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RESEARCH ARTICLE

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Preparation and application of cross-linked core-shell PBA/PS and PBA/PMMA nanoparticles

Abstract This paper reports the preparation of cross-linked core-shell poly(butyl acrylate)/polystyrene (PBA/PS) and poly(butyl acrylate)/poly(methyl methacrylate) (PBA/PMMA) nanoparticles via seeded emulsion polymerization and their application in nylon-based composites. A highly cross-linked structure was formed in both the cores and the shells by using a cross-linking agent, which could prevent the migration of hydrophobic PS shells to the inside of particles. There were covalent bonds on the interfaces between the cores and the shells of both particles. The average particle sizes were 40–50 nm, and the size distributions were narrow. The kinetics of polymerization was investigated. Well-defined core-shell structure and narrow particle size distribution could be achieved under starved conditions of monomer feeding. Furthermore, PBA/PMMA particles were used to fill nylon 6, good dispersion was obtained because of the strong interfacial interaction between the nanoparticles and the nylon 6 matrix and the good deformation ability of nanoparticles, and the toughness and rigidity of the composites were improved evidently.

Keywords seeded emulsion polymerization, crosslink, core-shell, starved conditions of feeding

Core-shell polymer nanoparticles are structured composite particles consisting of at least two polymers: one in principle forms the core and the other the shell. Because of their special double-layered or multi-layered structure, core-shell composite particles have drawn more and more attention from researchers during the past few years. Between the polymer core and the polymer shell there may be grafting, IPN or ionic bondings. For this reason, the core-shell nanoparticles have come to be used in a wide variety of polymer enforcement: they can evidently increase the polymer's wearability, abrasion resistance, anti-water property, weather fastness, UV-resistance, tensile strength, impact strength and interfacial interaction, improve the transparency, decrease the minimum film-forming temperatures (MFTs) and improve the processability [1–5].

An enormous amount of work has been done in the preparation of core-shell nanoparticles, involving the methods of embedment and seeded emulsion polymerization. In the former case, a kind of polymer particles with higher phase transition temperature is used as the cores, and another kind of polymer with lower phase transition temperature is used in its soft or melt states to wrap up the cores and form the shell [6–8]. In this way, the interfacial interaction between the polymer core and the polymer shell is weak, since only van der Waals force is involved. Under certain conditions, the core and the shell may separate from each other; besides this, it is difficult to control the composition and structure. The seeded emulsion polymerization gradually becomes the most widely-used way to prepare core-shell polymer nanoparticles, because through it we can obtain composite particles with different morphologies and properties [9, 10]. In most cases, we need to choose a monomer with lower hydrophilicity as the core monomer and a monomer with higher hydrophilicity as the shell monomer, so that well-defined core-shell structure particles will form. In the opposite case the core monomer or polymer with higher hydrophilicity will migrate to the water phase and form abnormal structure particles, for example, the strawberry-like, layer-like, snowman-like and inverted core-shell particles, etc. Min and his co-workers [11] reported that, if we choose butyl acrylate as the core monomer and styrene as the shell monomer, as the hydrophilicity of the former is obviously higher than that of the latter, the composition structure of core-shell particles prepared will be inverted after a year's storage, poly(butyl acrylate) (PBA) will gradually migrate to the outer part, while PS will migrate to the core part. Besides this, in previous research, the

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interfacial interaction between the polymer core and the polymer shell is weak, because no chemical bonding is involved, only physical encapsulation exist; the core-shell particles are in micro or sub-micro scale and do not possess the special properties of nanoparticles that we expected, since the diameter of the particles is big.

Based on the above discussion, this article focuses on the preparation of cross-linked core-shell nanoparticles via seeded emulsion polymerization. If both the core and shell parts form a cross-linked structure by using a cross-linking agent, the migration of the hydrophobic shell to the inside of particles will be prevented, so that a well-defined core-shell structure could be achieved. Meanwhile, the chemical bonding between the core and the shell is introduced through grafting for enhancing the interfacial interaction. The polymerization kinetics and the ways of monomer 2 addition are examined, and the influence of the amount of surfactant on the morphology and structure of the particle is investigated. The dispersion of these core-shell particles in the matrix and its effect on the mechanical properties of the composites are also discussed.

1 Experamental

1.1 Materials

The butyl acrylate (BA), methyl methacrylate (MMA) and styrene monomers were purified by distillation under vacuum before use. Ammonium persulfate (APS) was recrystallized from water before use. Cross-linking agent trimethylol propane trimethacrylate (TMPTMA), sodium dodecyl sulfonate (SDS), poly(ethylene glycol) mono-*p*-nonyl phenyl ether(OP-10), $AlCl_3$, $CHCl_3$, montmorillonite (MMT) and nylon-6 (PA6) were used as received.

1.2 Preparation of cross-linking core-shell particles

In a typical experiment a 250 mL four-necked flask with a mechanical stirrer, thermometer and condenser was used as a reactor. The reaction was carried out under nitrogen atmosphere and in a water bath. In the whole process, the stirring rate was fixed at 150 r/min.

SDS and OP-10 were charged into the reaction flask containing distilled water, and then a mixture of BA and TMPTMA was added at 50°C. A solution of APS in water was introduced to initiate the polymerization. The temperature was then raised to and held at 80°C for 2 h. After that, an additional portion of APS solution was added, and the mixture of monomer 2 (St or MMA) and TMPTMA was added drop-wise at a rate of 5 mL/h. After completion of addition of the mixture of monomer 2 (St or MMA) and TMPTMA, the reaction system was stirred at 80°C for 1.5 h. After demulsification with 20 mL of 20 wt% $AlCl_3$ solutions, the product was collected by suction filtration and was washed thoroughly with hot water and then dried.

1.3 Equipment and characterization

The conversion of the monomer was determined by a gravimetric method. To evaluate the polymer binding efficiency, the product was extracted with xylene for 12 h with a Soxhlet apparatus. According to the weight of unextracted and extracted product, the yield and gel efficiency were calculated.

$$\text{yield}(\%) = \frac{\text{polymer formed (g)}}{\text{monomer and crosslinking agent used (g)}} \times 100$$

$$\text{gel efficiency}\,(\%) = \frac{\text{product after extraction}}{\text{product before extraction (g)}} \times 100$$

The average particle size and size distribution (PDI) were measured by a ZETAPARTICLE HS3000 laser scattering particle size and zeta potential analyzer (LS). The latex sample was stained by RuO_4, and then used for the morphology observation by using a JEOL 200CX transmission electron microscope.

1.4 Measurements of mechanical properties

The nanoparticles obtained were blended with PA6, after extrusion and injection standard samples for measurements were obtained. For the sake of comparison, some samples were the blends of nanoparticles, PA6 and MMT. The samples were dried at 90°C in vacuo for 72 h before measurements. Then, tensile, flexural and Izod impact tests were carried out at 21°C, the final results were the average of five samples. The tensile testing was carried out using an Instron tensile strength tester TS-2000 at a cross-head speed of 50 mm/min. The flexural testing was carried out at a speed of 20 mm/min. Izod impact tests were carried out using a UJ-40 pendulum.

2 Results and discussion

2.1 Stable PBA/PS core-shell polymer nanoparticles

In most cases, in order to obtain well-defined core-shell structure particles, we need to choose a monomer with lower hydrophilicity as the core monomer and a monomer with higher hydrophilicity as the shell monomer. In this experiment, higher hydrophilic monomer BA performed as the core monomer while lower hydrophilic monomer St was chosen as the shell monomer, and cross-linking agent TMPTMA was added in both parts. The yield, gel efficiency, average particle size and size distribution were 91.2%, 94.4%, 45.1 nm and 0.0032, respectively. The latex sample was stained by RuO_4 and then used for the morphology observation by TEM. It can be observed that the composite nanoparticles have a core–shell structure, with PBA as the core and PS as the shell (Fig. 1a). After being kept for about 18 months in latex form without demulsification, the latex particles were also stained with RuO_4 for morphological

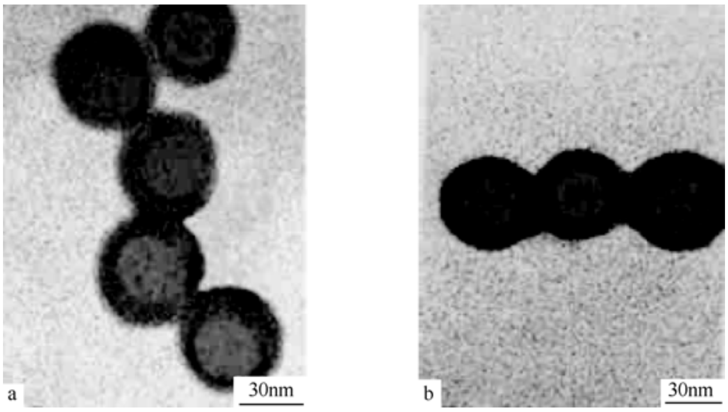


Fig. 1 TEM pbotographs of PBA/PS core-shell particles as-prepared (a) and after 18 months (b)

observations. It was found that the particles can keep their original well-defined core-shell structure; the lower hydrophilic PS didn't migrate to the core part (Fig. 1b). This evidence proved that a highly cross-linked structure formed in both the core and the shell prevented the migration of hydrophobic PS shell to the inside of particles.

2.2 Kinetics of emulsion polymerization

Taking the BA/St system as an example, Fig. 2 shows the time-conversion curve of the monomers in the BA/St system, the three periods of the reaction are marked with broken lines. During the preparation of the core, the conversion of the monomer 1 reaches its maximum at the end of the period I. In the period II, monomer 2 (shell monomer) is added drop wise. The conversion remains unchanged all along the course of shell monomer addition, implying that the shell monomer is in a state of starvation, as expected. During the period III the conversion is almost unchanged. The kinetic curve of the BA/MMA system is almost the same as that of the BA/St system.

2.3 The ways of monomer 2 feeding

To obtain the expected core-shell structure by seeded emulsion polymerization, two ways of monomer 2 addition (here taking MMA as monomer 2 as an example) were studied and compared. One involved a semi-continuous process, just as described in the experiment part, monomer 2 was added drop-wise to the reaction system to keep it in a starved condition, that is, the addition speed of monomer 2 should be slower than its polymerization rate. Another way of addition was a non-starved process, in which monomer 2 was added in one portion at the end of period I. The results are listed in Table 1.

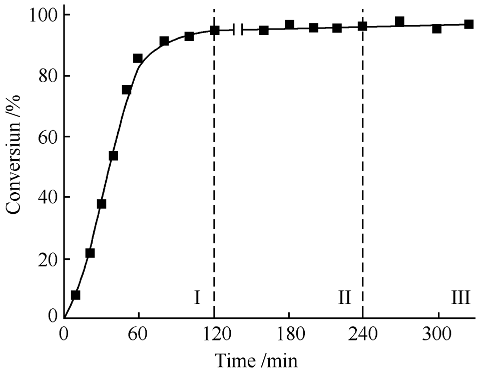


Fig. 2 Time-conversion curve of monomers in BA/St system

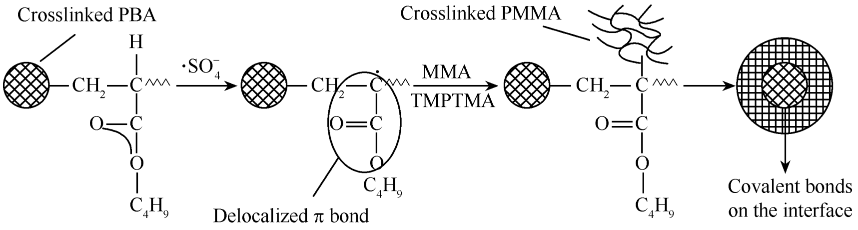
A starved process (sample A) gives high gel efficiency, which can be attributed to the following: (1) after the addition of monomer 2, the shell part also formed a cross-linked structure due to the addition of a cross-linking agent, which

Table 1 Influences of the way of mononer II[a] feeding

Sample	The condition of monomer II	TMPIMA in Monomer II (g)	Yield (%)	Cel efficiency (%)	Average patticle size (mm)	PDI
A	Starved	0.92	93.4	97.5	43.2	0.0019
B	Non-starved	0.92	91.7	93.8	39.8	0.078
C	Non-starved	0	92.0	62.8	40.7	0.094
D[b]	Starved	0.92	94.8	92.8	40.1	0.074
E[c]	Starved	0.92	94.1	95.2	37.6	0.112

[a] MMA was taken as nomomer II;

[b,c] The amounts of SDS (wt % to whole nomomers) in sample D and E are 4.6% and 5.5%, respectively



Scheme 1 Reaction mechanism of monomer II

led to higher gel efficiency; (2) monomer II was added in a starved process, and some new initiator was added at the same time. With the existence of the new initiator, the tertiary carbon of the PBA chain will be initiated to produce terminal free radicals, which is stabilized by the conjugated structure of the side group [12], as shown in scheme 1. In this way, grafting at the surface of the seed particles occurred at the same time of cross-linking, which also leads to higher gel efficiency.

Besides, the polydispersity index (PDI) of sample A was small, its low PDI value showed a narrow distribution of the size of the obtained particles, and the particle size of these composite particles obtained was about 40–50 nm. When monomer 2 was added in a non-starved process (sample B), though the gel efficiency was high, the particle size obtained was almost the same (slightly smaller); the size distribution obviously broadened. Figure 3 shows the TEM photographs of PBA/PMMA particles obtained under different ways of monomer 2 addition. Under starved condition, the product obtained showed a narrow size distribution, and a well-defined core–shell structure was observed after staining (Fig. 3a). Under the non-starved condition, a broader sized distribution was observed, and the border between the core and the shell was not very obvious (Fig. 3b). Rois and his co-worker claimed that the seed latex particle had a certain ability of absorbing and capturing monomer 2. We can speculate that the seed latex particles will have enough time to capture monomer 2 only when the addition speed of monomer 2 is slow enough so that monomer 2 would enter the seed particle to form well-defined core–shell particles. If monomer 2 is added in a non-starved state, some monomer 2 would still enter the seed particles and polymerize at the surface of seed particles, while the others would absorb surfactant to form micelles, and finally polymerize to form homo-polymer, which leads to a broader sized distribution and the abnormal core–shell structure. Because monomer 2 was added together with the cross-linking agent (TMPTMA), the homo-polymer obtained was also cross-linked, so the gel efficiency remained almost unchanged.

Even if we do not use any cross-linking agent, monomer 2 will enter the seed particles and graft onto the surface of the seed particles if it is added at proper speeds, so the gel efficiency will not decrease either. In order to prove whether monomer 2 in sample B mainly entered the seed particles, in sample C we did not add any cross-linking agent, while monomer 2 was added in a non-starved state. The TEM photograph (Fig. 3c) of the final product was almost the same as that of sample B, but the gel efficiency decreased obviously, implying that most monomer 2, in sample B, did not graft at the surface of the seed particles, but formed new micelles and produced a homo-polymer. The homo-polymer would be extracted in the absence of TMPTMA, so that its gel efficiency decreased evidently.

It made no difference in yield and gel efficiency to increase the amount of the surfactant, but the size distribution broadened obviously. Comparing samples D, E with sample A, we could find that the amount of SDS in samples D and E were very large at the end of period I, there were 31% and 40% surfactant forming empty micelles, respectively besides the seed particles (PBA core), while there were only 5% surfactant forming empty micelles in sample A. Because of this reason, the large amount of empty micelles increased

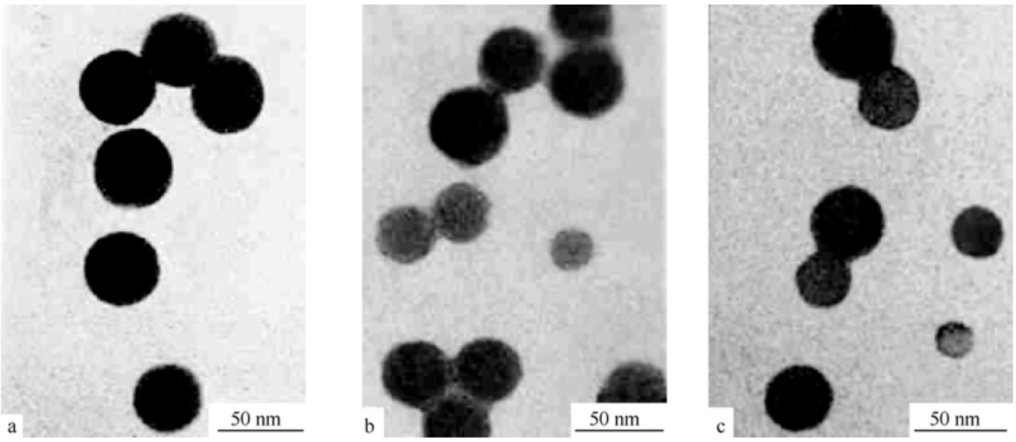


Fig. 3 TEM photographs of PBA/PMMA particles obcained under starved condition (a) noer starved condition in the preseace of TMPIMA (b) and nore starved condition in the abseace of TMPIMA (c) respectively

the opportunity of monomer 2 to enter the micelles, which led to the formation of homo-polymer particles with different size, so that the size distribution broadened obviously. Because monomer 2 was added together with the cross-linking agent (TMPTMA), the homo-polymer obtained was also cross-linked, so the gel efficiency remained almost unchanged.

2.4 Modification of PA6 matrix

In previous studies, inorganic rigid particles or rubber elastic particles were usually used to reinforce the polymer matrix. However, the addition of inorganic rigid particles would lead to a decrease in the toughness when the rigidity of the matrix was increased, while in the latter case, the improvement in toughness was usually at the cost of its rigidity. In this work the cross-linked core-shell PBA/PMMA nanoparticles were blended with PA6, and the results are listed in Table 2.

Table 2 The mechanical properties of PA6 filled with various inorganic particles

Sample	Tenisile strength (MPa)	Tensile modulus ($\times 10^3$) MPa	Flexural modulus ($\times 10^3$) (MPa)	Inpact strength (J/m)
A	83.9	3.08	2.62	26.0
B	80.9	4.26	2.73	34.1
C	81.9	4.84	2.86	34.5

A: PA6; B: PA6 with 5 wt%PBA/PMMA; C: PA6 with 5 wt% PBA/PMMA and 2 wt% montmorillonite

When the PA6 matrix was filled with the core–shell nanoparticles, the tensile strength and flexural modulus were almost unchanged, while the tensile modulus and impact strength increased by 38% and 31%, respectively. These results were obviously better than those in cases when inorganic rigid particles or rubber elastic particle were used. We also found that when MMT and PBA/PMMT nanoparticles were used together to reinforce the PA6 matrix, the properties of the composite could increase more evidently, a tensile modulus increase of 57% was obtained.

Figure 4 shows the TEM photograph of PA6 filled with PBA/PMMA nanoparticles. Most nanoparticles were dispersed individually in the PA matrix. In comparison with Figures 1 and 3, we can observe that the PBA/PMMA nanoparticles in the matrix take a deformed, elongated shape. It is believed that this kind of deformation is caused by the shear effect during processing, and it also implies a strong interfacial interaction between the PBA/PMMA nanoparticles and PA6 matrix. The strong hydrogen bonding between the ester-groups of PMMA chains and the PA6 matrix and the highly cross-linked core-shell structure of the PBA/PMMA nanoparticles not only made the nanoparticles disperse well in the PA6 matrix, but also greatly increased toughness of the composites.

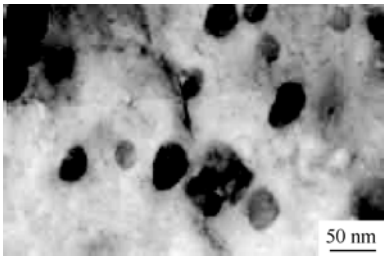


Fig. 4 FBA/PMMA particles dispersed in PA6 matrix

3 Conclusions

Cross-linked core-shell poly(butyl acrylate)/polystyrene (PBA/PS) and poly(butyl acrylate)/poly-(methyl methacrylate) (PBA/PMMA) nanoparticles can be prepared via seeded emulsion polymerization with chemical bonding between the core and the shell of the nanoparticles. The particle size of composite particles obtained was about 40–50 nm and had a narrow size distribution. Highly cross-linked structures were formed in both the core and the shell by using a cross-linking agent, which prevented the migration of hydrophobic PS shell to the inside of particles. The kinetics of the emulsion polymerization implied that the shell monomer was in a state of starvation, and nanoparticles with better core-shell structure and narrow size distribution could be obtained when monomer 2 was added in a starved process. Furthermore, PBA/PMMA particles can be well dispersed in nylon 6 matrix and result in increases of the tensile modulus and impact strength of the composites by 38% and 31%, respectively.

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