POLYMER
BLENDS

Effect of β-Cyclodextrin on the Preparation
of Poly(methyl methacrylate-*co*-lauryl methacrylate) Nanoparticles
and Their Latex Blending with Natural Rubber[1]

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Abstract—Poly(methyl methacrylate-*co*-lauryl methacrylate) (PMLMA$_1$) latex with two-layer spheroidal particles and low coagulum was successfully carried out using synthesized surfactants and β-cyclodextrin (β-CD) by suspension polymerization. PMLMA$_1$ was then latex blended with natural rubber (NR) compared to conventional core-shell poly(methyl methacrylate-*co*-lauryl methacrylate) (PMLMA$_2$) particles. The influences of reaction temperature, mass ratios of surfactants and β-CD, reaction time and initiator loading on conversion, coagulum and molecular weight of PMLMA$_1$ were firstly analyzed. Before contrast analysis of NR/PMLMA$_1$ and NR/PMLMA$_2$, the effect of surfactants and β-CD on NR was discussed. Characterizations of dynamic light scattering, scanning electron microscope (SEM), X-ray diffraction and mechanical strength clearly indicated the good interaction between these stabilizers and NR. According to the analysis of transmission electron microscope, PMLMA$_1$ and PMLMA$_2$ particles were homogeneously distributed on the surface of NR particles, while, SEM measurement showed that surface and cross section of NR/PMLMA$_1$ films were much denser and smoother than correspondingly NR/PMLMA$_2$ blends. The data from tensile strength and elongation at break also indicated that NR/PMLMA$_1$ films were superior to NR/PMLMA$_2$ due to high LMA molar ratio in chemical composition of PMLMA$_1$. Differential scanning calorimetry analysis further demonstrated the strong interfacial adhesion between PMLMA$_1$ phase and NR matrix compared to NR/PMLMA$_2$. Because the preparation was eco-friendly and economical, the novel PMLMA$_1$ latexes are expected to be directly used for the manufacture of dipped films.

INTRODUCTION

Latex blending is a convenient and effective method for the preparation of coating, paint and film products. In the field of dipped films products, natural rubber (NR) latex were often mixed with polymer for better properties, such as mechanical strength, anti-aging and solvent resistance [1–3]. Poly(methyl methacrylate) (PMMA) is an excellent material to possess good mechanical strength and aging resistance, and the products of NR/PMMA retaining individual properties have attracted much attention from academic and industrial area [4–6]. However, due to high glass transition temperature and hydrophilicity, undeformed PMMA particles tend to migrate into NR film surface during the process of film forming, resulting in limited reinforcement of mechanical strength [7].

Three methods are generally implemented to tackle the incompatible problems. The first way is to increase the polarity of NR by epoxidation, maleinization and graft copolymerization [8–10]. These modified NRs reduce interfacial tension of PMMA phase and NR matrix due to chemical interaction of blend two phases. But the preparing process involves organic reagent and reaction efficiency is relatively low in the presence of non-rubber materials [1, 10, 11]. The second way is to synthesize interpenetrating polymer network (IPN) by polymerizing swelling MMA monomers in NR film, which leads to a formation of homogenous films [12, 13]. However, the reaction is highly incomplete due to the difficulty in free movement of monomer and initiator inside NR film. The third way is to prepare MMA-based polymer latexes using natural materials as surfactants, such as casein, starch and sericin [14–16]. These polymers could improve the compatibility between MMA units and

NR phases by the adsorption of functional groups onto protein and phospholipid as outer layer of NR particles. Compared to latexes prepared by synthesized surfactants, these polymer latexes have several unfriendly disadvantages, such as poor mechanical stability and easy deterioration. Some researchers have discussed about the influence of synthesized surfactants on mechanical stability of NR particles and compactness of NR films. Lim et al. studied the latex blend of NR and two synthesized surfactants with twelve hydrocarbons [17]. The results showed that mechanical stability of NR particles increased by the addition of anionic surfactant but decreased by nonionic surfactant. It may be the fact that steric stabilization from nonionic surfactant is interior to molecules interaction from anionic surfactant. Singh et al. reported a long-chain surfactant with functional groups, such as hydroxyl and amino groups, and used it to modify NR [18]. They found that the evenness and compactness of NR films has been largely reinforced. Although these synthesized surfactants improve the strengths of NR films, inexpensive and easily available surfactants are more preferred in the modification of NR films. Tween 80 (T80) and sodium dodecylbenzene sulfonate (SDBS), as low priced and high-performance surfactants, are widely used in the emulsion/suspension polymerization to obtain sustainable latexes. It was also reported that T80 can adsorb on the surface of NR particles to form complexes by the interaction between poly(ethylene oxide) of T80 and carboxyl groups of protein as outside shell of NR particles, which caused the reinforcement in stability of these particles [19]. In addition, because protein and phospholipid have great impacts on the strain-induced crystallization of NR, it can be inferred that additional surfactants also benefit the process of strain-induced crystallization due to interactions between surfactants and protein or phospholipid [20, 21].

Because lauryl methacrylate (LMA) is a non-polar and soft monomer, which is highly similar to chemical character of NR units. Thus, one can expect that LMA can be used in the modification of NR. Unfortunately, LMA polymerizations in aqueous media frequently lead to the formation of suspension-like polymer particles, low molecular weight and poor conversion [22, 23]. In fact, propagating process of polymer chains mainly occurs in monomer droplets, which leads to oversized monomer droplets and coagulum formation [24]. Some papers had been reported on improving the problem. Ahmad et al. found that the addition of ethanol can increase solubility of LMA monomer in water phase and allow the synthesis of sub-micron sized PMLMA particles [25]. Additionally, some researches prepared PMLMA either by atom transfer radical polymerization or group transfer polymerization or living anionic polymerization inorganic medium other than water [26–28]. Because organic solvents are extremely harmful for NR latex, these PMLMAs are unable to be used in the modification of NR films. β-

cyclodextrins (β-CD) is a kind of cyclic carbohydrates in the shape of hollow truncated cones with hydrophilic surface and hydrophobic cavity [29]. The inner cavity diameter and height of β-CD is about 0.78 nm and 0.79 nm, respectively [30]. Because β-CD can solubilize hydrophobic monomer in the cavity to form complexing compounds, it is often used in the LMA polymerization as a phase transfer agent [31, 32]. But β-CD should be combined with other synthesized surfactants to obtain steady latexes due to its unsealed structure [31]. In our technique, small monomer droplets with hydrophilic surface can be prepared by controlling the adding orders of synthesized surfactants and β-CD. It can be explained from the mechanism of assembling between surfactants and β-CD as follows (see Scheme 1): (1) the mixture of LMA, MMA, initiator (AIBN) and β-CD result in the formation of complexing β-CD compound, defined as Particle 1; (2) the formation of Particle 2 by the absorption between carboxyl groups from sodium dodecylbenzene sulfonate (SDBS) and hydroxyl groups from β-CD as outer of Particle 1; (3) the formation of monomer droplets by the affinity between long alkyl chains from Tween-80 (T80) and dodecyl chains from SDBS as outer of Particle 2. These monomer droplets could stably become two-layer particles during the polymerization, which has been confirmed by transmission electron microscope in this paper. Few reports are available about the copolymerization of MMA and LMA in pure water medium. We hope that this work could contribute to the study on the polymerization of LMA monomer in water phase and modification of NR dipped-film.

EXPERIMENTAL

Materials and Instruments

Natural rubber (NR) latex (solid content: 60%) was provided by Hainan American International Xianghe Industrial (Hainan, China). Methyl methacrylate (MMA, 99%, Aldrich) and lauryl methacrylate (LMA, 96%, Aldrich) were purified by passing through an alumina column to remove inhibitor for three times and then kept in a refrigerator until use. 2,2-azobisisobutyronitrile (AIBN, 98%) was obtained from Shanghai Ling-Feng Chemical Reagent (Shanghai, China) and recrystallized using ethylalcohol for three times before use. Sodium dodecylbenzene sulfonate (SDBS), Tween-80 (T80) and sodium chloride (NaCl) were purchased from Shanghai Ling-Feng Chemical Reagent. β-cyclodextrin (β-CD, 99%) and hydroquinone (99%) were obtained from Adamas Reagent (Basel, Swizerland). Chloroform and ethyl alcohol were purchased from Aldrich (99%, St. Louis, America). D-chloroform (CDCl₃, 98%) was provided by Merck (Darmstadt, Germany). Phosphotungstic acid was purchased from Sinopharm Chemical Reagent (99%, Beijing, China) and used as negative
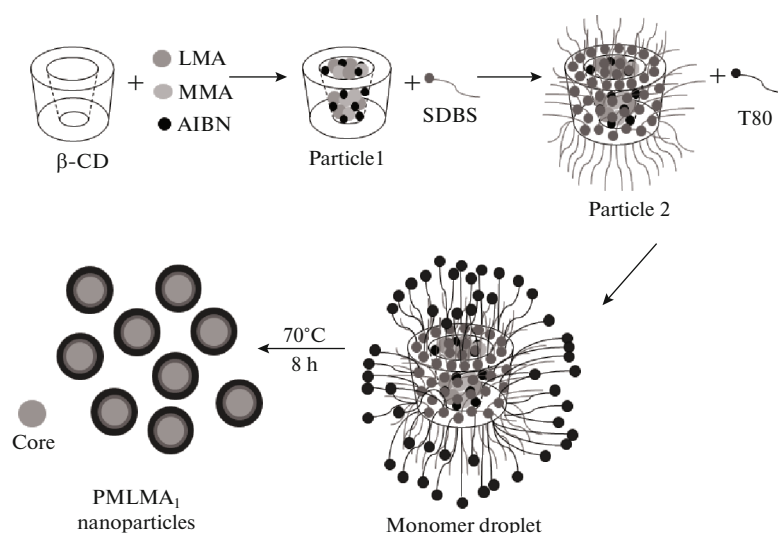
Scheme 1.

dying agent for TEM analysis. Deionized water was used throughout the entire experiment.

Dynamic light scattering instrument (DLS, ZEN3600, UK); scanning electron microscope (SEM, S-3400N, Japan); X-ray diffractometer (XRD, D/max 2550V, Japan); Bruker Avance 400 MHz NMR spectrometer (^{1}H NMR, Avance, Germany); gel permeation chromatography (GPC, PL-GPC50, UK); transmission electron microscope (TEM, JEM-1400, Japan); differential scanning calorimetry (DSC, Q2000, USA).

Preparation of NR/Stabilizer Blends, Copolymer Latexes and NR/Copolymer Blends

Preparation of NR/surfactant and NR/5% β-CD blend films. The blend processes of NR and stabilizers are shown as follows: Firstly, SDBS or T80 was solved in the deionized water and adjusted to pH 11 by adding ammonia aqueous solution. But for β-CD, it should be solved in heated water (80°C). Secondly, NR latex was respectively blended with the stabilizers at different loading by using mechanical agitation at 25°C. The blend latexes were stirred for 2 h and stayed overnight. Modified films could be obtained by pouring these blend latexes into plastic culture dishes and then drying at 70°C for 12 h.

Preparation of copolymer latexes and NR/copolymer blend films. PMLMA$_1$ latexes were synthesized via suspension polymerization according to the recipes (Table 1). The synthesis of PMLMA$_1$ was performed in a 250 mL four-necked flask equipped with magnetic stirrer, nitrogen gas inlet, thermometer and condenser. The process of copolymerization involved two steps. Initially, deionized water (82 g) was poured into flask and then stirred for 0.5 h under nitrogen atmosphere. Meantime, a mixture was obtained according to the

following procedures: (1) the blend of MMA (1 g), LMA (1 g), AIBN (20 wt % of total initiator) and β-CD (20 wt % of total β-CD) for 0.5 h; (2) the blend of (1) and SDBS (20 wt % of total SDBS) for 0.5 h; (3) the blend of (2) and T80 (20 wt % of total T80) for 0.5 h. Then, the mixture was added into the flask to obtain a white non-deposition compound and the reaction temperature was raised to designed temperature. Subsequently, the remaining mixture of stabilizers, MMA, LMA, AIBN and deionized water (8 g) was prepared as the above procedures and then slowly added into the reaction vessel during 4 h period. The copolymerization process was continuously performed for several hours to obtain a stable latex. The preparation of PMLMA$_2$ (see Table 2) was similar to that of PMLMA$_1$ and the preparation of NR/copolymer film was similar to that of NR/stabilizer film.

Samples must be purified before the measurement of ^{1}H NMR, GPC and DSC. The procedures of purification were shown as follows: Some precipitates were firstly formed by adding 100 mL of NaCl aqueous solution into synthesized copolymer latex (1 g) and then solved in the mixture of chloroform and ethylalcohol (1/1, w/w) to prepare 2% polymer solution. Secondly, the solution was slowly added into deionized water to form unsolved film. Purified samples could be prepared by drying the unsolved film in an oven at 110°C for 2 h.

Characterization

Particle size and zeta potential of NR/stabilizer particles and particle size of copolymer particles. The analysis of particle size and zeta potential can be used to confirm the interaction between NR particles and stabilizers. The characterization of particle size and zeta potential were performed by using a dynamic light

Table 1. The results of characterizations of PMLMA$_1$ latexes

Run	SDBS, g	T-80, g	β-CD, g	AIBN, g	Reaction time, h	T, °C	Coagulum, %	Conversion, %	Particle size, nm	$M_n \times 10^4$	PDI
1	0.3	0.3	0.3	0.08	8	60	3.3	81.8	129	4.6	1.88
2	0.3	0.3	0.3	0.08	8	65	3.5	85.3	125	5.7	1.79
3	0.3	0.3	0.3	0.08	8	70	3.9	90.6	132	6.8	2.13
4	0.3	0.3	0.3	0.08	8	75	4.0	92.1	137	5.6	2.03
5	0.2	0.2	0.3	0.08	8	70	10.2	76.2	132	4.3	2.36
6	0.3	0.3	0.4	0.08	8	70	5.6	91.5	123	5.9	2.35
7	0.4	0.4	0.4	0.08	8	70	3.6	92.5	118	5.5	2.28
8	0.3	0.3	0.3	0.08	4	70	1.9	54.6	125	4.7	2.28
9	0.3	0.3	0.3	0.08	6	70	3.5	72.5	131	5.5	2.02
10	0.3	0.3	0.3	0.08	10	70	4.5	91.2	132	6.9	2.05
11	0.3	0.3	0.3	0.07	8	70	3.5	85.6	122	5.7	2.15
12	0.3	0.3	0.3	0.09	8	70	4.1	91.5	133	6.4	2.28
13	0.3	0.3	0.3	0.10	8	70	4.2	92.7	136	5.8	2.26

Table 2. The results of characterizations of PMLMA$_1$ and PMLMA$_2$

Samples	SDBS, g	T80, g	β-CD, g	Mean diameter, nm	$M_n \times 10^4$	PDI	LMA, mol %	Conversion, %	Coagulum, %
PMLMA$_1$	0.3	0.3	0.3	127	6.7	2.08	8.57	91.3	3.8
PMLMA$_2$	0.3	0.3	0	73	7.8	2.34	6.67	93.2	12.6

scattering instrument at 25°C. All samples were diluted to about 0.1 wt % by adding deionized water before measurement. Each sample was repeated for three times and the average value was reported in the graphs.

SEM characterization of surface and cross sections of modified NR films. The surface and cross-section morphologies of blended films were examined by scanning electron microscope. All film samples were coated with thin gold in a sputter coater for 60 s and then photographed at an appropriate magnification.

XRD measurement of NR/stabilizers blend films. X-ray diffractometer was used to examine the compatibility of NR and stabilizers using an analyzer with CuK_α radiation (λ = 0.1542 nm). The generator operating voltage and current of X-ray source were 40 kV and 100 mA, respectively, with an angle of 5°−50° and a step angle of 2°/min.

Calculation of conversion, coagulum and LMA molar percentage. Copolymer latex was withdrawn from the flask and poured into a weighed beaker with an amount of hydroquinone solution for preventing further polymerization. Subsequently, the beaker was kept in an oven at around 100°C until a constant weight was reached. Conversion of polymerization can be calculated from the solid content. During the copolymerization process, some coagulum was generated

due to the hydrophobic LMA monomer. The suspending-flock can be obtained by filtering copolymer latex through a sieve (10 µm). Then, coagulum percentage of copolymer was calculated by measuring the dried flock.

The purified sample was dissolved into CDCl$_3$ and analyzed with a NMR spectrometer. The molar percentage of LMA in the copolymer was calculated by Eq.:

$$M_{LMA} = \frac{3A}{3A + 2B} \times 100\%.$$

M_{LMA} is the molar percentage of LMA in the copolymer, A and B represent integral area for −OCH$_2$ (3.9 ppm) and −OCH$_3$ (3.6 ppm) protons, respectively.

Molecular weight and PDI measurement of PMLMA$_1$ and PMLMA$_2$ copolymer. The number-average molecular weight and polydispersity index (PDI) of copolymer were examined by gel permeation chromatograph. The GPC measurement was performed with poly(methyl methacrylate) as a standard and N,N-dimethylformamide (DMF) as the eluent at a flowing rate of 0.8 mL/min.

TEM analysis. The morphologies of PMLMA$_1$, PMLMA$_2$, NR/PMLMA$_1$ and NR/PMLMA$_2$ nanoparticles were directly observed by TEM mea-

surement. The copper grid was wetted by 5% latex and then dyed by 2% phosphotungstic acid for analysis.

DSC characterization of NR/PMLMA blend films. DSC can directly confirm the interaction between copolymer phase and NR matrix by the analysis on endothermic transition of substances. The sample (5 mg) was placed in the DSC pan and run in the instrument from −100 to 150°C at a heating rate of 10 deg/min under a liquid nitrogen atmosphere.

Mechanical strength of NR/PMLMA blend films. Tensile strength and elongation at break of dumbbell-shaped samples were performed by using universal tensile testing machine (CMT2202) at a rate of 400.0 mm/min according to GB 7543-2006 at room temperature. Eight samples were examined for each blend film, and the average value was reported.

RESULTS AND DISCUSSION

Preparation of $PMLMA_1$ Latexes Based on Different Reaction Conditions Effect of Reaction Temperature on Copolymerization (Run 1−4)

From Table 1, the amount of coagulum, conversion and molecular weight increase from 60 to 70°C. When the temperature is further raised to 75°C, molecular weight decreases due to the appearance of side reactions, such as chain termination and chain transfer. It may be the fact that the best decomposition temperature of AIBN initiator is 60~70°C, low temperature or high temperature both have unfavorable impacts on the formation of initiator free radicals and propagation of polymer free radicals [33].

Effect of Mass Ratios of Surfactants and β-CD on Copolymerization (Run 3, 5−7)

When loading of SDBS and T80 are constant, the amount of coagulum and conversion increase but molecular weight decreases with the increasing β-CD loading, suggesting that β-CD plays an important role in reinforcing polymerization. However, due to the lack of protection from SDBS and T80, synthesized polymers would be precipitated from excess β-CD and finally cause an increase in the amount of coagulum. When the loading of SDBS, T80 and β-CD is increased to 0.4 g, respectively, the amount of coagulum reduces and conversion increases. It might be explained by the fact that most of monomers have been protected by these stabilizers to form monomer droplets, and hence residual monomers are difficult to form suspension-like particles. Besides, the concentration in each a monomer droplet falls for the increasing number of monomer droplets, leading to decreased molecular weight.

Effect of Reaction Time on Copolymerization (Run 3, 8−10)

The amount of coagulum, conversion and molecular weight gradually ascend with increasing reaction time, indicating that the increase in reaction time enhance the completion of polymerization. Compared to 8 h, the conversion and molecular weight are basically unchanged while the amount of coagulum slightly increases at 10 h, suggesting that a further increase beyond 8 h has no obvious assistance on polymerization but minimizes mechanical stability of polymer latex due to poor emulsification of magnetic stirring.

Effect of Initiator Loading on Copolymerization (Run 3, 11−13)

From Table 1, the amount of coagulum and conversion increase with increasing initiator loading. But excess initiator loading could raise the chance of chain termination and lead to a decrease in molecular weight. Thus, a suitable dosage is very crucial for the polymerization. In this work, 0.08 g is the best loading based on the combination of coagulation, conversion and molecular weight.

Because molecular weight of additional polymer has a major role in intensifying mechanical strength of matrix. Thus, it may be proper to decide reaction conditions mainly according to molecular weight and coagulation. From Table 1, at the reaction condition of Run 3, a fine $PMLMA_1$ latex with low coagulum, high conversion and molecular weight could be obtained and used for modifying NR latex.

Effect of Species of Stabilizer on the Natural Rubber

Interactions between NR latex particles and stabilizers in the latex stage. The interactions between NR particles and stabilizers can be investigated by particle size and zeta potential. It is reported that negative charges of NR particles are derived from amino groups and carboxyl groups of protein and long-chain fatty acid soaps as outer of NR particles [34]. For NR/SDBS blends, due to the formation of hydrogen bonds between carboxyl groups of SDBS and carboxyl, amino groups of NR particles, particle size and negative charge of NR/SDBS particles increase. For NR/T80 blends, because T80 is a nonionic surfactant, the particle size increases but zeta potential decreases with increasing loading. For NR/β-CD blends, particle size increases as increasing amount of β-CD. However, zeta potentials of NR/β-CD particles show different changes. From Fig. 1, it can be found that zeta potential of NR/2.5% β-CD is −49.1 mV while one of NR/5% β-CD is −42.3 mV. It may be fact that β-CD is a rigid cyclic polymer with Lewis base character [30, 35]. At the low loading, zeta potentials of NR/β-CD particles increase by the interaction
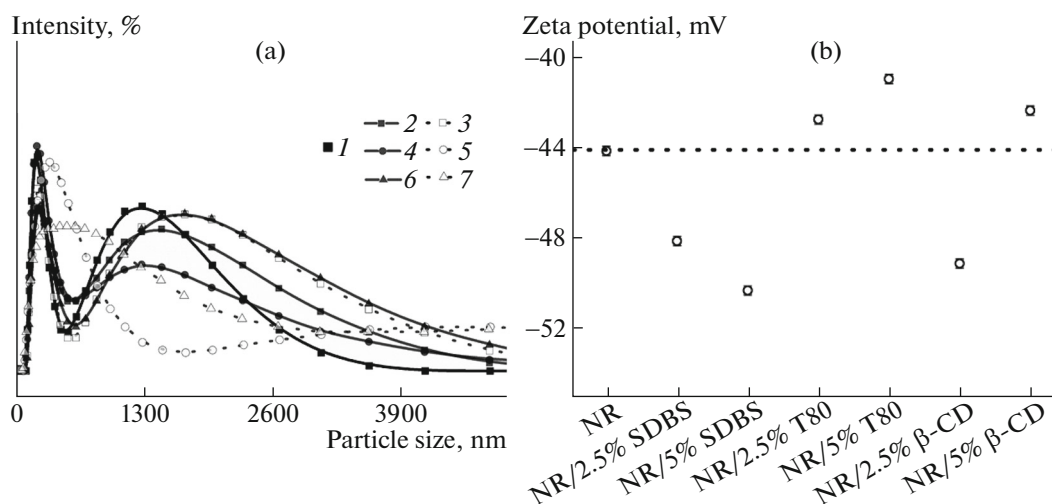
Fig. 1. (a) Particle size and (b) zeta potential of (*1*) pure NR and modified NR particles: (*2*) NR/2.5% SDBS, (*3*) NR/5% SDBS, (*4*) NR/2.5% T80, (*5*) NR/5% T80, (*6*) NR/2.5% β-CD, and (*7*) NR/5% β-CD.
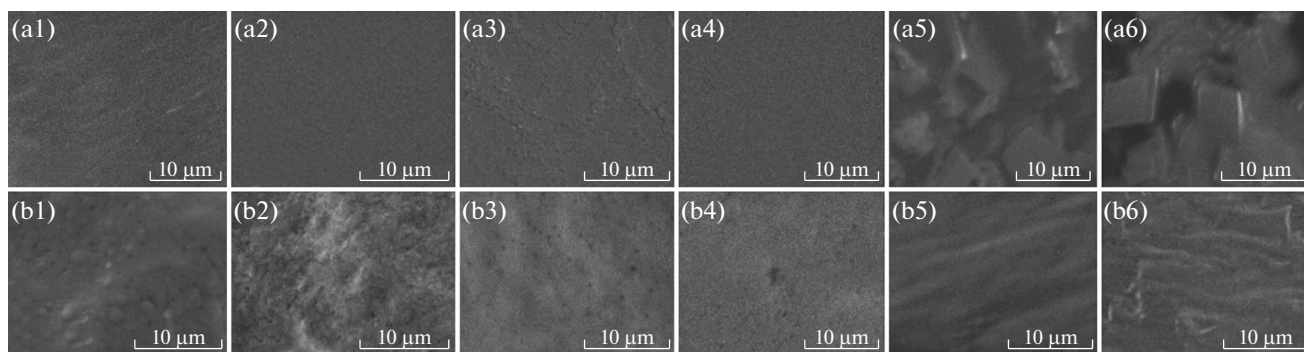

Fig. 2. SEM characterization of (a) surface and (b) cross sections of modified films: (a1), (b1) NR/2.5% SDBS, (a2), (b2) NR/5% SDBS, (a3), (b3) NR/2.5% T80, (a4), (b4) NR/5% T80, (a5), (b5) NR/2.5% β-CD, and (a6), (b6) NR/5% β-CD. Scale bar 10 μm.

between β-CD and NR particles. However, many β-CD may aggregate with the increasing loading and then absorb on the big NR particles to form flocculation, causing a decrease in zeta potential. According to the measurements of particle size and zeta potential, it can be inferred that SDBS and β-CD increase stability of NR particles by electrostatic repulsion while T80 acts by steric repulsion.

Effect of stabilizers on the morphologies of NR films. From Fig. 2a, the surfaces of NR/2.5% SDBS and NR/2.5% T80 films are uneven and coarse. It may be the reason that the absorption of SDBS or T80 on the shell of NR particles is unfavorable for the complete inter-diffusion between rubber chains during film formation. In addition, with increasing amount of SDBS or T80, the corresponding blend films are getting smooth. It may be the fact that the addition of surfactants with long alkyl chain can induce weak flocculation and contribute to the formation of a more uniform film [36]. The surface morphologies of NR/β-

CD films show that massive β-CD particles accumulate on the film surface, which results from the incompatibility between polar outer of β-CD and non-polar rubber chains.

From cross-section morphologies of modified NR films, the interaction of two phases can be directly observed to indicate the compatibility between stabilizers and NR matrix. In Fig. 2b, NR/SDBS films show rugged and dense morphologies with small mounds, which are formed from the interaction between SDBS and non-rubber materials. After the addition of T80, NR films show plat fractures with some pores, which maybe stems from moisture absorption of T80. Compared to NR/SDBS and NR/T80 blends, cross-sections of NR/β-CD are homogeneous. It can be explained by the fact that β-CD is a hollow cone with hydrophobic cavity so that nonpolar rubber chains can freely migrate through the cavities of β-CD due to the similar chemical properties
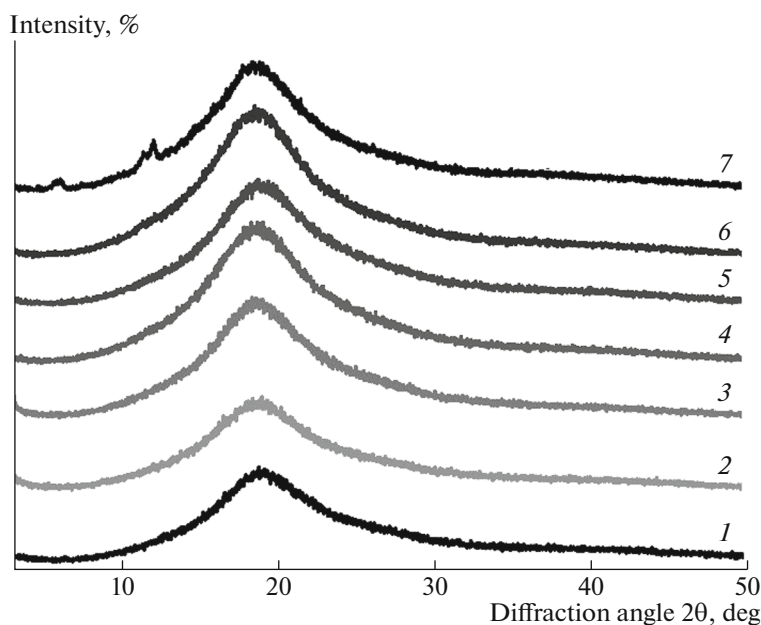
Intensity, %

Fig. 3. XRD characterization of (*1*) pure NR film and modified films: (*2*) NR/2.5% SDBS, (*3*) NR/5% SDBS, (*4*) NR/2.5% T80, (*5*) NR/5% T80, (*6*) NR/2.5% β-CD, and (*7*) NR/5% β-CD.

during the film formation of films, resulting in the good dispersion of β-CD among NR matrix.

From the analysis on morphologies of modified NR films, it can be concluded that SDBS and T80 have a fine interaction with NR matrix for the presence of long alkyl chains and functional groups. However, β-CD would aggregate on film surfaces and uniformly distribute inside NR matrix. Thus, it is necessary to find a method to prevent it from migrating into film surfaces.

Study on the compatibility between NR and stabilizers. The XRD measurements of modified NR films with stabilizers are shown in Fig. 3. The XRD results of NR/SDBS and NR/T80 are similar to that of pure NR film at two loadings, suggesting the good compatibility between NR phase and SDBS or T80. The spectrum of NR/2.5% β-CD has no new peaks while some crystalline peaks are observed on the spectrum of NR/5% β-CD. The new peaks might derive from aggregating β-CDs on the film surface, which is harmful for crystalline property of NR film due to the semicrystalline character of β-CD through intermolecular hydrogen bonding. In addition, these results are also consistent with the surface and fracture morphologies of modified NR films.

Tensile strength and elongation at break of NR/stabilizers blend films. Figure 4 shows the effect of three stabilizers loading on tensile strength and elongation at break of NR films. As shown in Fig. 4a, the addition of SDBS or β-CD reinforces tensile strength of NR films but T80 decreases. Because non-rubber materials of NR, such as protein and phospholipids, connect with two active ends of linear polyisoprene of NR to form networks and enhance strain-induced crystallization of rubber chains [20]. Thus, SDBS can reinforce crystallization by the interaction with non-rubber materials and contribute to the increase in tensile strength. Because rubber chains can migrate through the β-CD cavity to form many entanglements, reinforcement in tensile strength can be also observed. For NR/T80, air bubbles are formed inside modified films due to moisture absorption of T80, which causes the decrease in tensile strength of NR films. In addition, elongation at breaks of all modified films are lower than that of pure NR films since the extension of green polymer is abated through the formation of entanglements between rubber chains and copolymer chains.

Preparation of PMLMA$_1$ and PMLMA$_2$ and Comparison of NR/PMLMA$_1$ and NR/PMLMA$_2$ Blend Films

Chemical composition of PMLMA$_1$ and PMLMA$_2$. The chemical compositions and conversions of PMLMA$_1$ and PMLMA$_2$ are shown in Table 2. As seen in Table 2, PMLMA$_2$ generates 12.6% suspension-like particles while the coagulum of PMLMA$_1$ polymerization reduces to 3.8%, and particle size of PMLMA$_1$ is almost twice as that of PMLMA$_2$. The results indicate that β-CD acts as a protecting agent during polymerization. The spectra of ^{1}H NMR (Fig. 5) show two peaks at 3.6 and 3.9 ppm, which respectively correspond to the −OCH$_3$ protons for MMA and −OCH$_2$ protons for LMA [27]. The molar ratios of LMA can be calculated according to integrated areas of 3.6 and 3.9 ppm. From Table 2, LMA
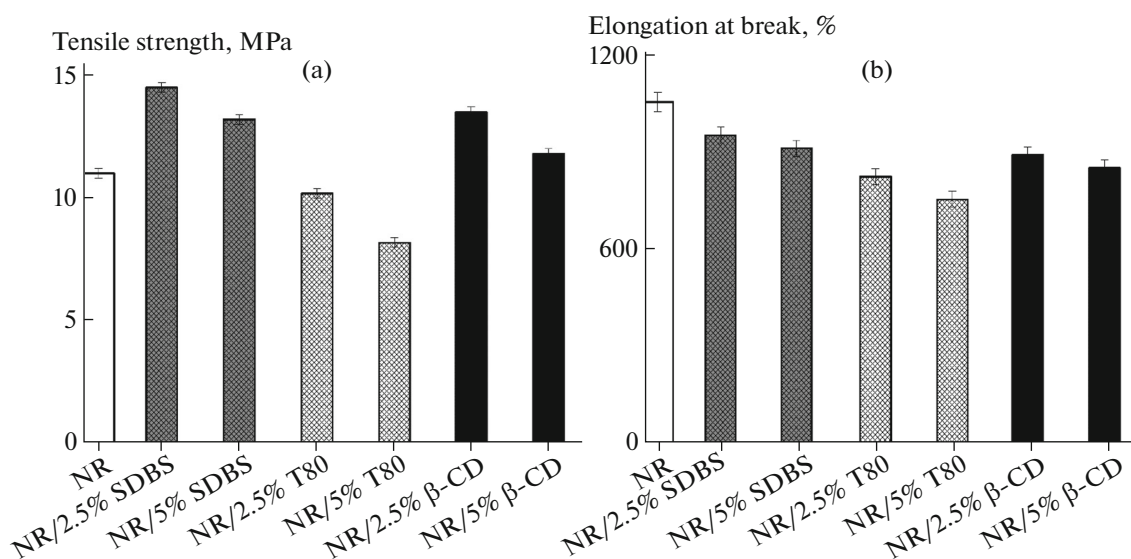
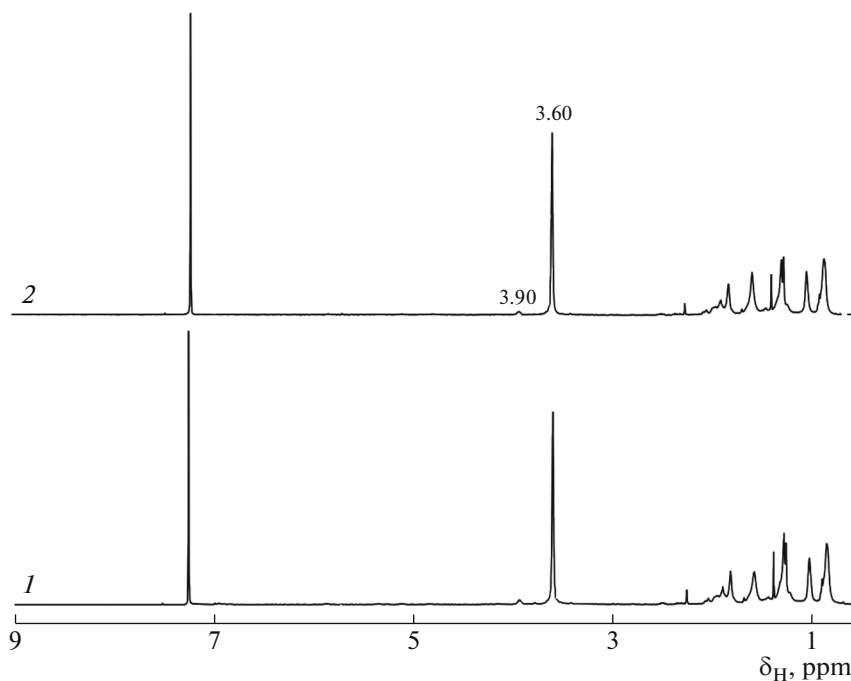**Fig. 4.** (a) Tensile strength and (b) elongation at break of modified NR films with surfactants.

Fig. 5. ^{1}H NMR spectra of (*1*) PMLMA$_1$ and (*2*) PMLMA$_2$.

molar ratio of PMLMA$_1$ is 8.57%, which is close to feed ratio (8.95%) of LMA and is superior to one of PMLMA$_2$. The results show that the addition of β-CD contributes to improving reaction efficiency of LMA and MMA and controlling chemical composition. However, not all of monomers are able to be completely coated into β-CD to form monomer droplets due to the limitation of magnetic stirring, thus, the monomer conversion of PMLMA$_1$ (91.3%) is lower than that of PMLMA$_2$ (93.2%).

TEM analysis of PMLMA$_1$, PMLMA$_2$, NR/PMLMA$_1$ and NR/PMLMA$_2$ particles. From TEM characterization, we can directly observe microstructure of PMLMA$_1$, PMLMA$_2$, NR/PMLMA$_1$ and NR/PMLMA$_2$ particles. Figure 6a displays that PMLMA$_1$ particles possess two-layer structure with diameter around 100−130 nm, which is consistent with DLS measurement. Compared to PMLMA$_1$, PMLMA$_2$ particles (Fig. 6b) are core-shell structure
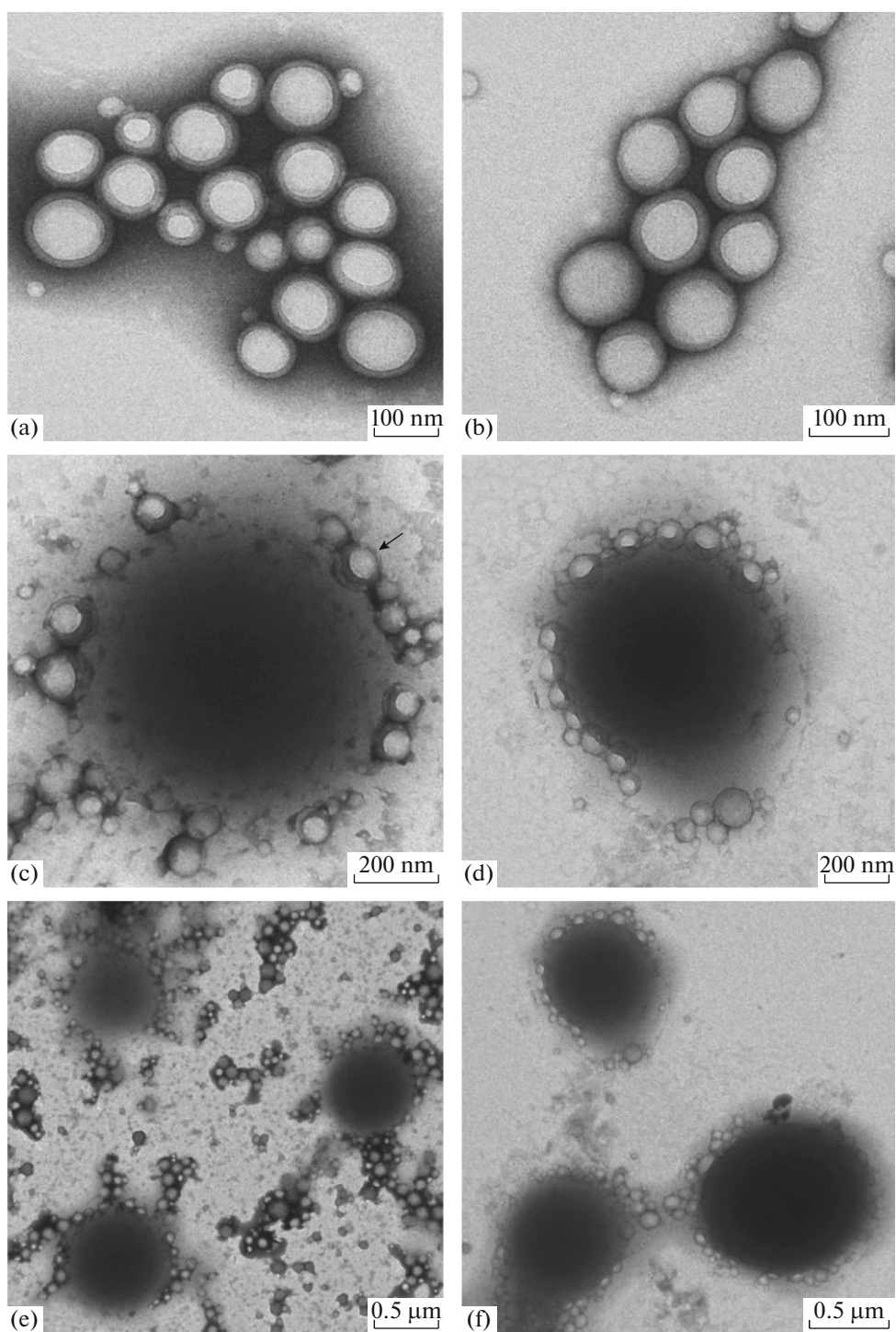
Fig. 6. TEM images of (a) PMLMA$_1$, (b) PMLMA$_2$, (c), (e) NR/10% PMLMA$_1$ and (d), (f) NR/10% PMLMA$_2$.

with diameter around 60−100 nm. The results confirmed the assembling mechanism between surfactants and β-CD for the presence of two-layer particles. Besides, it is also found that some core-shell particles are irregularly distributed among two-layer particles, and the thickness of each layer on two-layer particles is variable. These results might originate from heterogeneity of magnetic stirring. NR particle consists of *cis*-polyisoprene core and non-rubber shell, including protein and phospholipids. After latex blends of copolymers and NR, PMLMA$_1$ or PMLMA$_2$ particles homogeneously absorb on the gray halo layer of NR particles by the formation of hydrogen bonds between stabilizers and proteins or phospholipids.
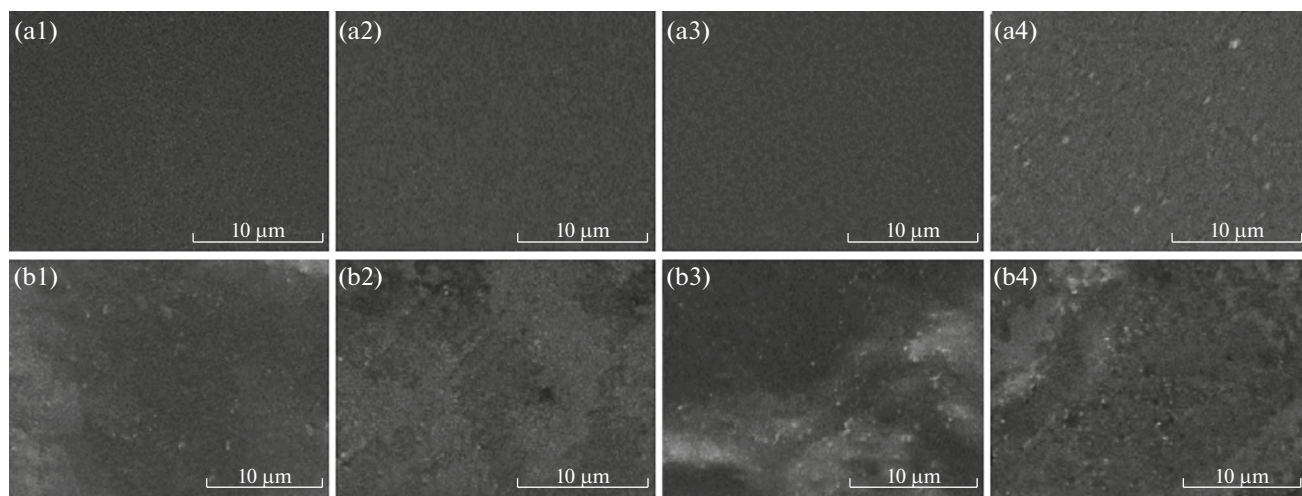
Fig. 7. SEM (a) surfaces and (b) cross sections of blend films with copolymers: (a1), (b1) NR/10% PMLMA$_1$, (a2), (b2) NR/15% PMLMA$_1$, (a3), (b3) NR/10% PMLMA$_2$, and (a4), (b4) NR/15% PMLMA$_2$. Scale bar 10 μm.
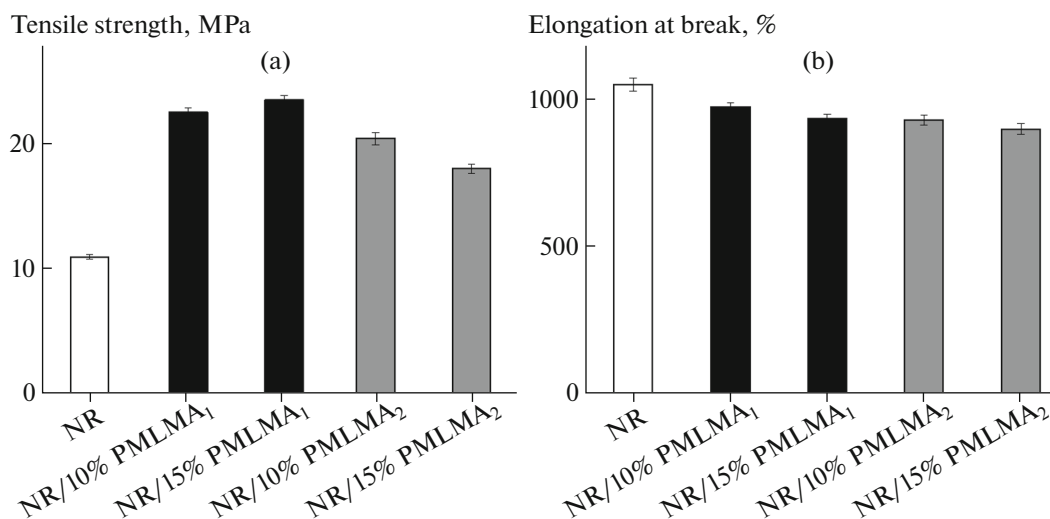

Fig. 8. (a) Tensile strength and (b) elongation at break of blend films.

Comparison of NR/PMLMA$_1$ and NR/PMLMA$_2$ blend films. It has been reported that the compatibility of NR/PMLMA$_2$ blend was superior to that of NR/PMMA due to strong chain mobility and low polarity of PMLMA$_2$ chains. Thus, the film morphologies of NR/PMLMA$_2$ were more coherent and dense than ones of NR/PMMA. From Fig. 7, film surfaces of NR/PMLMA$_1$ are smooth at two blend ratios, indicating that β-CD of PMLMA$_1$ are homogeneously distributed among the blend phase by the interaction of blend components. In addition, fracture surfaces of NR/PMLMA$_1$ have less incompatible particles and more grey section than those of NR/PMLMA$_2$. According to our previous work, the grey section is the copolymer of MMA and LMA [23]. The result of frac-ture sections can be rationalized by the fact that PMLMA$_1$ chains with low molecular weight and high LMA molar ratios can freely migrate into rubber phase and contribute to obtaining homogeneous films. Consequently, it can be suggested that NR/PMLMA$_1$ has a better compatibility than NR/PMLMA$_2$.

Tensile strength and elongation at break of NR/PMLMA$_1$ and NR/PMLMA$_2$ blend films. Figure 8 shows the effect of PMLMA$_1$ and PMLMA$_2$ on tensile strength and elongation at break of NR films. From Fig. 8a, tensile strengths of NR/PMLMA$_1$ films are stronger than those of NR/PMLMA$_2$ at all blend ratios. Due to weak polarity of PMLMA$_1$ compared to PMLMA$_2$, the strong inter-diffusion between PMLMA$_1$ chains and rubber chains benefits the large formation
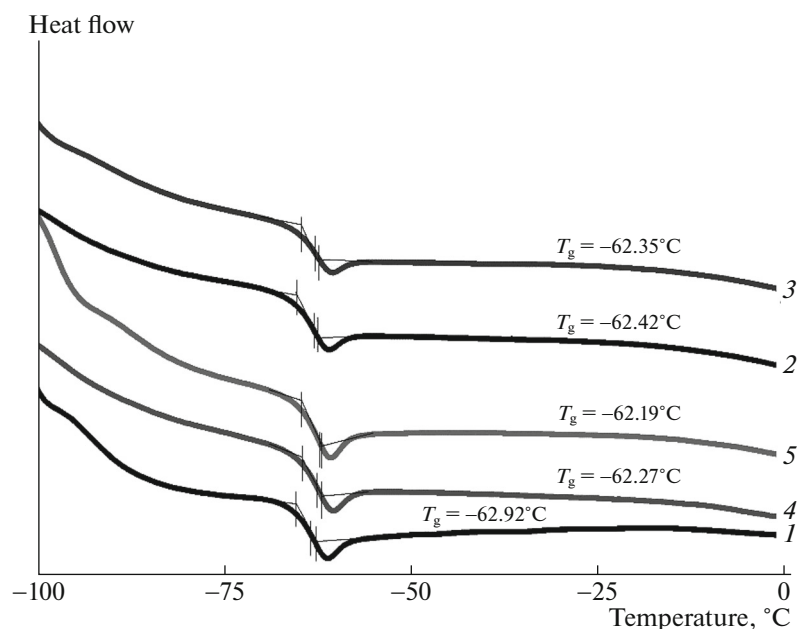
Fig. 9. DSC spectroscopy of (*1*) pure NR and modified NR films: (*2*) NR/10% PMLMA₁, (*3*) NR/15% PMLMA₁, (*4*) NR/10% PMLMA₂, and (*5*) NR/15% PMLMA₂.

of entanglements and thus improves mechanical strength of NR films. From Fig 8b, elongations at breaks of NR/PMLMA₁films are superior to the corresponding NR/PMLMA₂ films, indicating the good elasticity of NR/PMLMA₁ films. It may be the fact that LMA molar ratios of PMLMA₁ is higher than that of PMLMA₂, resulting in the increment of rubber-like ability.

DSC thermograms of NR/PMLMA₁ and NR/PMLMA₂ blend films. To further explain the effect of PMLMA₁ and PMLMA₂ on NR film, DSC was employed to analyze glass transition temperature T_g of blend components. Because DSC spectra of NR/copolymer only show the T_g of NR phase when the loading is less than 20%, in this experiment we mainly focus on the changes in T_g of NR phase. From Fig. 9, it is found that T_g of NR/PMLMA₁is close to the T_g of pure NR compared to corresponding NR/PMLMA₂, suggesting the good compatibility between NR and PMLMA₁. This is due to the fact that the LMA molar ratio of PMLMA₁is higher than that of PMLMA₂, so that PMLMA₁chains are more flexible than PMLMA₂ chains. In addition, because the molecular weight of PMLMA₁ is lower than PMLMA₂, short PMLMA₁ chains have no much effect on the movement of NR chains compared to PMLMA₂. Thus, the analysis of DSC spectra further indicated that the compatibility of NR/PMLMA₁ is stronger than that of NR/PMLMA₂.

CONCLUSIONS

In this study, two-layer PMLMA₁ and core-shell PMLMA₂ nanoparticles were respectively synthesized via suspension polymerization using traditional surfactants in the presence/absence of β-CD. A fine PMLMA₁ latex with low coagulum, high conversion and molecular weight can be obtained by choosing a proper polymerizing conditions. Compared to normal suspension polymerization, monomer droplets are of the small size and the formation of coagulum thus abated. However, due to the limitation in magnetic stirring, thickness and amounts of two-layer particles were difficult to control. Meantime, we study the effect of synthesized surfactants and β-CD on NR. The results showed that these stabilizers have strong inter-diffusion with NR. Lastly, the PMLMA₁ and PMLMA₂ latexes were incorporated into NR by latex compounding. TEM showed that PMLMA₁ or PMLMA₂ particles homogeneously distribute on the gray halo layer of NR particles by the formation of hydrogen bonds between stabilizers and proteins or phospholipids. However, due to high LMA molar ratios of PMLMA₁, the strong inter-diffusion of NR/PMLMA₁ contributed to obtaining smooth surface and dense cross-section morphologies. The fine interfacial adhesion between PMLMA₁ and NR benefited the formation of entanglements, which largely improves the mechanical strength of NR films. Because PMLMA₁ was more flexible than PMLMA₂, NR/PMLMA₁ possessed good elasticity compared to NR/PMLMA₂. DSC analysis further indicated that

the compatibility of NR/PMLMA$_1$ is stronger than that of NR/PMLMA$_2$.

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