

STUDY ON NYLON 6/SUPERFINE RUBBER PARTICLES COMPOSITES VIA IN SITU POLYMERIZATION

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Abstract Two highly cross-linked superfine styrene-butadiene rubber particles, one with 1 wt% of carboxyl groups and the other without such groups having particle sizes of 130–150 nm and 80–100 nm respectively, were used to prepare nylon 6/rubber composites via *in situ* polymerization. It was found that carboxylic styrene-butadiene dispersed uniformly in nylon matrix and there was strong interfacial interaction because of the graft polymer formed by the reaction of nylon with carboxyl group of the rubber, resulting in considerably improved impact strength with almost unchanged tensile strength. However, the addition of styrene-butadiene without carboxyl groups showed intensive agglomeration of the rubber particles and weak interfacial interactions, and the toughness of the materials was improved slightly. The crystallization and rheological behavior of the composites were also discussed.

Keywords Nylon 6, Superfine rubber particles, *In situ* polymerization

INTRODUCTION

As a main class of engineering plastics, nylon 6 exhibits excellent tensile properties, wearability, chemical resistance, thermostability and good processability. However, it also has disadvantages such as low moisture resistance, low dimensional stability, and low impact strength in dry state or at low temperature, limiting its application in some fields^[1]. For the composite materials based on nylon 6, the filling of rigid particulates usually results in improved strength and decreased toughness; whereas toughening with rubber or elastomer usually results in the loss of strength and modulus^[2–4].

In recent years, the preparation of nanocomposites has received wide interest in material science. Owing to the nanometer dimension effect, large specific surface area and highly activated surface atoms of nanometer materials, they can strongly interact with a polymer matrix. At present, the methods used for the preparation of polymer based nanocomposites include the sol-gel process, intercalation, blending and *in situ* polymerization^[5–8]. As to *in situ* polymerization, it is a good means to prepare polymer based nanocomposites, in which the fillers are dispersed in the monomer first, and the process is carried out similarly to bulk polymerization. By this method, the nanometer or quasi-nanometer particles could be better dispersed in the polymer matrix, and the characteristics of the particles retained, yielding nanocomposites with good processability^[9, 10]. In the previous reports, *in situ* polymerization has been applied to the preparation of nylon 6 based nanocomposites, such as nylon 6/clay^[11–14] or nylon 6/silica nanocomposites^[15–17], and so on. As to nylon 6/clay nanocomposites, the strength and modulus of nylon matrix could be improved significantly, whereas its toughness could only be maintained or even slightly decreased. The use of modified nanometer silica could improve the strength and toughness of the composites simultaneously, but perfect dispersion was hard to achieve due to the strong self-assembly tendency of nanoparticles, especially when the particle size was much smaller^[16].

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Owing to the dimension effect of nanoparticles, large specific surface area and the particular structure, highly cross-linked superfine rubber particles (nanometer or quasi-nanometer) are expected to be different from the ordinary rubber in plastic toughening. Liu *et al.*^[18] reported the special effect of superfine rubber particles on the toughening of polypropylene and epoxy resin. As to nylon based composites prepared by *in situ* polymerization, their application has not been reported so far.

In this study, two kinds of superfine rubber particles, styrene-butadiene (SB) and carboxylic styrene-butadiene (CSB), were used to prepare nylon 6/rubber composites via *in situ* polymerization. The morphology and the interfacial interactions in the two composite systems were discussed. Crystallization of the composites was studied by DSC and X-ray diffraction. The influence of superfine rubber particles on the rheological and mechanical properties of the materials was also investigated.

EXPERIMENTAL

Materials

ϵ -Caprolactam and *n*-aminocaproic acid were used to prepare nylon 6. Styrene-butadiene with particle size of 80–100 nm and carboxylic styrene-butadiene with particle size of 130–150 nm were kindly provided by SINOPEC Beijing Research Institute of Chemical Industry, and the particles were prepared by irradiating the latex with γ ray or an electron beam, aiming at changing the latex particle from linear or slightly cross-linked to highly cross-linked structure, then desiccated by direct spraying. For carboxylic styrene-butadiene used in this study, the content of carboxylic groups was 1 wt%.

Preparation of Nylon 6/ Superfine Rubber Particles Composites

A typical procedure is described as follows: a 500 mL four-necked flask, equipped with a mechanical stirrer, was used as the reaction vessel. In the vessel, 200 g of ϵ -caprolactam, 22 g of *n*-aminocaproic acid, 0.6 g of antioxidant and certain amount of rubber particles (SB or CSB, both varied between 2.6 wt% and 6.7 wt%) were placed. The mixture was heated to and held at 220°C for 1 h, then held at 260°C for 4 h under a nitrogen atmosphere. After completion of the reaction, the product was cooled and mechanically crushed, then washed with water at 85°C for 1 h to extract the unreacted monomer and the oligomers.

Characterization

FT-IR and Molau test were employed to investigate the interfacial interactions of the composite systems. In FT-IR measurements, the product was fully extracted with formic acid, then the rubber particles were isolated and the spectra of the original powder were recorded on a Nicolet 560 FT-IR spectrometer. Since the CSB particles were difficult to isolate from the composites containing a smaller addition, they were instead extracted from nylon 6/20 wt% CSB composite. Fine pellets of the composite were dissolved in formic acid, and a small amount of toluene was added to facilitate the coagulation of particles; then the suspension was filtered using a sintered glass filter. The procedure was repeated until no more polymer could be detected in the filtrate. The residue was washed with methanol and dried. The molau test was conducted by mixing 0.8 g of the composites and 8 mL of formic acid in a test tube, and the mixture was put aside for over 30 days.

The morphology of nylon 6/superfine rubber particles composites was examined with a Hitachi-800 transmission electron microscopy (TEM) on cryogenically microtomed ultra-thin sample sections. Phase contrast between the components was revealed by exposing the sample sections to OsO₄ vapor to stain the rubber phase.

Differential scanning calorimetry (DSC) and X-ray diffraction method were employed to investigate the crystallization behavior of the composites. DSC was performed on a TA DSC-2910 calorimeter and before measuring all samples were held at 250°C for 5 min to eliminate their heat history, then quenched in liquid nitrogen. The samples were then heated to 250°C at a heating rate of 10 K/min under a nitrogen atmosphere and held for 2 min, then cooled down to 100°C at a rate of 10 K/min. X-ray diffraction was performed at room temperature on a D/MAX-III A diffractometer, in a range of $2\theta = 10\text{--}40^\circ$ with a scan rate of $2^\circ/\text{min}$.

Dynamic viscosity measurements were undertaken using a rheometer (Rheometric Scientific ARES) in the parallel-plate mode, and the test specimens were prepared by compression molding. The diameter of both upper

and lower plates was 25 mm, and the gap between the two parallel plates was 1 mm. The measurements were conducted at a strain of 15% (within the linear viscoelastic range) over a frequency range of 10^{-1} – 10^2 rad/s. The experimental temperature was set at 260 °C.

The samples for mechanical tests were obtained by injection molding, and all tests were conducted on dry samples at 23 °C. Tensile properties were measured using a TS-2000 Testing Machine, and a crosshead speed of 50 mm/min was employed. The flexural tests were also carried out on the same instrument with a crosshead speed of 20 mm/min. The Izod impact strength was carried out with an impact test machine (UJ-40).

RESULTS AND DISCUSSION

FT-IR Analysis

Figure 1 shows the IR spectra of original rubber particles and the particles isolated from the composites after thorough washing with formic acid. As for nylon 6/CSB composite, several new peaks appeared in the spectrum of the isolated particles as compared with that of the original CSB. The bands at 1640 cm^{-1} and 1540 cm^{-1} are the characteristic peaks of amides, while the peak at 3300 cm^{-1} corresponds to the stretching vibration of the N—H group. These spectral characteristics suggest that there is chemical bonding between carboxylic styrene-butadiene and nylon 6 matrix via amide bond formation during the polymerization process, resulting in grafting of nylon chain on the surface of CSB particles. The characteristic stretching vibration of the carboxyl group at 700 cm^{-1} does not disappear in the spectrum of the isolated particles, because the grafted nylon chain has carboxyl group as its end group. However, for nylon 6/SB composite, the FT-IR spectrum of the isolated particles shows no obvious grafting of nylon 6, as indicated by the weak amide bond at 1540 cm^{-1} , suggesting that there are no chemical interactions between SB and the matrix. The presence of small amount of nylon may arise from physical penetration of nylon into the cross-linked particles. The peak at 1637 cm^{-1} in Fig. 1(d) does not mainly originate from the presence of nylon, as it was also observed in other treatments which do not involve nylon; *e.g.*, it arose when the original rubber particles were extracted with $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$. Its origin, however, is not clear at present. In addition, it is noted that FT-IR spectra of the original styrene-butadiene (Fig. 1c) and carboxylic styrene-butadiene (Fig. 1a) all have a weak peak at 1735 cm^{-1} , derived from the ester group of the surfactant used in the preparation of the rubber particles through emulsion polymerization.

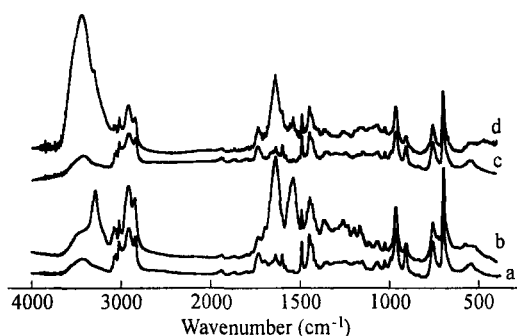


Fig. 1 FTIR spectra of the original rubber particles and the particles isolated from the composites: (a) CSB; (b) CSB isolated from nylon 6/CSB composites; (c) SB; (d) SB isolated from nylon 6/SB composites

Molau Test

Both highly cross-linked SB and CSB rubber particles are insoluble in formic acid. This fact makes it possible to investigate the interface interactions in the composites by the Molau test. As seen in Fig. 2, when same amount of rubber particles was added (*i.e.* 4.3 wt%), nylon 6/SB composite was evidently delaminated in formic acid, and the insoluble SB particles coagulated in the upper layer while the lower layer became a pellucid solution. On the contrary, when nylon 6/CSB composite was dissolved in formic acid, a uniform emulsion was obtained when left aside for over 30 days or even centrifuged at high speed, showing that the particles could uniformly and stably

disperse in nylon 6/formic acid solution rather than undergoing phase separation. This experimental phenomenon shows clearly that the interactions between the dispersed phase and the matrix are different in the two composite systems. For the composite containing SB particles, there is no reactive bonding between the two phases, resulting in weak interfacial interaction. Moreover, in consideration of the difference of polarity between SB and nylon 6 matrix, the compatibility between them is inferior, which resulted in phase separation in the solution. As to the composite containing CSB, the interfacial interaction is strong owing to the formation of graft polymer and the higher polarity of CSB.

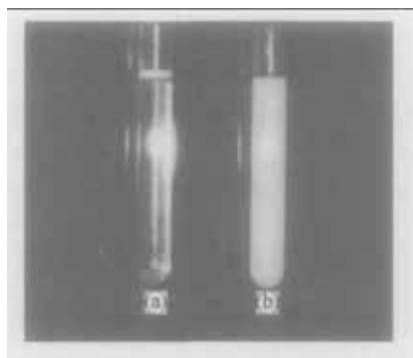


Fig. 2 Photograph of Molau test: (a) nylon 6/SB composite; (b) nylon 6/CSB composite dissolved in formic acid

TEM Observation

Figure 3 shows the phase morphology of the two composites via TEM observation. With the same amount of rubber particles (*i.e.* 4.3 wt%), CSB is monodispersed retaining its original dimensions in nylon matrix, whereas SB particles are obviously agglomerated, indicating poor dispersion. This comparison reveals that the grafting resulting from the existence of reactive groups on CSB improves the dispersion of rubber particles. At the same time, there is good binding between CSB and nylon matrix, thus strong interactions are formed.

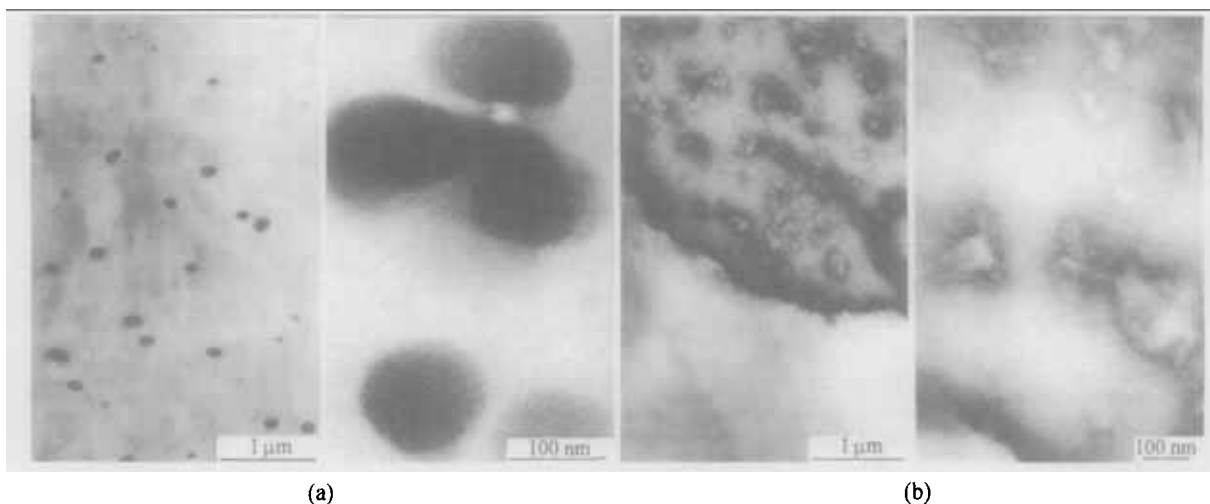


Fig. 3 TEM photomicrographs of nylon 6/superfine rubber particles composites: (a) nylon 6/CSB composite (4.3 wt%); (b) nylon 6/SB composite (4.3 wt%)

SB particles have smaller size and larger specific surface area, and thereby higher surface energy, as well as a lack of reactive groups compared to CSB. During polymerization, the compatibility between SB and nylon matrix is poor; therefore the rubber particles tend to agglomerate. However, owing to the distinct cross-linked

structure of SB particles, they could not agglomerate into a separate phase, and the interface between SB particles and nylon matrix would not diminish even when the particles assembled together. Accordingly, the agglomerate showed a special phase containing structure, inside the SB particles acted as dispersed phase while nylon was the continuous phase. Moreover, there is a clear boundary between SB particles and nylon, indicating that the interface interaction was poor. For the two composite systems in this study, these structural characteristics would surely play a role in the performance of the composites.

Crystallization Analysis

In Table 1, the values of melting point (T_m), the melting enthalpy (ΔH_m), the crystallization temperature during melt cooling (T_{mc}), the crystallization enthalpy (ΔH_{mc}), and the supercooling degree ($T_m - T_{mc}$) were obtained from DSC analysis. The melting points of the composites containing SB or CSB are almost the same as that of the neat nylon 6. Meanwhile, slight changes of ΔH_m , T_{mc} and ($T_m - T_{mc}$) indicate that the addition of both types of rubber particles will result in an inconspicuous effect on the non-isothermal crystallization behavior of the nylon matrix.

Table 1. DSC characteristic parameters of nylon 6 and nylon 6/rubber particles composites

Sample	T_m (°C)	ΔH_m (J/g)	T_{mc} (°C)	ΔH_{mc} (J/g)	$T_m - T_{mc}$ (°C)
Nylon 6	219.5	62.7	182.9	58.9	36.6
Nylon 6/CSB (2.6 wt%)	218.8	58.6	180.4	54.4	38.4
Nylon 6/CSB (4.3 wt%)	219.8	59.1	179.8	55.5	40.0
Nylon 6/SB (2.6 wt%)	219.6	60.1	182.8	57.6	36.8
Nylon 6/SB (4.3 wt%)	220.5	63.1	184.1	59.6	36.3

The crystal structure of nylon is determined by the configuration of hydrogen bonds existing among the amide groups in adjacent molecular chains. Since the molecular chains of nylon 6 are non-centrosymmetric, nylon 6 molecules could crystallize into two phases: the α crystal of anti-parallel chain and γ crystal of parallel chain. Generally, the α crystal is stable and usually formed; the molecular chains are entirely extended, the methylene segments and the amide groups are located in one plane, and the molecular chains are linked by hydrogen bonds, turning into planar lamellae. As to γ crystal, usually it is less stable, in which the hydrogen bonds existed among molecular chains are almost perpendicular to the plane of carbon skeleton^[19, 20]. In the present study, WAXS was used to gain an insight into the influence of rubber particles on the crystalline structure of nylon 6. With regard to the crystals, the α phase gives rise to two peaks at 20° and 24°, respectively, while the γ phase manifests itself as a peak around 21°. As can be seen in Fig. 4, the curves indicate the presence of both crystal phases for either neat nylon 6 or nylon 6/rubber particles composites, with higher diffraction intensities of the γ phase for CSB and SB filled nylons, especially notable when the content of rubber particles is increased.

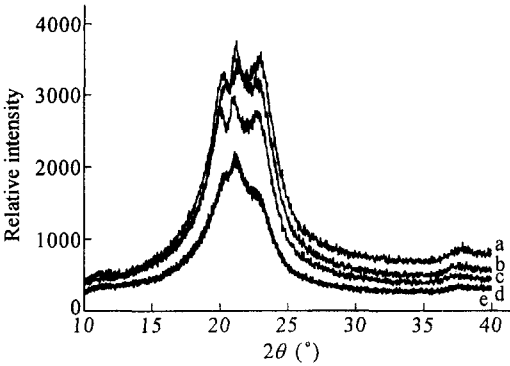


Fig. 4 X-ray diffraction scans for (a) nylon 6; (b) nylon 6/SB (2.6 wt%); (c) nylon 6/CSB (2.6 wt%); (d) nylon 6/SB (4.3 wt%); (e) nylon 6/ CSB (4.3 wt%)

Rheological Analysis

For nylon 6/SB and nylon 6/CSB composite systems, the dispersion of rubber particles and the interactions between the dispersed phase and the matrix will consequentially influence the rheological properties. As it can be seen from Fig. 5(a), there is little change in dynamic viscosities. Comparatively, the change in dynamic viscosity of nylon 6/SB is higher than that of the others, which may be due to the agglomeration of SB particles as well as the weaker interfacial interaction in the composites. As to nylon 6/CSB composites, the dynamic viscosities are higher than that of neat nylon 6 at higher frequency, owing to the existence of chemical bonding between the carboxylic groups on CSB particles and the nylon matrix, which restrains the response of nylon segments to the operation. In Fig. 5(a), the influence on dynamic viscosity is not obvious as the content of CSB increases. This fact is advantageous for the processability of the composite materials.

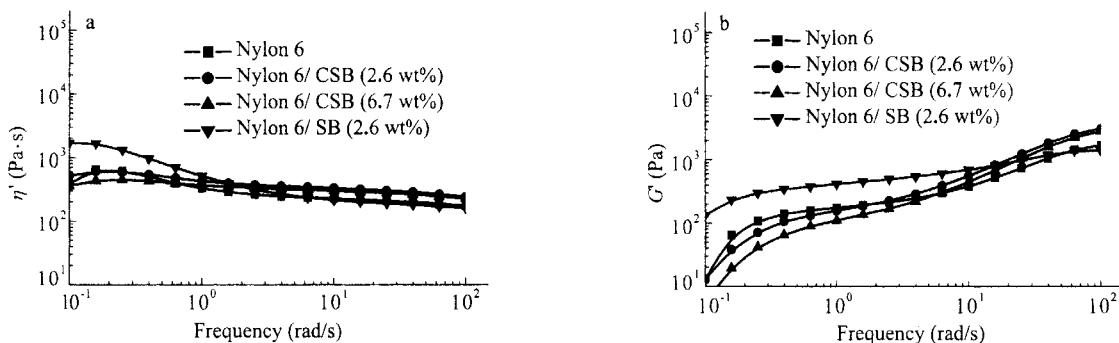


Fig. 5 Rheological behavior of nylon 6 and nylon 6/superfine rubber particles composites
a) η' versus frequency; b) G' versus frequency

Figure 5(b) indicates that the storage moduli (G') of nylon 6/SB composite change slightly with increasing frequency, and are basically higher than that of neat nylon 6. Comparatively, the storage modulus of nylon 6/CSB composite is lower at low frequencies, but it rises at a certain frequency. This may be due to the uniform dispersion of rubber particles in nylon 6/CSB composites, and the formation of graft polymer on the particle surface, leading to strong interactions with the matrix. At lower frequency, the movement of macromolecular chains is sufficient, meanwhile the CSB particles have larger strain, which leads to the decrease of storage modulus; as the frequency increases, the action time becomes shorter, then the movement response of small dimension units of nylon 6 accounts for the dominant degree, at the same time the highly cross-linked rubber particles could maintain their intrinsic elasticity, thus leading to a higher storage modulus of the composites. However, as to nylon 6/SB composites, the interfacial interactions between nylon matrix and the rubber particles are comparatively weaker, therefore the changing tendency of G' should correspond to the specific phase containing structure mentioned above, which results from the agglomeration of rubber particles. For instance, the movement of nylon macromolecular chains accounts for a major role at lower frequency, simultaneously the special phase containing structure bears the stress as a whole, accordingly resulting in abnormally higher storage modulus than that of neat nylon 6; as the frequency increases, the movement response of small dimension units plays a major role. Then the G' value of nylon 6/SB composites gradually tends to the same value as that of neat nylon 6. The changing tendency of η' for nylon 6/CSB and nylon 6/SB composites within the investigated frequency range can also be explained in this view. In addition, as it can be seen from Fig. 5(b), the storage modulus of nylon 6/CSB composites decrease as the CSB content increases at lower frequency; whereas at higher frequency, the influence of CSB content becomes un conspicuous. This changing tendency is in agreement with the discussion above.

Mechanical Properties

Mechanical tests reveal that within the experimental range, the addition of SB and CSB particles causes a slight decrease in tensile strength and flexural strength of nylon matrix, or even brings about an increase under some

circumstances. As to nylon 6/CSB composites, its toughness is significantly improved in the dry state. For instance, when 4.3 wt%–6.7 wt% of CSB was added, the Izod impact strength was improved almost twofold. As to nylon-rubber blends, previous studies^[21, 22] showed that poor results were obtained with particle size below 200 nm. But the CSB used in this study having particle size of 130–150 nm manifests a distinct toughening effect when present in only small amounts. However, as to nylon 6/SB composite, the impact strength is only increased slightly as compared with that of neat nylon 6, indicating a slight increase in toughness of the matrix; however, the tensile elongation is sharply decreased. As mentioned above, the dispersion of the two kinds of rubber particles and the interactions between the dispersed phase and the matrix play an important role in changing the macroscopic characteristics of the composites. Since CSB particles are uniformly dispersed in nylon matrix and a certain amount of graft polymer is formed on the particle surface owing to the presence of carboxyl groups, there is strong interface adhesion in nylon 6/CSB composites, therefore causing a notable improvement in matrix toughness with only slight decrease in rigidity. As to nylon 6/SB composites, due to the worse dispersion of rubber particles, the agglomeration of SB particles with special phase structure formed in the composite leads to the almost unchanged modulus and tensile and flexural strengths, and the impact strength increases to a less extent compared with neat nylon 6, whereas the elongation at break obviously decreases with the increase of SB content.

Table 2. Mechanical properties of nylon 6 and nylon 6/rubber particles composites

Sample	Tensile strength (MPa)	Tensile elongation (%)	Impact strength (J/m)	Flexural strength (MPa)	Flexural modulus (MPa)
Nylon 6	71.9	172	33.9	84.6	2153
Nylon 6/CSB (2.6 wt%)	69.6	281	52.8	78.6	1937
Nylon 6/CSB (4.3 wt%)	73.6	284	66.8	90.2	2230
Nylon 6/CSB (6.7 wt%)	68.6	223	67.9	80.6	2100
Nylon 6/SB (2.6 wt%)	69.8	122	44.4	82.0	2044
Nylon 6/SB (4.3 wt%)	68.1	37	38.5	85.5	2213
Nylon 6/SB (6.7 wt%)	64.8	31	42.3	84.3	2113

CONCLUSIONS

Nylon 6/ rubber composites have been successfully prepared via *in situ* polymerization, using two kinds of highly cross-linked superfine rubber particles. The dispersion of rubber particles and the interactions between the dispersed phase and the matrix are quite different in the two systems. For nylon 6/CSB composites, the particles are dispersed uniformly in nylon matrix, and the graft polymer is formed on the particles through chemical bonding during the polymerization, leading to strong interface adhesion. However, SB particles are obviously agglomerated in the nylon 6/SB composite and have no chemical bonding with nylon matrix, resulting in poor interfacial interactions. Compared with neat nylon 6, the addition of both SB and CSB rubber particles results in slight change in its crystallizability, but facilitates the formation of γ crystal. Owing to the differences in the dispersion state and the interfacial interactions, the storage modulus of nylon 6/SB composite changes slightly as the frequency increases, being basically higher than that of neat nylon 6. The storage modulus of nylon 6/CSB composite is lower at low frequencies, then it rises above a certain frequency. Mechanical tests indicate that nylon 6/CSB composites have considerably higher toughness with almost unchanged rigidity, as compared with nylon 6 and nylon 6/SB composites.

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