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ORIGINAL PAPER

Rheology, mechanical, and thermal properties of core–shell silicon-acrylic copolymer emulsion films and its application on surface sizing: role of silane coupling agent

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Abstract With the assistance of polymerisable maleate surfactant and costabilizer, core–shell emulsions with poly(butyl acrylate) core (PBA) and poly(butyl acrylate–styrene–methacryloxypropyl trimethoxysilane) shell (PSBM) were prepared through seeded emulsion polymerization. Effects of MPTS on rheological, mechanical, and thermal properties were investigated. Simultaneously, the emulsions were utilized as paper surface sizing agents, and corresponding properties were studied. It was found that the emulsion possessed viscoelastistic nature and changed from viscous to elastic with MPTS addition. At the same time, enhanced internal network strength among particles was detected, which was weakened when MPTS concentration was 8%. The tensile strength and thermal stability of copolymer films were therefore increased accordingly. However, decrease in tensile strength, elongation at break and thermal properties was observed with higher MPTS concentration due to weakened interaction among different shells. It was also found that glass transition temperature (T_g) did not influence greatly by MPTS, and two phases corresponding to core and shell copolymer were observed with low degree of microphase separation. Furthermore, the interaction between polymer and fiber was improved, resulting in improved sizing degree, ring crush strength, surface strength, and folding strength. While the surface strength and folding endurance decreased due to the increase of brittleness with higher crosslinking degree.

Keywords Core–shell emulsion · Rheology · Mechanical property · Thermal property · Surface sizing

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Introduction

Siloxane containing polymers have been studied intensively because of their many desirable properties, such as the low-surface energy, high flexibility, good thermal stability, and weather resistance [1–4]. Siloxane containing polyacrylate or poly(acrylate–styrene) emulsions, as one of these materials, gained special attention and extensive application due to excellent film-forming properties and mechanical properties [5–10]. While for polyacrylate and poly(acrylate–styrene), they have disadvantages in water resistance and weather resistance, and their mechanical properties are often temperature dependent [11, 12]. As a consequence, incorporation of siloxane monomer into polyacrylate and poly(acrylate–styrene) is demonstrated to be an effective method to improve variety of physical/chemical properties of final materials [13–15].

However, it is common sense that siloxane monomer is more expensive than most of vinyl monomers, how to minimize the amount of silane monomer whereas reasonable properties can be maintained becomes a concern for researchers. Core–shell particle structure therefore attracted special and deep attention [16–18]. The function of siloxane monomer can become more effective if core–shell particles with siloxane monomer as the shell were prepared. In recent years, novel core/shell emulsion particles with polyacrylate core and polysiloxane as a shell were successfully synthesized through some special seeded polymerization methods [19–21]. However, decrease in tensile strength, monomer conversion, and emulsion stabilities is observed with the increase of silicone concentration, which can be attributed to the eventual microheterogeneous structure in copolymer emulsion films resulting from different polymer polarities [6]. Vinyl trialkoxysilane has often been used as crosslinking agent to form a middle transition layer between the core and shell to improve the compatibility, and therefore improve the mechanical and thermal properties [6, 22, 23].

The synthesis of stable poly(butyl acrylate) (PBA)/poly(butyl acrylate–styrene–methacryloxypropyl trimethoxysilane) (PSBM) core–shell emulsion using polymerisable maleate surfactant has been studied in our previous study [24]. The main objective of this article is to systematically investigate effects of silane coupling agent on phase behavior, the mobility of polymer chain and interactions among emulsion particles, and further study how the interactions among polymer chains and particles influence the phase behavior, mechanical and thermal properties of core–shell copolymer emulsion film, as well as its application performance on paper surface sizing.

In this research, with the assistance of polymerisable maleate surfactant, core–shell PBA/PSBM emulsion was prepared in the presence of methacryloxypropyl trimethoxysilane as coupling agent in the shell. Effects of MPTS on the rheological properties of core–shell emulsion were studied, as well as mechanical properties, crystallinity, and thermal properties of emulsion films. In addition, the emulsions were utilized for paper surface sizing agents, and corresponding properties such as sizing degree, surface strength, folding endurance, and ring crush strength were investigated.

Experimental part

Materials

3-Methacryloxypropyl trimethoxysilane (MPTS) (Wuhan Institute of Applied Technology, China) and nonyl phenol ethoxylate (TX-10) (Tianjin Kermel Chemical Reagent Co., Ltd, China) were used as received. Maleic anhydride (MAH), sodium bisulfite ($NaHSO_3$), potassium persulfate, ferric chloride, ammonium thiocyanate (NH_4SCN), and aqueous ammonia ($NH_3 \cdot H_2O$) from Tianjin Dengfeng Chemical Reagent Co. (China) were all analytically pure grades, and were used without further purification. The analytical reagents butyl acrylate (BA), methacrylic acid (MAA), styrene (St), and octadecyl acrylate (ODA) were all purchased from Tianjing Chemical Reagent Factory (China) and were distilled under vacuum before use.

Synthesis of polymerisable surfactant (MT)

1 mol MAH and 1 mol nonyl phenol ethoxylate were stirred in a melted state at 70 °C for 3 h. $NH_3 \cdot H_2O$ was then added dropwise to the reaction mixture to adjust pH value of reaction system to 6 and thereafter the temperature was maintained in the range of 90–95 °C until the solution became transparent. Polymerisable surfactant (MT) can be obtained by keeping the reaction for additional 2 h [24].

Preparation of poly(BA-*n*-ODA) seed emulsion

1.5 g polymerisable surfactant (MT) and distilled water were introduced into a 250 mL four-necked flask equipped with a reflux condenser, a mechanical stirrer, and a digital thermometer. Then, 16 g BA, 0.5 g MAA, 0.1 g $NaHSO_3$, and 0.2 g ODA were added into the flask. After additional 30 min equilibration at 70 °C, 6 g 5% potassium persulfate aqueous solution was dropped into the flask in 1 h, then the system was kept at 70 °C with constant stirring for additional 2 h.

Seeded emulsion polymerization

0.2 g $NaHSO_3$ and 50 g water was added into the abovementioned seed emulsion. Then, the mixture of 16 g St, 16 g BA, 1.0 g MAA, and MPTS of different concentration was dropped into the flask under starved-feed addition, and simultaneously 10 g 5% potassium persulfate aqueous solution was introduced slowly into the reaction system. The reaction was kept for another 2 h after the addition was completed. Then, the obtained emulsion was cooled to room temperature. Finally, ammonia was adopted to adjust the pH value of emulsion in the range of 7–8.

Preparation of hybrid films

The emulsions were cast on a tetrafluoroethylene plate to allow them to dry at room temperature for 5 days, and then at 60 °C for 12 h. After demoulding, the films were kept into a desiccator to avoid moisture.

Preparation of surface sizing agent

Mixture of 10 g starch and 190 g distilled water was added into a three-neck flask, and then the reaction was kept at 90 °C for 30 min with constant stirring to get starch fluid. Surface sizing agent can thereby obtained by mixing 20 g PBA–PSBM core–shell emulsion with the starch fluid.

Characterization

The rheological properties of emulsions were analyzed in an American TA Instrument® AR2000ex Rheometer. All tests were carried out at 25 °C using DIN concentric cylinders geometry. Strain amplitude experiments (0.01–100%) were performed at a frequency of 0.1 Hz to determine the linear viscoelastic region. Then, frequency sweeps (0.01–1000 Hz) were performed with a strain of 2% at 25 °C.

The tensile strength and elongation at break of the films were measured on a multifunctional electronic strength tester TS 2000-S (Scientific and Technological Limited Company of High Iron in Taiwan). Tensile test bars ($5 \times 70\ \text{mm}^2$) were cut from hybrid films of 0.4–0.7 mm thickness. The standard tensile test performed was an adaptation of ASTM 412-83, D 638-84, and D 882-83 methods.

Temperature dependence of dynamic mechanical properties was conducted using an America TA Q800 dynamic viscoelastometer at an operating frequency of 1 Hz from −70 to 150 °C at a heating rate of 3 °C min^{-1}.

Thermogravimetric analysis (TG) and differential thermogravimetry (DTG) were performed in an American TA Q500 thermal analyzer. Film samples about 10 mg were placed in a platinum sample pan and heated from 20 to 600 °C under N_2 atmosphere, at a heating rate of 10 °C min^{-1}.

Paper sheets preparation and characterization

For each experiment, four 60 g m^{-2} paper sheets for physical property testing were prepared according to TAPPI method T205 [25]. All paper samples were dried, conditioned (for 24 h before any physical testing) and tested in the standard environment (22 ± 2 °C and 50 ± 2% relative humidity).

Sizing efficiency was measured as Stöckigt sizing degree (JIS P 8122, JIS method 1979) [26]. The specimens of paper were placed on the surface of 2% NH_4SCN solution; the temperature was maintained at 20 ± 1 °C. Then, a drop of 1% ferric chloride solution was dropped onto the surface of the specimen. Switch off timer when three red spots were detected, and the time was recorded as Stockigt sizing time. For each test unit, five specimens with the felt side and five with the wire side were measured.

For each surface strength test unit 6 specimens (200 × 15 mm) were prepared, all tests were measured by IGT picking speed detector (Sichuan Changjiang Paper Instrument Co., Ltd).

For each folding endurance test unit 10 specimens (15 × 100 mm) were prepared, all tests were performed on YQ-Z-31 vertical folding tester (Sichuan Changjiang Paper Instrument Co., Ltd).

For each ring crushing strength test unit 10 specimens (15 × 120 mm) were prepared, all tests were performed on DCP-KY3000 computer control compression tester (Sichuan Changjiang Paper Instrument Co., Ltd).

Results and discussion

Rheological behavior of core–shell PBA/PSBM emulsion

The frequency dependence of storage and loss moduli for emulsions with different MPTS concentration was shown in Fig. 1. Similar as polymer fluid, emulsions have an internal network structure resulting from intermolecular interactive forces. At high frequencies, the mobility of molecular chain and droplets is highly restricted,

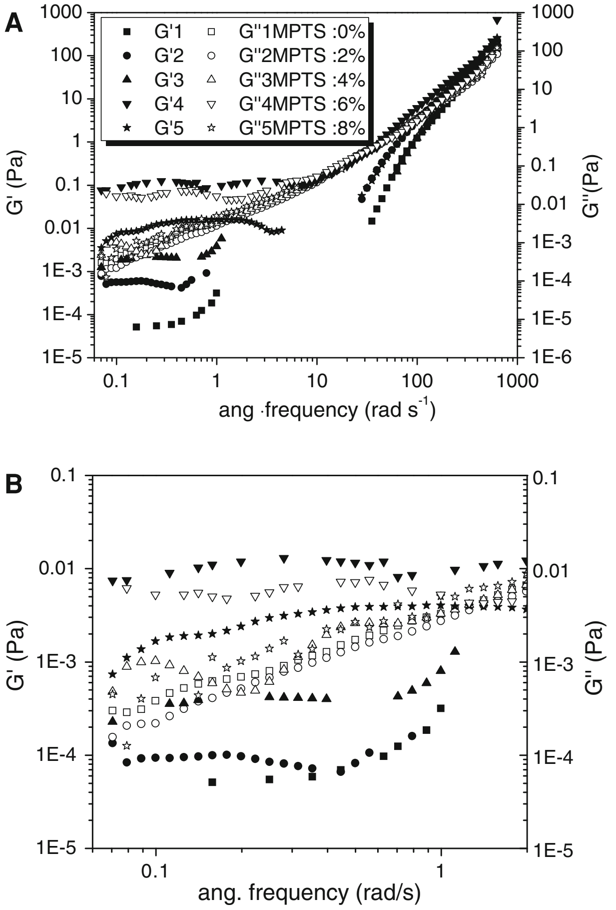

Fig. 1 **a** Frequency dependence of storage and loss moduli with variation in MPTS concentration and **b** partial enlargement of (**a**)

resulting in higher storage moduli. While the energy can no longer stored and storage moduli decrease with lower frequency.

A plateau was detected for each emulsion at lower frequency, demonstrating the formation of internal network among particles. It was also observed that storage modulus (G') in the plateau region increased with increasing MPTS concentration, indicating enhanced internal network strength among particles. However, G' decreased when MPTS concentration was 8%, the interaction among particles was weakened, therefore it can be concluded that self-crosslinking reaction among different shells was reduced, and the increase of MPTS concentration may just contribute to the increase of self-crosslinking reaction occurring in the same shell. However, at higher frequency, the change was not that pronounced.

Furthermore, it was shown that the storage modulus (G') and loss modulus (G'') crossovered each other and the crossover was shifted to higher frequency, manifesting the system possessed viscoelastistic nature and displaying a decrease in relaxation time. Another observation was that, G'' remained over G' when MPTS concentration was <4%; the viscous characteristic occupied the predominant role in the system. While for the emulsion with MPTS concentration >6%, G' became the dominant factor, so it was evident that the system changed from viscous to elastic with MPTS addition.

Mechanical properties

The tensile strength and elongation at break of emulsion films with different MPTS concentration were shown in Fig. 2. It can be seen that the tensile strength increased as MPTS was incorporated, followed by a slight decrease when MPTS concentration was >8%, indicating that the mechanical response of the copolymers was affected by the MPTS self-crosslinking. This is ascribed to higher interchain interaction and interaction among different shells with MPTS addition. However, the decrease of tensile strength with the further increase of MPTS suggested that the

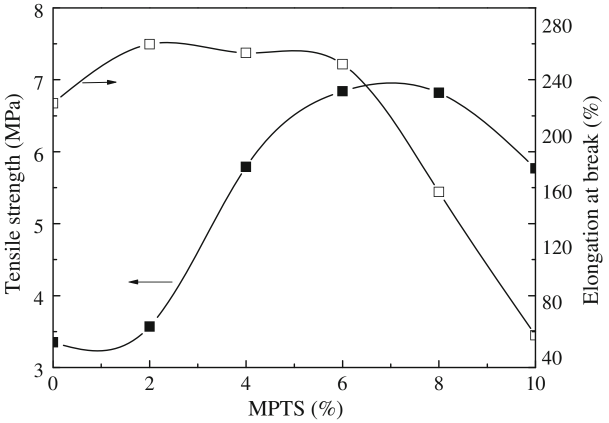

Fig. 2 Effect of MPTS concentration on tensile strength and elongation at break of emulsion films

crosslinking interaction occurring in the same shells contributed less to the mechanical properties of films; simultaneously the crosslinking interaction among different shells, which can enhance the tensile strength, is in contrast reduced.

It was also found that the elongation at break was increased with MPTS addition, but marked decrease was detected when MPTS concentration was >8%. The main reason was that the brittleness of the films was increased at the same time due to the increase of crosslinking degree.

Dynamic mechanical thermal analysis

Temperature dependence of storage modulus (E') and loss tangent (tanδ) with different MPTS concentration was presented in Figs. 3 and 4, respectively. An increase of E' was observed both in glassy region and at temperatures above the glass transition by increasing MPTS concentration to 6.0%. This phenomenon can be attributed to the enhanced intermolecular interactions produced by silane coupling agent MPTS. However, significant decrease in E' was detected with 8% MPTS addition, indicating the weakened interactions.

Another observation to consider was the decrease in the intensity of tanδ peaks and glass transition temperature (T_g) shifted to higher temperature, which can be attributed to the restriction of polymer chain mobility. However, insignificant change in T_g was found when MPTS concentration exceeded 4%, and the intensity of tanδ peaks almost kept invariable with 6 and 8% MPTS addition. According to theory, the T_g should increase since the motions of polymer chains can be restricted by silane coupling agent. However, effects of more MPTS on T_g were not that apparent with further increase in MPTS concentration, this was reasonable since core–shell copolymer was itself high crosslinked with the assistance of certain amount of silane coupling agent, so slight change took place in the T_g [27, 28].

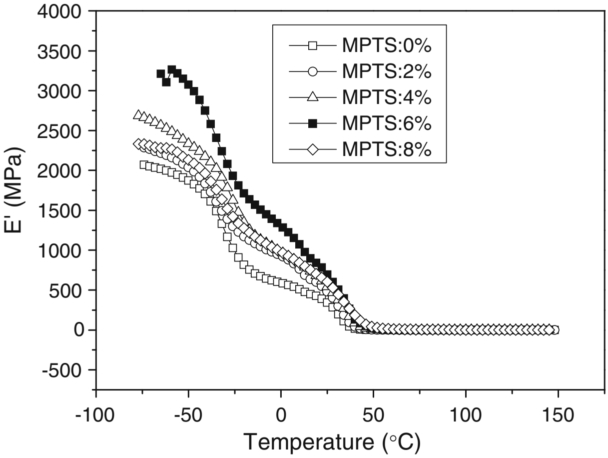

Fig. 3 Temperature dependence of storage modulus with different MPTS concentration

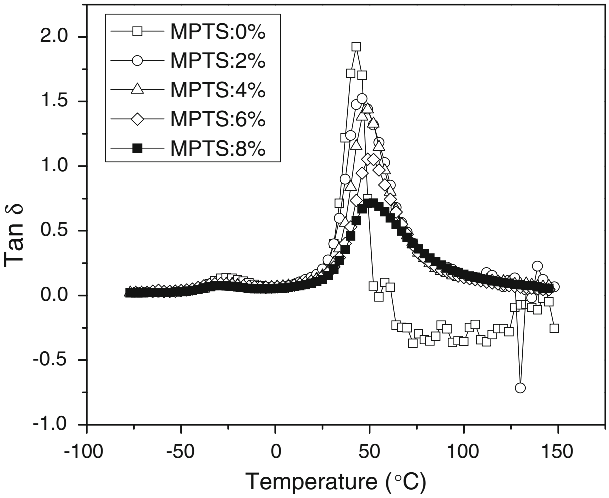

Fig. 4 Temperature dependence of loss tangent (tan*δ*) with different MPTS concentration

In addition, the tan*δ* peaks became broadened with MPTS addition, indicating the greater dynamic mechanical losses in this region [21]. Furthermore, two tan*δ* peaks around −25 and 50 °C were observed for all the samples, which can be attributed to seed phase and shell phase, respectively, thereby demonstrating that two different phases were formed in the core–shell particles. One phase comprises mainly PBA, and the other phase is formed mainly by copolymer of St, BA, and MPTS. It was also found that the intensity of tan*δ* peaks for seed phase was very low, suggesting seed copolymer chain was highly restricted and low degree of microphase separation was detected.

Thermal stability of hybrid emulsion films

The typical TG and DTG curves of hybrid films with different MPTS concentration were shown in Figs. 5 and 6, respectively. As shown in Fig. 5, the thermal decomposition temperature of hybrid materials shifted to higher temperature range accompanied with an increase of MPTS concentration, which confirmed the enhancement of thermal stability. However, the thermal stability became weaker when MPTS concentration reached 6%, further demonstrating the reduction of internal network strength.

Similar phenomena were detected in the DTG curves. The temperature at maximum degradation rate shifted to higher temperature with the increase of MPTS concentration, and then decreased with further increase in MPTS concentration. It was also found that only one stage of degradation for all samples was observed, indicating no microphase separation, which was not coincidence with DMA results to some extent. The main reason was that DTG method was not sensitive enough to detect the microphase separation phenomena.

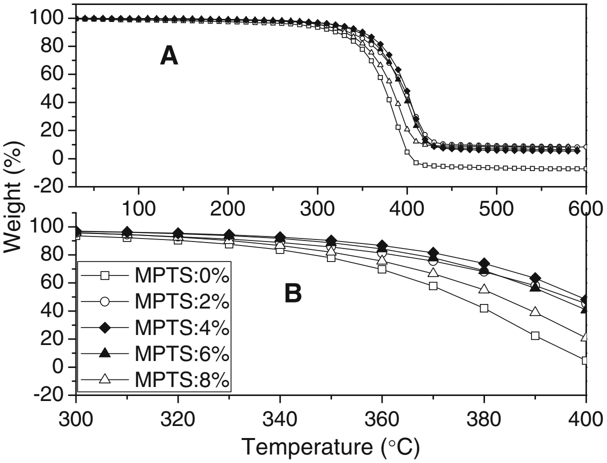

Fig. 5 TG curves of hybrid films with different MPTS concentration **a** TG curve from 30 to 600 °C and **b** TG curve of partial enlargement from 300 to 400 °C

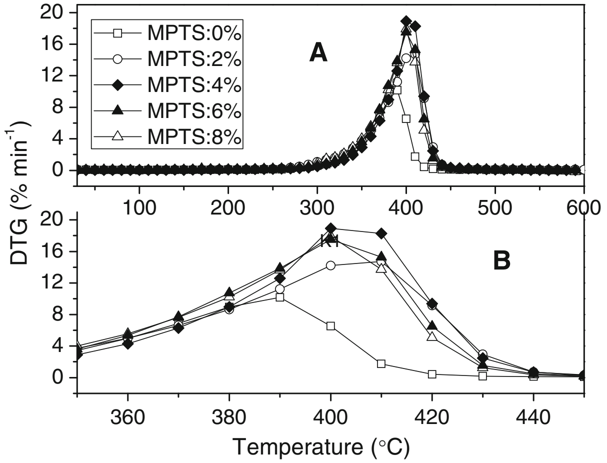

Fig. 6 DTG curves of hybrid films with different MPTS concentration **a** DTG curve from 30 to 600 °C and **b** DTG curve of partial enlargement from 350 to 450 °C

Surface sizing properties of PBA–PSBM emulsion

Effects of MPTS concentration on paper sizing degree, surface strength, folding endurance, and ring crush strength were shown in Figs. 7 and 8, respectively. It was found that Stockigt sizing time increased with MPTS addition and kept almost invariable when MPTS concentration was >8%. And continue increase in ring crush strength was observed, as shown in Fig. 8. The interaction between polymer and fiber can be improved with the increase of MPTS concentration, so it became more difficult for water to penetrate into paper fiber through crosslinking copolymer films.

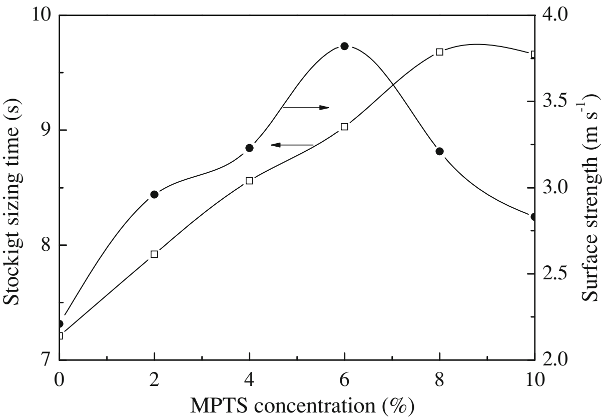

Fig. 7 Effects of MPTS concentration on Stockigt sizing time and surface strength of sized paper

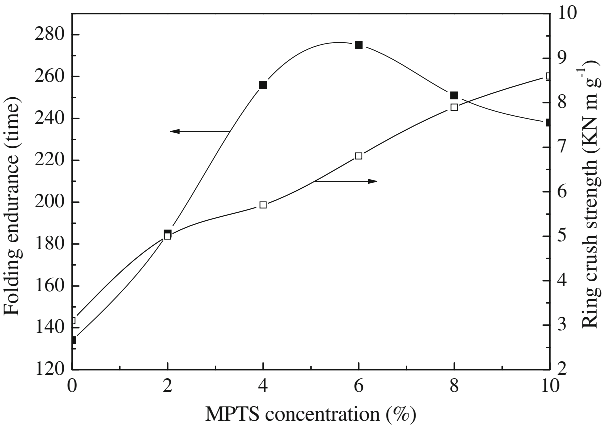

Fig. 8 Effects of MPTS concentration on folding endurance and ring crush strength of sized paper

Furthermore, the continue increase in ring crush strength certified the increase of paper stiffness.

However, the optimum surface strength and folding endurance were detected when MPTS concentration was 6%, followed by decrease in these properties. The main reason was that the brittleness of film increased simultaneously with further increase in crosslinking, it was easy for rupture to take place with external force, which will destroy combination among fibers and decrease the surface strength and folding endurance.

Conclusion

Core–shell emulsions exhibited viscoelastic nature and the system changed from viscous to elastic with the increase of MPTS concentration. It was demonstrated that internal network strength among particles got enhanced with MPTS addition. However, when MPTS concentration was >6%, the self-crosslinking reaction among different shells was reduced; the increase of MPTS concentration contributes to the increase of self-crosslinking reaction occurring in the same shell. The tensile strength, elongation at break, and thermal properties can be improved with certain amount of MPTS, as well as the sizing degree, ring crush strength, surface strength, and folding endurance of paper sized with PBA/PSBM core–shell emulsion, demonstrating enhanced intermolecular interaction and interaction among particles. However, decrease of these properties was observed due to reduced interaction among different shells and enhanced brittleness.

Simultaneously, the motion of polymer chains was highly restricted with certain amount of MPTS addition. And insignificant change in T_g was found when MPTS concentration exceeded 4%. In addition, the tanδ peaks became broadened with MPTS addition, indicating greater dynamic mechanical losses. Furthermore, lower intensity of tanδ peak for seed phase and low degree of microphase separation were observed in core/shell copolymer.

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