the size of the particles, the homogeneity of the shell coverage. Therefore, it is important to prepare the structure-controlled core-shell polyacrylic modifier with suitable core-shell weight ratio and compatibility with PBT matrix^[15].

In this study, a core-shell structured poly(butyl acrylate)/poly(methyl methacrylate) (CSSP) modifier in the absence of other functional monomers was synthesized as the latex particle with a predetermined size of about 353 nm, and different core-shell weight ratios by seed emulsion polymerization. The CSSP modifiers and PBT matrix were blended with a weight ratio of 1/5. The effects of core-shell weight ratios of CSSP particles on the rheological and mechanical properties of PBT/CSSP blends were evaluated. The morphology was confirmed by means of transmission electron microscopy (TEM). Scanning electron microscope (SEM) was used to observe the fractured surfaces. Dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) were used to explore the molecular movement and crystallization of PBT/CSSP blends.

EXPERIMENTAL

Materials

The initiator potassium persulfate (KPS) and sodium hydrogensulfite (NaHSO_3) were purchased from Tianjin Chemical Agent Co., (China). The anionic surfactant used in this study was Aerosol MA Series from Cytec, (the Netherlands). Allyl methacrylate (ALMA), and 1,4-butanediol diacrylate (BDDA) was purchased from Tianjiao Chemical of China (China). All the above materials were used without further purification. *n*-Butyl acrylate (BA) and methyl methacrylate (MMA) were purchased from Beijing Dongfang Chemical Co., (China). The BA monomer was freed of inhibitor, which was washed with a 2 wt% of NaOH solution and deionized water until the filtrated water was neutral, dried with CaCl_2 overnight, and distilled under reduced pressure. The MMA monomer was purified by distillation under reduced pressure before use. Hydroquinone was used as an inhibitor of the latexes taken from the emulsion polymerization. Deionized water was used in all the experimental work in this study. PBT resin (I100-211M) was provided by Changchun Industry (China).

Seed Emulsion Polymerization Process

Core-shell structured latexes were synthesized as 50% of solid latexes *via* a two-stage semicontinuous emulsion polymerization. The surfactant (0.3 g), KPS (0.27 g) and water (140 g) were added to a 0.5 L flanged reaction flask under nitrogen, and heated at about 63 °C. After 30 min, the seed-stage BA monomer (10.0 g, 5 wt% of total monomer) was added to the surfactant solution and stirred for 10 min. Then, a solution of 0.013 g NaHSO_3 in 5 g water was added, and after 30 min the same addition was repeated. The seed stage was 60 min with an average diameter of 140 nm. The growth stage involved three layers: the first layer was preemulsified monomers of BA (150 g) and ALMA (1.35 g) with surfactant (1.89 g), with an increase of 308 nm in the particle diameter, the second layer was preemulsified monomer of MMA (10 g) with surfactant (0.125 g), and the third layer was preemulsified monomer mixture of MMA (30 g) with surfactant (0.446 g), with an increase of 353 nm in the particle diameter. Based on the weight of the monomer, preemulsified monomers of the first two layers were dropped into the flask successively at a constant rate over 1.5 h. At the same time, a solution of 0.104 g NaHSO_3 in 40.0 g distilled water was added to the reaction flask at a constant rate over 1.5 h. Then, the third layer of

preemulsified monomers and a solution of 0.026 g NaHSO_3 in 10.0 g water were added to the reaction flask at a constant rate for 15 min. After 60 min, the latex was cooled down to room temperature and filtered through a 53 μm sieve to obtain the coagulate content. The CSSP modifier sample was obtained by freeze-thaw cycling and washed with deionized water several times. Based on the above latex preparation, the weight ratios of core-shell structured particles corresponded to 90/10, 85/15, 80/20, 75/25, 70/30, 65/35, 60/40, respectively.

Blends Preparation

The PBT and the CSSP modifier were sufficiently dried in a vacuum oven at 120 °C and 40 °C, respectively. A TE-34 twin screw extruder ($L/D = 28$, Nanjing Institute of Extrusion Machinery, China) was employed to prepare PBT/CSSP blends with the weight ratio of 5/1 at a screw speed of 65 r/min and barrel temperatures of 227–235–245–240 °C. The pelletized materials were dried and injection molded into standard specimens in an injection-molding machine (JPH-30, Guangdong Hongli Machine, China) at 240 °C.

Conversion and Particle Size Measurement of the Latexes

At 30 min intervals, the samples of the latex (10 mL) were removed into preweighed vials containing 1 mL of hydroquinone solution (2 wt%) to prevent further polymerization, which were cooled down with ice to quench the polymerization and then analyzed gravimetrically to determine the instantaneous conversion (on the basis of the monomer fed until the sampling time) and overall conversion (on the basis of the monomer fed in the full emulsion polymerization process). Particle sizes were measured online with a fixed 90° scattering angle with dynamic light scattering (DLS) on a Malvern Zetasizer NANO-ZS90 (UK) and the cell temperature was kept at 25 °C. The particle diameters quoted are the mean values of z -average diameters ($d_{z,s}$) calculated by cumulate method.

Morphology of the CSSP Modifier

The CSSP latex morphology was examined by TEM (JEM-2100). The latex was dispersed in water sufficiently with ultrasonic waves before characterization and then prepared by casting one drop of diluted solution onto a carbon-coated copper grid.

Impact and Tensile Tests

The mechanical testing was performed at 23 °C and 50% of relative humidity, and the samples were climatized under this condition for 48 h before testing. The notched Charpy impact strength was measured with an impact testing machine (ZBC-4) based on National Standard Testing Methods (GB 1043-1993), China. The type of the specimen is 1 and the type of notch is C. The impact speed was 2.9 m/s and energy was 4.0 J. The tensile testing was carried out on a universal tensile tester (CMT-6104) according to ASTM D-638 and the type of the specimen is V. The tensile strength was measured at a crosshead speed of 20 mm/min. The average value of at least six tests was used.

Thermal Analysis

Differential scanning calorimetry (DSC) measurements were conducted with a differential scanning calorimeter (Perkin-Elmer, Diamond). Samples of PBT/CSSP blends were heated from room temperature to 250 °C at a rate of 50 K/min and held for 3 min to destroy any residual nuclei, followed by cooled at 10 K/min to room temperature and reheated at 10 K/min to 250 °C. All DSC measurements were performed under a nitrogen atmosphere.

Dynamic Mechanical Analysis

Dynamic mechanical analysis tests of PBT/CSSP blends were performed under nitrogen atmosphere at a frequency of 1 Hz between –80 °C and 150 °C with a heating rate of 3 K/min by using a Tritec-2000 dynamic mechanical analyzer (UK) under a dual-cantilever beam blending mode.

Rheological Measurements

Torque rheometry of PBT/CSSP blends was performed in a HAAKE PolyLab OS RheoDrive 7 equipped with a Rheomix 600 mixer with roller rotors. The measurements were performed at 30 r/min and at a set point temperature of 230 °C with 45 g of samples.

Fractured Morphology

The notched Charpy impact-fractured surfaces of PBT/CSSP blends were observed with a JSM-6490LV scanning electron microscope (SEM) operated at 10 kV. The surface was coated with gold prior to SEM observation.

RESULTS AND DISCUSSION

Latex Preparations with Different Core-Shell Weight Ratios of CSSP Latexes

Emulsion polymerizations of CSSP latexes were carried out at a temperature of 63 °C. Samples were taken at 30 min intervals during the polymerization to monitor the conversion and the particle growth. Instantaneous and overall conversions were calculated from a mass balance of the reagents in the polymerization with the percentage solid content measured at each sampling time^[16]:

$$\text{Instantaneous percentage conversion (\%)} = [\text{Mass of polymer formed} / \text{Mass of monomer added}] \times 100 \quad (1)$$

where the mass of monomer added is the sum of the monomer in the seed stage and all the monomer that has been added during the growth stage.

$$\text{Overall percentage conversion (\%)} = [\text{Mass of polymer formed} / \text{Total mass of monomer}] \times 100 \quad (2)$$

where the total mass of monomer is the sum of the monomer in the seed stage and all of the monomer in the growth stage.

Figure 1(a) plots the conversion-time data for the CSSP latex preparation with a core-shell weight ratio of 75/25. Table 1 lists the results of final percentage conversion and percentage coagulum for the latexes with different core-shell weight ratios. For each preparation listed in Fig. 1 and Table 1, all the CSSP polymerizations were observed to proceed at high instantaneous conversion (> 95.7%), *i.e.*, the reaction was carried out in a semi-continuous mode under “starved conditions” where the addition rate of the monomers was slower than the consumption rate of reaction. Under these conditions, the copolymer composition would be uniform and approximately equal to the composition of the BA/MMA comonomer feed mixture. Final conversions were found to be high (> 99.7%) for all of the polymerizations, which showed that a continuation of the polymerization for 1 h after the end of the monomer addition stage was adequate to allow complete conversion.

Table 1. Latex parameters for different core-shell weight ratios of CSSP particles

Core-shell weight ratio	Final conversion (wt%)	Coagulum content (wt%)	Final latex particle size (nm)	Polydispersity index (PDI)
90/10	99.08	2.62	345	0.021
85/15	99.50	2.71	346	0.004
80/20	99.33	0.93	344	0.056
75/25	99.75	1.80	353	0.024
70/30	99.89	1.31	349	0.065
65/35	99.54	1.13	349	0.025
60/40	99.53	2.15	344	0.075

The DLS technique was used to obtain quantitative information about the particle sizes of colloidal systems. In this study, DLS provided a rapid means of monitoring the particle size of the latex particles during both the seed stage and the growth stage of polymerization. With this information, it is possible not only to establish a latex system of the known particle diameter but also to determine whether, during the growth stage of polymerizations, the latex particles grew sequentially or the secondary nucleation occurred.

Latex particle diameters were determined by DLS and then were compared with those theoretically calculated from the following equation^[16]:

$$d_t = (M_t I_t / M_s)^{1/3} \times d_s \quad (3)$$

where d_t is the diameter of the particle at time t , M_t is the total mass of the monomer added at time t , I_t is the

instantaneous conversion at time t , M_s is mass of monomer added in the seed stage, and d_s is the seed particle diameter as measured by DLS.

Figure 1(b) shows the variation of particle size versus the reaction time. The CSSP particle diameter was consistent with the theoretical size. Moreover, the final CSSP particles are of 353 nm in diameter and the polydispersity index (PDI), referred as a Malvern polydispersity index (M-PI), has a very low value, shown in Table 1. Figure 1(c) exhibits the distribution of its final particle size PDI with a core-shell weight ratio of 75/25. The PDI of the latex was 0.024. These results showed that the final particle sizes of the latex presented narrow distribution. The good agreement shown between the measured and theoretical particle diameters throughout the polymerization for all the latexes provided strong evidence that the observed particles grew without significant secondary nucleation. This showed that the appropriate conditions were used in the growth stage of the CSSP polymerization. In conclusion, the instantaneous composition of polymer particles was close to that of the feed at every moment, and the polymerization process could control the composition and the structure of polymer particles with different weight ratios of core and shell layers. In next section, we just considered the effects of the core-shell weight ratios on the thermal and mechanical properties of PBT/CSSP blends.

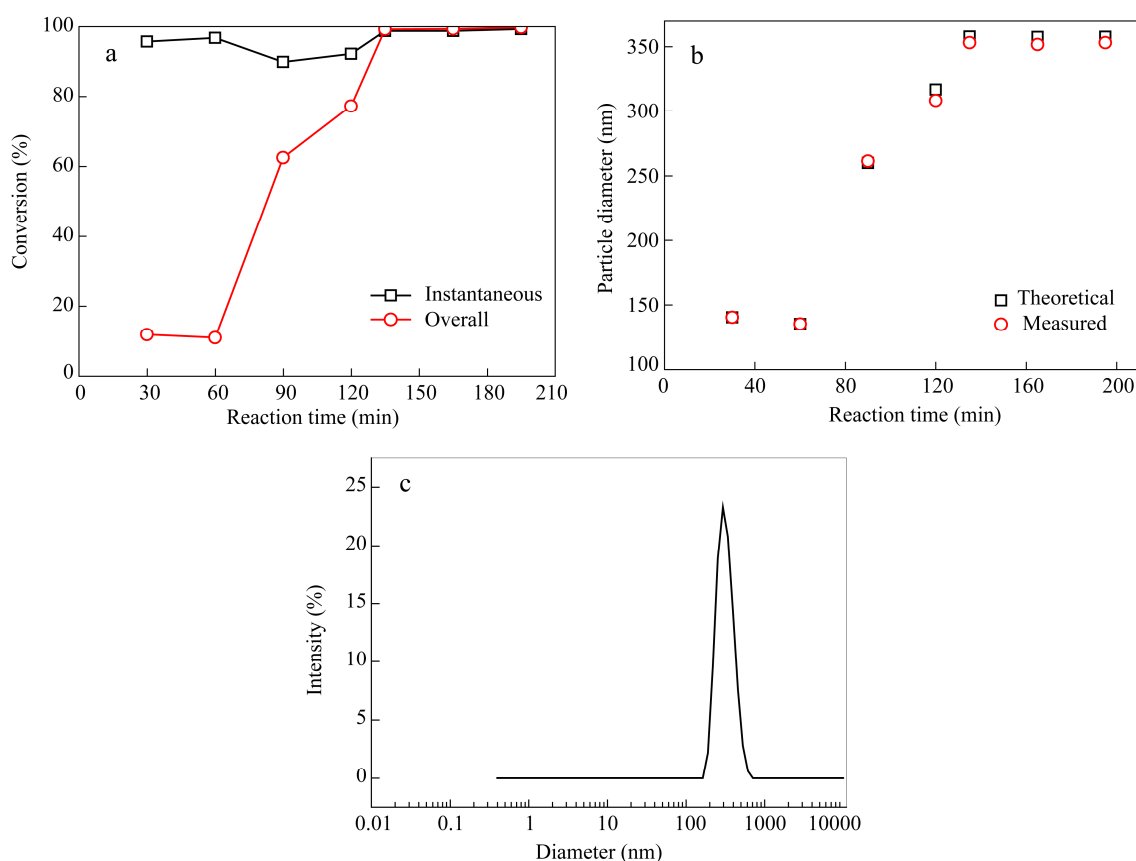


Fig. 1 Variation with reaction time of (a) overall and instantaneous conversion, (b) measured and theoretical particle diameter and (c) the distribution of CSSP final latex particle size with core-shell weight ratio of 75/25

The morphology of CSSP latex with the core-shell weight ratio of 75/25 was observed by TEM, as shown in Fig. 2. It could be seen that the particles consisted of a dark core of poly(BA) and a brighter shell of poly(MMA), indicating the obvious core-shell structure of CSSP latexes. Based on the TEM and DLS results, it could be proved that the final CSSP latex was spherical particles with narrow distribution.

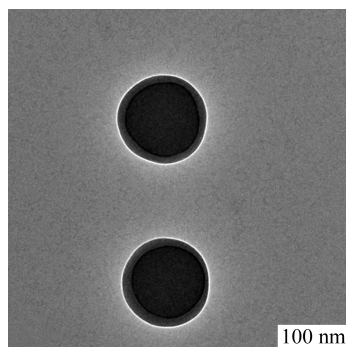


Fig. 2 TEM image of the CSSP particles with core-shell weight ratio of 75/25

Molecular Movement

The melting and crystallization behaviors of PBT/CSSP blends were studied by DSC, and the corresponding results of the second heating scan is shown in Fig. 3 for the CSSP modifiers with different core-shell weight ratios. It can be observed that the second heating showed a minor melting peak, which was a well-known feature of thermoplastic polyesters crystallized in DSC. It might be ascribed to the occurrences of initial melting, recrystallization, and remelting processes in the melting region^[17]. It has been reported that PBT could have two kinds of spherulites depending on the cooling and processing conditions^[18]. As shown, no crystallization exotherm was observed despite of the rapid cooling in the injection mold. As also shown in Fig. 3, the T_m of PBT remained constant and did not change obviously with the addition of CSSP particles. This indicated that the modifier phase did not disturb the crystallization process of PBT. The result agreed with the melting behavior observed in PBT/PEO-*g*-MA^[19] and (PBT-Ph)/PEO-*g*-MA^[20] blends and with reported results in other semi-crystalline matrix/elastomer blends^[21, 22].

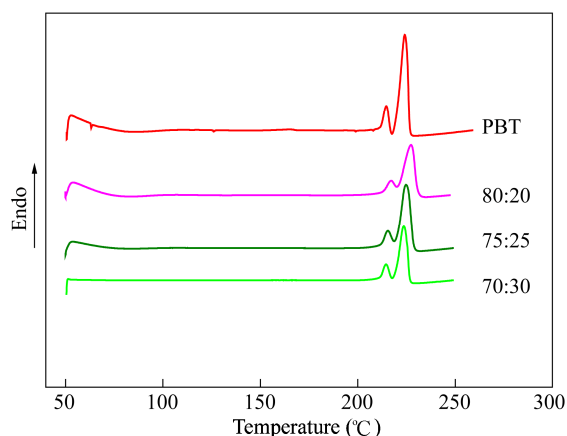


Fig. 3 DSC heating scans of the pure PBT and PBT/CSSP blends with different core shell weight ratios

The DMA results are shown in Fig. 4, illustrating the temperature dependence of the loss tangent ($\tan\delta$) and storage modulus of the PBT/CSSP blends with different core-shell weight ratios of CSSP and that of pure PBT. The values of the relaxation peaks observed in the blends with different core-shell weight ratios are listed in Table 2. DMA spectra showed that the internal friction peak of the rubber phase moved to higher temperatures and the internal friction peak of PBT moved to lower temperature. The lower glass-transition temperature (T_{g1}) corresponds with the T_g of the poly(BA) rubbery core polymer, and the higher temperature (T_{g2}) belongs to the CSSR shell polymer and the matrix. The difference between T_{g1} and T_{g2} glass transition temperatures was also

shown in Table 2. It is well-known that it is immiscible if the blend displayed two glass transitions^[16]. On the other hand, if it showed a single transition or two transitions between those of the pure components, the blend could be regarded as miscible or partially miscible. This was consistent with the case of PS modified by Poly(BA)/Poly(MMA)^[23]. The difference between the glass transition temperatures of PBT and PMMA was the least when the core-shell weight ratio was 75/25. So Fig. 4 and Table 2 indicate good compatibility between the PBT and the CSSP particles, which is the necessary qualification for an effective toughening modifier.

Table 2. Some glass transition temperature parameters for the PBT/CSSP blends with different core-shell weight ratios of CSSP particles

Core-shell weight ratio	T_{g1} (°C)	T_{g2} (°C)	$T_{g2}-T_{g1}$ (°C)
80/20	-55.4	67.5	122.9
75/25	-54.7	64.0	118.7
60/40	-54.2	66.5	120.7

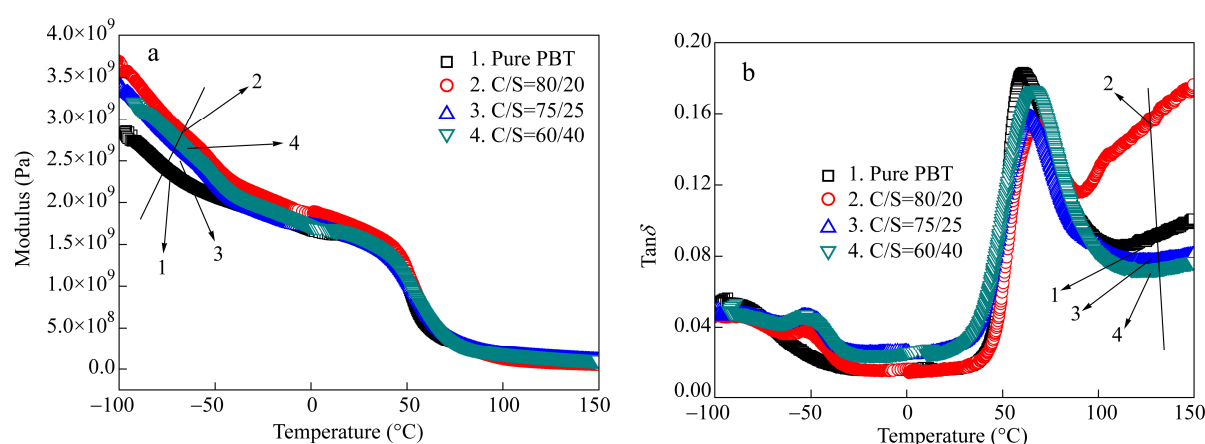


Fig. 4 DMA spectra of the PBT/CSSP blends with different core-shell weight ratios in CSSP: (a) storage modulus and (b) $\tan\delta$

Rheological Measurements

In polymer systems it was possible to form grafts, branches, or crosslinking during melt mixing. Effects such as an increase in the overall molecular weight of the materials, which could lead to an increase in the melt viscosity, were also likely to be observed. Therefore, the analysis of the viscosity allowed one to indirectly follow the progress of the reactions^[24–26]. Figure 5 shows the torque responses versus the time for the neat PBT and PBT/CSSP blends. We could observe that for PBT/CSSP blends with the different core-shell weight ratios of CSSP modifiers, the torque is similar to that for the neat PBT matrix. This is a clear evidence that no interfacial reactions between PBT and the CSSP modifier molecules had occurred.

Mechanical Properties

The tensile and impact strengths of the PBT/CSSP blends as a function of the core-shell weight ratio of CSSP modifiers are shown in Fig. 6(a). The tensile strength is an important characteristic of PBT materials, because it indicates the limit of stress in applications. The small decrease represents the existence of an interface region by which two phases are bonded strongly because the tensile strength is highly dependent on the interface structure of the blends. The stress has to transfer across the interface to avoid the fracture. The impact strength of the blends changes noticeably with the addition of CSSP with different core-shell weight ratios. The notched impact strength rapidly increases to 55.26 kJ/m² for the blend with the core/shell weight ratio of 80/20. Meanwhile, as the weight ratio of core to shell of the CSSP approached 75/25, the notch impact strength increases up to the maximum value of 75.20 kJ/m², which is roughly 8.64 times as high as that of pure PBT (8.71 kJ/m²). Meanwhile, the elongations at break of the PBT/CSSP blends significantly increase with different core-shell

weight ratios, as exhibited in Fig. 6(b). The improved toughness clearly indicates that CSSP acts as an effective modifier for PBT.

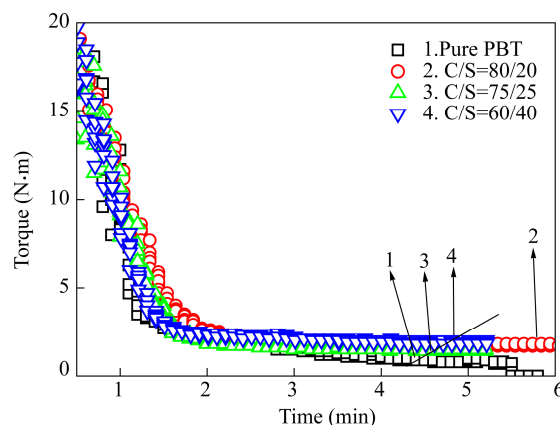


Fig. 5 Torque-time curves of PBT/CSSP blends as a function of core-shell weight ratios of CSSP modifiers

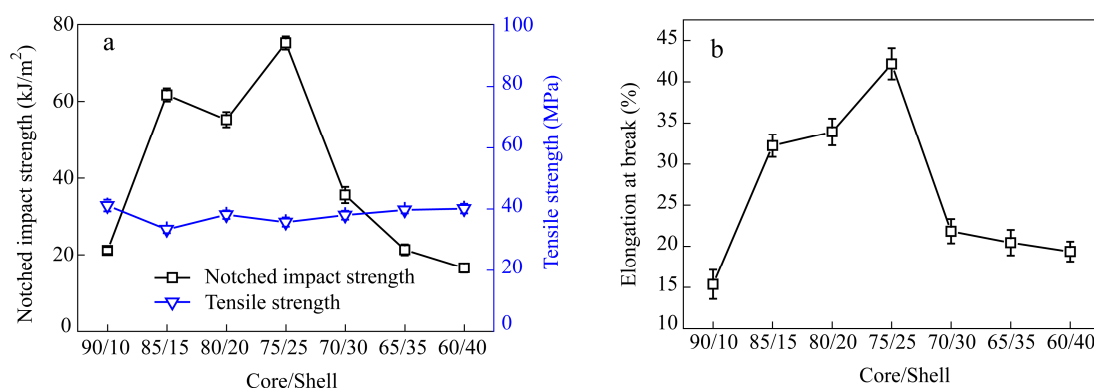


Fig. 6 Mechanical properties versus the core shell weight ratios of CSSP for PBT/CSSP blends: (a) tensile and notched impact strength, and (b) elongation at break

The impact property of PBT blends is very important for the end use. An important factor which influenced the impact strength in rubber toughened plastic blends is the core-shell weight ratio of the modifier. Because the rubber core, rather than the shell, plays an important role in toughening PBT, the toughness of PBT/CSSP blends depends on the rubber content. If the rubbery phase (BA) in the modifier is too low to absorb energy effectively in the failure process, the toughening effect will be not enough. Nevertheless, the PMMA which is a hard shell plays two important roles: the first is to act as compatibility agent in PBA and PBT system, as thickening PMMA shell could increase interfacial adhesion; while the second is to provide a means of stress transfer from the matrix to the particles in the modified PBT. For these reasons, just when the shell is thick enough, poly(BA) could disperse well in the matrix and the brittle-ductile transition point could emerge^[27]. Considering the above factors, a brittle-ductile transition occurred around the core-shell weight ratio 75/25, which has an optimum value, as shown in Fig. 6(a).

Fractured Morphology

The fractured morphologies of pure PBT and PBT/CSSP blends are shown in Fig. 7. As expected, only a few smooth lines could be seen, and a large area of the fracture surface is smooth while almost no stress whitening could be found on the fractured surface, as shown in Fig. 7(a) for pure PBT. It indicates the absence of a significant energy absorption-related deformation mechanism. Fractured morphologies of PBT/CSSP blends are

shown in Figs. 7(b–d). Compared with that of the pure PBT, as the core-shell weight ratios decreased, the fractured surface presents different morphologies. When the core-shell weight ratio changes from 90/10 to 75/25, the fractured surface becomes rougher. Specially, Fig. 7(c) displays the fractured morphology of PBT/CSSP-5:1 blend. The fractured surface shows the characteristics of ductile fracture, and extensive plastic deformation occurs, which indicates that the shear yielding of the PBT matrix has taken place. The notched impact surface morphology is consistent with the mechanical testing results. When the core-shell weight ratio of the CSSP particles further decreases to 60/40, the fractured surfaces of the blends become smooth again. All these evidences prove that the core-shell weight ratio of 75/25 for CSSP modifier is more suitable for the toughening PBT. On the basis of the above results, it could be concluded that the interfacial adhesion and morphological features are important for toughening PBT and this material shows wide prospects of use in industry.

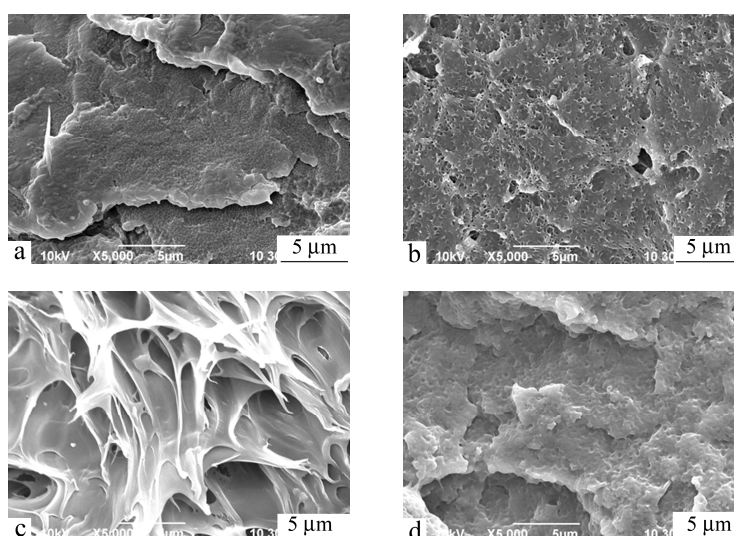


Fig. 7 SEM micrographs of the fracture surface of notched impact samples of PBT and its blends: (a) PBT, (b) PBT/CSSP-80/20, (c) PBT/CSSP-75/25 and (d) PBT/CSSP-60/40

CONCLUSIONS

CSSP modifiers were synthesized by seed emulsion polymerization and PBT/CSSP blends were prepared by melt blending. The morphology, mechanical and rheological properties and crystallization behavior were investigated. The CSSP latex particles had an obvious core-shell structure, and the mechanical properties showed that the notched impact strength of the PBT/CSSP blends was greatly improved. When the core-shell weight ratio was 75/25, it showed the highest notched impact strength (75.20 kJ/m^2), which was almost 8.64 times as high as that of pure PBT (8.71 kJ/m^2) which was corresponded to the SEM morphology for fracture surfaces. The torque of blends was almost coincident with that of the pure PBT which was an obvious evidence that no reactions between PBT and the CSSP modifiers occurred. DMA results indicated good compatibility between PBT and the CSSP particles, which was the necessary qualification for an effective toughening modifier. SEM observation showed that the PBT matrix had yielded, which was initiated by the stress concentrations associated with rubber particles. This method of employing core-shell particles is a very promising approach to achieving well-compatible PBT with high toughness.

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