

Design and Preparation of Cross-Linked α -Methylstyrene-Acrylonitrile Copolymer Nano-Particles for Elastomer Reinforcement

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ABSTRACT: Crosslinked α -methylstyrene and acrylonitrile (MStAN) copolymer particles in a latex form were synthesized by free radical emulsion polymerization. The particles took a spherical shape with an average size of 53.1 nm in a narrow distribution. When filled into styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR), and natural rubber (NR), the MStAN nanoparticles exhibited excellent reinforcing capabilities and the best in NBR. By the employment of heat treatment, mechanical properties of the MStAN-filled SBR compo-

sites had got remarkable further improvements. But mechanical properties, together with the morphology, of the MStAN-filled NBR composites, varied little after heat treatment, which, however, divulged the naturally good compatibility between the MStAN particles and the NBR matrix. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2459–2467, 2011

Key words: α -methylstyrene; acrylonitrile; copolymer; elastomers; reinforcement

INTRODUCTION

In most applications of elastomer, the elastomeric matrix requires reinforcement before utilization because of its weaknesses in modulus and strength. As this case stands, great parts of the rubber products are actually composites made of the elastomeric matrix, fillers, and some other curatives as well. And the filler, especially the reinforcing filler, plays an important role in determining the ultimate performance of the filled rubber compounds.^{1–10}

In the rubber industry, many types of reinforcing agents have already been developed; carbon black and silica are the ones that are commonly used. These conventional fillers usually are solid powders. It takes great energy and efforts to blend them with the high-viscous elastomer matrix in a mechanical blender. What's worse, because of the incompatibility with the rubber matrix, there is a tendency for the filler

particles to aggregate forming a strong filler network which may do harm to the dispersion of the fillers and the performance of the composites as well.

For further enhancing the performances of the filled elastomer composites, we had raised a concept of the ideal fillers for elastomer reinforcement.^{6,11} To be such an ideal filler, it should possess some distinctive features: (1) size in the nano scale, so as to provide excellent reinforcement to the elastomer matrix; (2) spherical shape, helping to reduce the processing-viscosity of the filled rubber; (3) easy access to a fine dispersion in the rubber matrix, holding back filler aggregation and weakening the filler network; (4) some chemical activity on the surface, providing certain chemical interaction between the filler and the matrix; (5) lower density, reducing the dynamically driving energy of the filled elastomer composites; (6) lower price. However, the conventional fillers, like carbon black and silica, do not possess all these features.

Different from the conventional fillers which have taken certain structure and surface properties as born, polymeric fillers can be designed and synthesized as the designer's intention. It made possible not only the control to the structure of fillers but also some needed modification to the fillers for adjusting the filler–rubber interactions.

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Few literatures in early days reported some work in rubber academy, using some polymeric filler, usually some rigid emulsion particles like polystyrene nano-particles, as the model fillers for the investigations on the mechanisms of elastomer reinforcement.^{12–16} Recently, rubber industry also started to show some interests in developing novel elastomer reinforcing agents from polymeric fillers. Zheng et al.¹⁷ from Goodyear Tire and Rubber Company have synthesized some model hairy nano-particles of crosslinked polystyrene cores and polybutadiene brushes, and Wang et al.¹⁸ from Bridgestone Americas have prepared various core-shell nano-particles with different shapes and sizes. In their work, the living anionic polymerization and living free radical polymerization were employed to prepare the core-shell structured polymers. They both thought the polymeric fillers capable as a novel elastomer reinforcing agents. But the end products of the polymeric fillers in their work were in a powder state, and to the best of our knowledge, aggregates of the filler particles would inevitably come into being as the result of the flexible, rubber-like polybutadiene shell that they both had in their powdered products. When preparing the rubber compound mixture, they had to take extra great energy and efforts to disperse these polymeric fillers into the high-viscous rubber matrix again.

Gauthier and Munam¹⁹ have prepared 400-nm sized polymeric particles of crosslinked polystyrene grafted with uniformly sized polyisoprene chains by a new grafting-onto method. With such a grafting-onto approach, the synthesis of the core part and the shell part could be carried out respectively, thus making precise control to the shell part polymer chains possible. But in our opinion, with a size of 400 nm, the particles might be too big in size to provide efficient reinforcement to the elastomer matrices. Besides, their grafting onto strategy employed a reaction of acetylation functionalized polystyrene particles coupling with the living polyisoprenyllithium chains, consequently, resulting in the complexity of the preparation process.

Our work was carried out in an attempt to provide a commercially viable method to prepare ideal fillers for elastomer reinforcement. Considering that most rubber types in use have their latex forms, we intended to prepare a kind of latex-formed polymeric fillers for the reinforcement of the elastomeric matrices. Specifically in this work, α -methylstyrene (α -MSt) and acrylonitrile (AN) were chosen as the monomers due to easy access and their compatibility with the commonly used elastomer matrices such as styrene-butadiene rubber (SBR) and nitrile-butadiene rubber (NBR). Furthermore, the introduction of acrylonitrile could improve the glass transition temperature (T_g) of the copolymers. Divinyl benzene (DVB) was also introduced into the polymerization

system as the crosslinking agent for further enhancing the T_g and stiffness of the polymer particles in case of possible applications in hot environment. Emulsion radical polymerization was employed as the synthesis technique to prepare such latex-formed polymeric fillers.

In our work, the synthesized crosslinked α -methylstyrene-acrylonitrile copolymer (MStAN) in the latex form was compounded with certain rubber latex in the energy-saving latex compounding method (LCM).^{20–23} As a water-mediating compounding method, LCM greatly reduced the viscosity of both the filler system and the bulk matrix system, thus saving tremendous amount of energy and resulting in better dispersion of the fillers.

A soft shell (like polyisoprene) over the particles, composed of some polymer compatible with the elastomer matrix, helping to adjust the filler–rubber interactions, has also been designed. We had also developed such a grafting-onto strategy by employing carboxylation functionalized then acyl-chlorinated core particles and living anionic polymerization prepared end-hydroxylated polyisoprene chains. The coupling reaction of acyl chloride and the hydroxyl groups made the preparation process much easier. The work covering that part will be reported in another paper.

In this work, we focused on the MStAN particles themselves. The influence from composition and crosslinking density on the properties of the MStAN particles, the reinforcement of the MStAN spherical nano-particles to the elastomer matrices and the influence of heat treatment to the filled composites were investigated, respectively.

EXPERIMENT

Materials

α -methylstyrene [α -MSt, Alfa Aesar China (Tianjin) Co., Ltd.], acrylonitrile [AN, Alfa Aesar China (Tianjin) Co., Ltd.], divinyl benzene [DVB, Jinke Fine Chemical Agent (Tianjin) Co., Ltd., China], ammonium persulfate (APS, Beijing Chemical Agent Co., Ltd., China), polyoxyethylene octylphenol ether [emulsifier OP-10, Vason Chemical Agent Co., Ltd (Tianjin), China], and sodium dodecyl sulfonate (SDS, Beijing Yili Fine Chemical Co., Ltd., China) were used as received. Rubber latexes were used as received, and the basic property information was provided in Table I. All other chemicals for rubber compounds are reagent-grade commercial products, and were used as received without further purification.

Synthesis of the MStAN copolymer

A four-necked flask equipped with a stirrer, a reflux condenser, a dropping funnel, and a thermometer,

TABLE I
Basic Property Information of the Rubber Latexes Used

Rubber type	Manufacture brand	Manufacturer	Basic information	Solid content
Styrene-butadiene rubber (SBR)	SBR-1502	Jilin petrochemical, China	of which styrene content is 23 wt %	21%
Nitrile-butadiene rubber (NBR)	LHN-212	Lanzhou petrochemical, China	of which acrylonitrile content is 26 wt %	46%
Natural rubber (NR)	Yun-Biao 1#	Beijing latex products factory, China	–	63%

was first charged with appropriate emulsifier SDS/OP-10 and deionized water. Start the stirrer at an appropriate speed for a while until an evenly blended mixture was obtained. The batch was then charged with certain amount of monomers of α -MSt, AN, and DVB at given ratio. Following another 30-min emulsification, the batch was heated to 70°C. When temperature got stable, polymerization was initiated by adding APS water solution. NaHCO₃ water solution was added to adjust the pH value of the latex equal to 7. The batch temperature of 70°C was maintained during the entire polymerization process. Remaining monomers were added by dripping since 30 min after the initiation. Hours later, the emulsion polymerization reaction completed. And obtained was the crosslinked α -methylstyrene-acrylonitrile copolymer (MStAN) latex.

Preparation of the MStAN-filled elastomer composites

The MStAN-filled elastomer composites were prepared by means of LCM. The crosslinked MStAN latex and rubber latex were mixed at given ratio by a mechanical stirrer for a period of time. After that, the even mixture was poured into the CaCl₂ water solution in stirring for coagulation. The master batch was washed several times before drying in an air oven at 50°C for 24 h. All the ingredients of curatives were added in a two-roll miller (see Table II). The master batch was then vulcanized at given temperature (150°C for SBR, 160°C for NBR, and 145°C for NR) for a time period of T_{90} under the pressure of 15 MPa.

Characterization techniques

Tensor 27 Fourier transform infrared spectrometer (FTIR, German Bruker Optik GmbH) was employed to detect the composition of the MStAN copolymer. The particle size and the particle size distribution were measured by Zetasizer Nano ZS particle analyzer (UK Malvern Instruments) in the means of dynamic light scattering (DLS) with a 633-nm red laser at the measuring angle of 135° and at the test-

ing temperature of 25°C. The morphologies of the copolymer particles in the tensile-fractured surface of the filled elastomer composites were detected by S-4700 scanning electron microscope (Japan Hitachi) under the operation of 20 kV. TEM images of the copolymer particles were obtained on a Hitachi H-800 transmission electron microscope (Japan Hitachi) operated at 200 kV; samples were prepared by dropping 10 times diluted copolymer particles latex onto carbon-film-covered copper meshes. DSC tests were carried out with DSC-2C different scanning calorimeter (US Perkin-Elmer) in N₂ gas flow with a heating rate of 10°C min⁻¹. Measurements of dynamical mechanical rheology were performed with the rheometer RPA 2000 (Alpha Technologies, USA) at the temperature of 60°C with the frequency of 1 Hz.

Dumbbell-shaped specimens, possessing a gauge length (benchmark) 25-mm long and a gauge width of 6 mm, were cut from a vulcanized flat sample sheet with die C in ASTM D412. The test specimens were preconditioned to 20% relative humidity and 23°C to standardize the test conditions. The mechanical properties tests were conducted on an Instron-type tensile testing machine at 23°C and a grips-separating speed of 500 mm min⁻¹ according to ASTM D412

TABLE II
Recipes for SBR, NR, and NBR Composites

Ingredients	Loading (phr ^a)	
SBR or NR	100	–
NBR	–	100
MStAN	Varied	
ZnO	3.0	5.0
Stearic Acid (SA)	1.0	1.0
Accelerator D ^b	0.5	–
Accelerator DM ^c	0.5	1.0
Accelerator TT ^d	0.2	–
Antioxidant 4010NA ^e	1.0	2.0
Sulfur	2.0	1.5

^a Parts per hundred rubber parts in weight.

^b Diphenyl guanideine.

^c 2,2'-dibenzothiazole disulfide.

^d Tetramethylthiuram disulfide.

^e N-isopropyl-N'-phenyl-p-phenylenediamine.

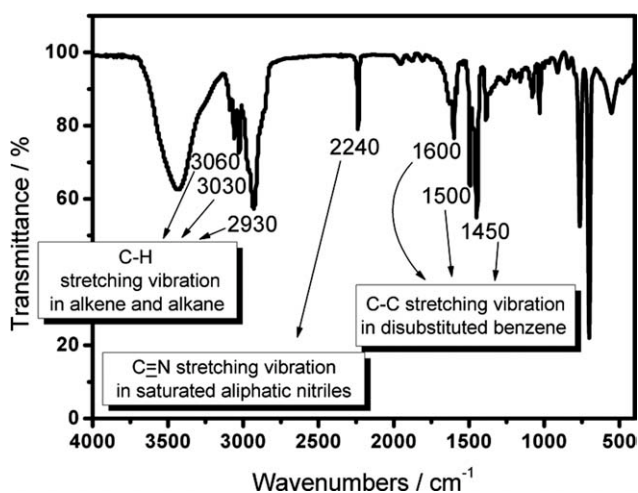


Figure 1 FTIR spectrum of the MStAN copolymer.

(Method A), and five specimens were tested to give the average. Shore A hardness of the vulcanizates was measured according to ASTM D2240, using a XY-1 Type A durometer (No. 4 Chemical Machinery Plant of Shanghai Chemical Equipment, China); three different spots on each over 6-mm-thick sample were measured to give the average. Tear strength was determined according to ASTM D624 using specimens cut from a vulcanized flat sheet with a right-angle tear die C; tearing tests were performed on the same Instron-type tensile machine as the tensile tests did at 23°C and a grips-separating speed of 500 mm min⁻¹.

RESULTS AND DISCUSSION

Characterization on spherical nano-particles of MStAN copolymer

With α -MSt, AN, and DVB consumption at varied ratio, the crosslinked MStAN spherical nano-particles were prepared by radical emulsion polymerization. And the composition, size, morphology, and glass-transition temperature (T_g) of the crosslinked MStAN spherical nano-particles were analyzed, respectively.

Composition

The composition of the MStAN copolymer with α -MSt and AN at a ratio of 2 : 1 in weight was analyzed by FTIR. As seen in Figure 1, the characteristic peaks of C—C stretching vibration of disubstituted benzene and the C≡N stretching vibration of saturated aliphatic nitrile were observed, respectively. The stretching vibration of C—H observed at 2930 cm⁻¹ indicated that a transition from alkene (the C—H stretching vibration in C=C is 3100–3010 cm⁻¹) to alkane (the C—H stretching vibration in C—C is

3000–2850 cm⁻¹) took place. All the information from the FTIR analysis suggested that a copolymer of α -methylstyrene and acrylonitrile was obtained.

Morphology, size, and size distribution

Such crosslinked MStAN copolymer particles were also analyzed with Zetasizer Nano ZS particle analyzer, SEM, and TEM. Results showed that the MStAN nano-particles took a spherical shape with an average size of 53.1 nm, as shown in Figure 2. Polydispersity index (PDI) of the particle size distribution was 0.038, proving a narrow distribution was achieved.

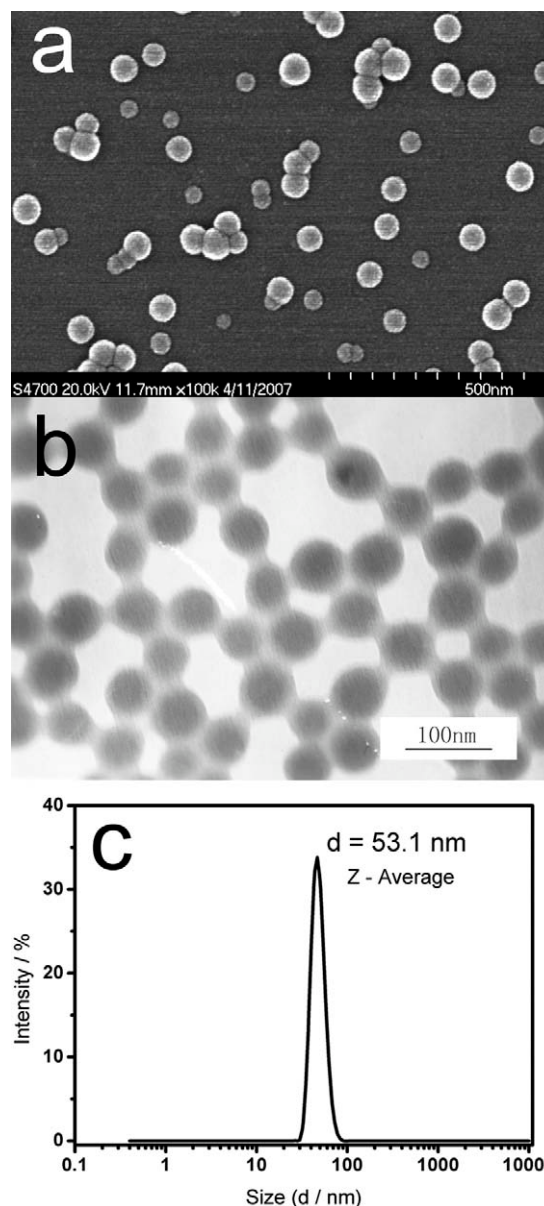


Figure 2 Morphology, size, and size distribution of MStAN particles (a is the image from SEM; b is the image from TEM; c is the result from DLS test).

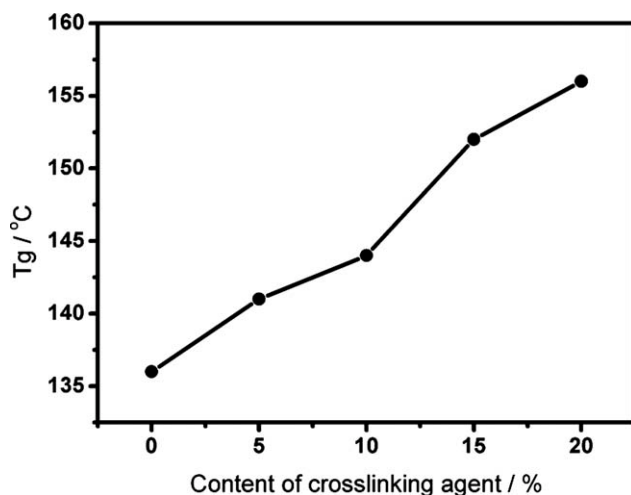


Figure 3 Influence on T_g of the crosslinked MStAN copolymer from crosslinking density.

The nano-sized particles are essential to the reinforcement of the elastomer matrix. Because of the high specific surface area, they provide sufficient interphase for the filler–rubber interactions, and make the elastomer molecular chain segment orientation possible in the stretching process. The elastomer molecular chains stick to the filler particles because of the filler–rubber interactions; when in tension, the elastomer molecular chains may slip along the filler particle surface to some extent; then the chains stick back to the filler particles again. In further tension, the stick-slip process goes round and round, resulting in the orientation of the elastomer molecular chain segments. Between the neighboring filler particles, several oriented elastomer chain segments at the same length become to bear the outer force simultaneously. The inside details turn out to be higher modulus of the sample shown as strain-hardening in the stress–strain curve.

Glass-transition temperature (T_g)

Varied ratios of α -MSt and AN monomers in copolymerization lead to differences in composition of the MStAN copolymers, and furthermore, alter the properties of the MStAN spherical particles. The influence on T_g of the MStAN copolymers from composition, therefore, was investigated. It was found that with the increase of AN content in monomers, the T_g of the MStAN copolymer went up subsequently, but the emulsion polymerization system exhibited a loss in stability as well. On balance, a composition of α -MS and AN consumption at the ratio of 2 : 1 was made the choice.

The crosslinking density is another factor that will affect the properties of the MStAN spherical particles. As shown in Figure 3, with composition of

α -MS and AN fixed at 2 : 1, the T_g of the crosslinked MStAN copolymer increased with higher DVB consumption. Meanwhile, there were also some effects to the emulsion polymerization system. When the DVB consumption increased, a loss of the stability of the emulsion polymerization system was also observed in our experiments. When filtering the copolymer latex obtained after the emulsion polymerization, we found the gel part in the latex increased with higher DVB consumption. Thus, taking into account of both the effects on T_g and the stability of the emulsion polymerization system, we took the DVB consumption of 15 wt % of the α -MS and AN monomer loading.

Reinforcement to the elastomeric matrix

The crosslinked MStAN spherical nano-particles with α -MS and AN at a ratio of 2 : 1 in weight and DVB consumption of 15 wt % of the α -MS and AN loading were employed as an attempt of such polymeric ideal fillers to study their reinforcement to the elastomeric matrices. The master batches of the MStAN-filled elastomer composites were prepared by LCM.

Properties of filled NBR composites with varied loadings

A series of NBR composites filled with the crosslinked MStAN spherical nano-particles were prepared at the loading of 0, 10, 20, 30, and 40 phr. The tensile tests were conducted with dumbbell-shape samples; and the tear tests were carried out with right-angle samples.

As can be seen in Table III, with varied loading of the MStAN particles, the filled NBR composites exhibited remarkable improvements in stress at given elongation, tensile strength, and tear strength compared with those of the neat NBR. The hardness of the filled composites went up with the increased filler loading; while the elongation at break varied a little.

The improved mechanical performances of the MStAN-filled NBR composites were resulted from the good compatibility and strong interactions between the crosslinked MStAN spherical nano-particles and the NBR matrix, and also a fine dispersion of the filler achieved by LCM.

In varied elastomer matrices

The composites filled with MStAN in several elastomer matrices were prepared by the means of LCM. And the mechanical properties of the composites with the same filler loading were investigated with the results listed in Table IV.

TABLE III
Mechanical Properties of the MStAN-Filled NBR Composites at Varied Loadings

Samples	Shore A hardness		Stress at 100% elongation/MPa		Stress at 300% elongation/MPa		Tensile strength/MPa		Elongation at break (%)		Permanent set (%)		Tear strength/(KNm ⁻¹)	
	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.
Pure NBR	55	1	1.2	0.1	2.2	0.1	3.5	0.8	438	42	0	0	16	2
MStAN (10)/NBR	62	0	1.6	0.0	4.4	0.1	10.0	1.1	451	22	4	0	27	3
MStAN (20)/NBR	70	1	2.0	0.1	5.9	0.2	15.9	2.2	485	21	8	0	33	1
MStAN (30)/NBR	75	1	2.3	0.2	7.9	0.8	17.1	0.8	455	23	8	0	37	2
MStAN (40)/NBR	82	1	3.3	0.2	12.2	0.9	16.0	1.1	353	16	8	0	39	1

Note: S.D. stands for standard deviation; and the unbiased standard deviation (S_{N-1}) was calculated by eq. (1), in which N is the number of values in the set of data, x_i is a value in the set of data, and \bar{x} is the mean value of all values in the set of data.

$$S_{N-1} = \sqrt{\frac{1}{N-1} \cdot \sum_{i=1}^N (x_i - \bar{x})^2} \quad (1)$$

As shown in the results, compared with neat SBR and NBR matrices, the MStAN-filled composites performed great improvements in stress at given elongation, tensile strength, and tear strength as well. Especially in the NBR matrix, a tremendous enhancement in the mechanical properties was observed. However, in the NR matrix, the stress at given elongation and the tear strength got enhanced; while the tensile strength of the filled composites decreased a lot compared with that of the neat NR matrix because of the poor compatibility between the NR matrix and the MStAN spherical nano-particles which had a strong polarity introduced by the cyano group. Another reason for the deterioration in tensile strength is that the NR matrix has a property of stretch-induced crystallization, which helps to self-reinforce the matrix while stretching. When introduced with the MStAN spherical nano-particles, such stretch-induced crystallization of the molecular chains may get restricted, finally resulting in reduction in tensile strength.

The MStAN spherical nano-particles had strong polarity induced by the cyano group, which thus, led

to poor compatibility with the nonpolar SBR and NR matrix, resulting in the agglomeration of the particles as can be seen in Figure 4(a,c). However, in a polar matrix like NBR, the MStAN spherical nano-particles had a good compatibility with the matrix, and this helped to achieve a fine dispersion of the filler particles in the matrix as seen in Figure 4(b). It was the difference in the morphologies of the filled composites bringing about by the compatibility between the matrix and the MStAN spherical nano-particles that resulted in the different performances in mechanical behaviors.

The compatibility or interactions between the matrix and the polymeric filler particles can be modified by designing a core-shell structure which means to introduce a compatible zone of some other polymers like polyisoprene covering the core of some hard polymers like the MStAN copolymers here. And the work we have done on this idea will be reported in another article.

Besides the introduction of the compatible zone, there is another alternative way to improve the dispersion of the MStAN spherical nano-particles in the

TABLE IV
Mechanical Properties of MStAN-Filled SBR, NBR, and NR Composites

Samples	Shore A hardness		Stress at 100% elongation/MPa		Stress at 300% elongation/MPa		Tensile strength/MPa		Elongation at break (%)		Permanent set (%)		Tear strength/(KNm ⁻¹)	
	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.
Pure SBR	48	1	1.1	0.1	1.5	0.1	2.0	0.5	461	39	4	0	11	1
MStAN/SBR	76	0	2.2	0.1	3.2	0.1	6.7	0.5	619	18	28	1	28	2
Pure NBR	55	1	1.2	0.1	2.2	0.1	3.5	0.8	438	42	0	0	16	2
MStAN/NBR	75	1	2.3	0.2	7.9	0.8	17.1	0.8	455	23	8	0	37	2
Pure NR	35	1	0.7	0.1	1.6	0.1	28.3	1.1	801	45	16	0	30	1
MStAN/NR	75	0	1.9	0.1	3.5	0.2	12.4	2.0	601	20	48	1	36	1

Note: the loading of MStAN fillers was 30 phr.

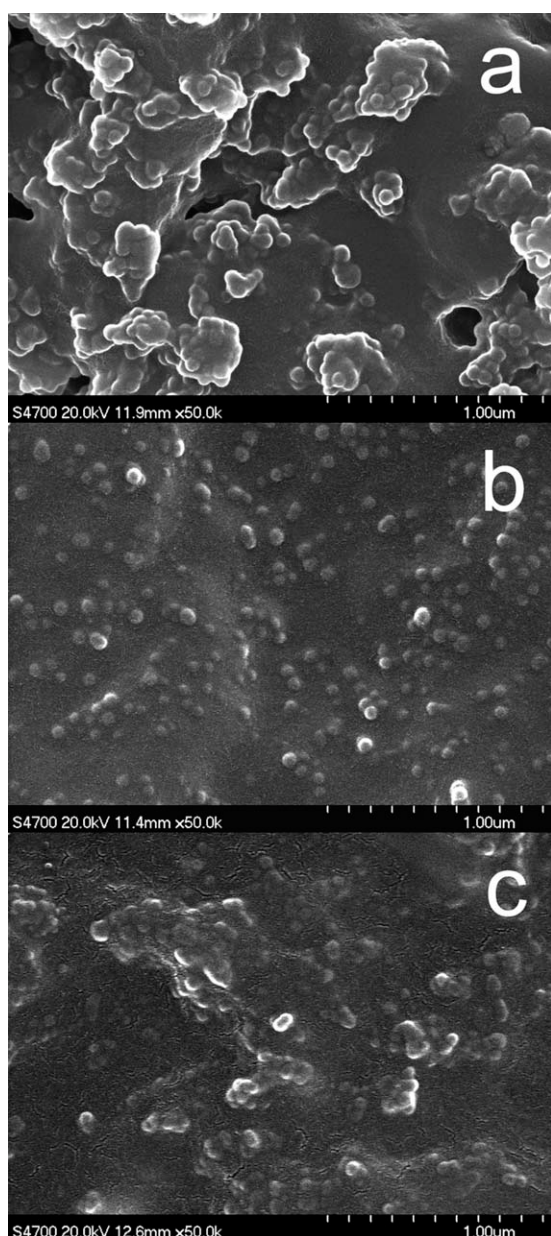


Figure 4 Morphologies of the MStAN spherical nano-particles in different elastomer matrices (a is the SEM image of the tensile-fractured surface of MStAN/SBR nanocomposites, b is that of the MStAN/NBR nanocomposites, and c is that of the MStAN/NR nanocomposites).

nonpolar matrix like SBR. Heat treatment can also work to promote the interactions between the filler particles and the elastomer matrix, therefore, achieving better dispersion of the filler in the matrix and enhancing the mechanical properties of the composites.

Heat treatment effect for MStAN/SBR and MStAN/NBR nanocomposites

In MStAN/SBR nanocomposites

Heat treatment on a heated two-roll miller at 140°C for 15 min was employed to solve the problem that the MStAN spherical nano-particles agglomerated in the SBR matrix due to the poor compatibility of the filler and the matrix. Mechanical properties and morphologies of the heat-treated samples were compared with those of the samples which didn't take the heat treatment at the same loading of the MStAN spherical nano-particles.

It was observed in Table V that through heat treatment, the mechanical properties of the MStAN-filled SBR composites such as stress at given elongation and tensile strength got great enhancement, while the hardness of the composites showed a slight decrease from no heat treatment to heat treatment on the heated two-roll miller. The changes in the mechanical properties revealed that the employment of the heat treatment reduced the agglomeration of the MStAN spherical nano-particles in the SBR matrix, the filler network was weakened, and the interaction between the MStAN particles and the SBR matrix got improved.

Results were proven by the environmental scanning electron microscopy (ESEM) observation and the dynamical mechanical rheology measurements. As seen in Figure 5(c), the Payne effect was weakened through heat treatment, which indicated that the filler network had been weakened. Shown in the images in Figure 5(a,b), the agglomerates of the MStAN particles before the heat treatment turned into well-dispersed particles in the SBR matrix. The heat treatment promoted the dispersion of the MStAN particles in the SBR matrix and weakened the filler network.

TABLE V
Comparison of the Mechanical Properties of the MStAN-Filled SBR Composites with and Without Heat Treatment

Samples	Shore A hardness		Stress at 300% elongation/MPa		Tensile strength/MPa		Elongation at break (%)		Permanent set (%)	
	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.	Median	S.D.
No heat treatment	76	0	3.2	0.1	6.7	0.5	619	18	28	1
Heat treated on a miller	65	0	5.0	0.1	9.6	0.4	460	15	16	1

Note: The loading of the MStAN filler was 30 phr.

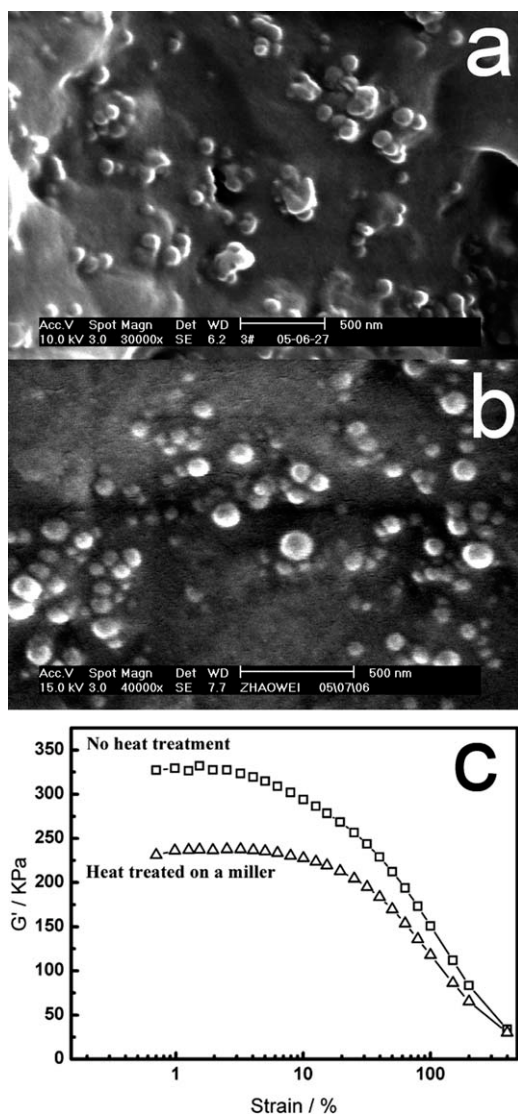


Figure 5 Morphologies and strain amplitude dependence of storage modulus (G') of the MStAN-filled SBR composites before and after the heat treatment (a and b, respectively, are the ESEM images of the tensile-fractured surfaces of the MStAN(30)/SBR composites with no heat treatment and heat treated at 140°C for 15 min; c is the strain amplitude dependence of storage modulus (G') of the composites with and without heat treatment).

In MStAN/NBR composites

The influence of heat treatment to the MStAN-filled NBR composites was also investigated with the intention of further enhancing the performances of the filled composites. Heat treatments to the MStAN/NBR composites at a filler loading of 40 phr were carried out on a heated two-roll miller at varied temperature for 15 min.

However, as shown by the mechanical results [the plot in Fig. 6(a)], there was no distinguishing further improvements after the heat treatment. But that was not something bad; it just revealed that the MStAN

particles achieved a well dispersion and had a strong filler–rubber interaction in the NBR matrix even before the heat treatment, leaving little room for further enhancement by the heat treatment. This could also be proved by the slight differences in filler network shown in Figure 6(b) and the morphologies in Figure 7.

CONCLUSIONS

A crosslinked copolymer of α -methylstyrene, acrylonitrile and divinyl benzene was successfully synthesized by radical emulsion polymerization. The MStAN copolymer took a spherical shape with an average diameter of 53.1 nm and a narrow particle size distribution. The glass-transition temperature of the copolymer increased with higher AN content and higher DVB consumption.

When filled into elastomeric matrices, the MStAN copolymer nano-particles were found to be both

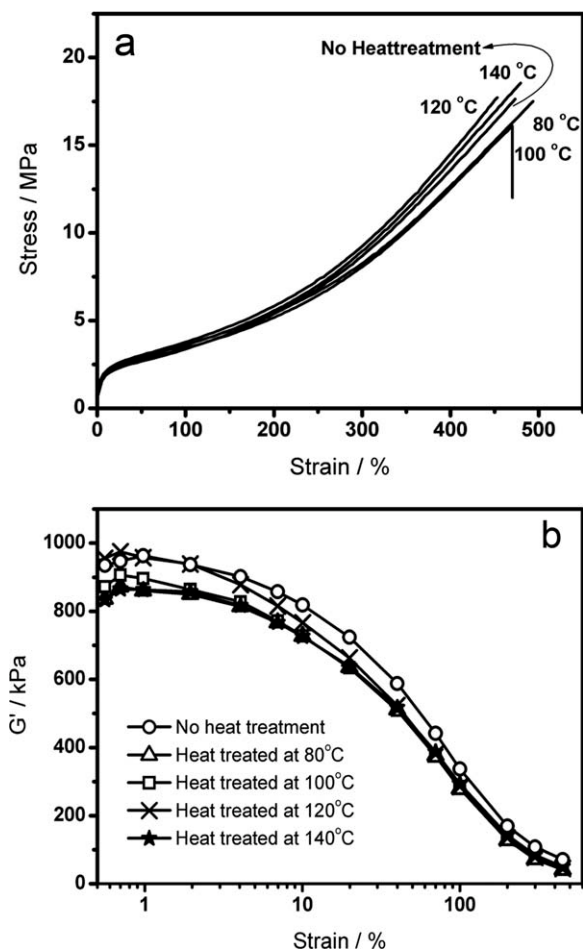


Figure 6 Stress–strain performance and strain amplitude dependence of storage modulus (G') of the MStAN-filled NBR composites at varied heat treatment temperatures (a is the stress–strain performance; b is the strain amplitude dependence of storage modulus).

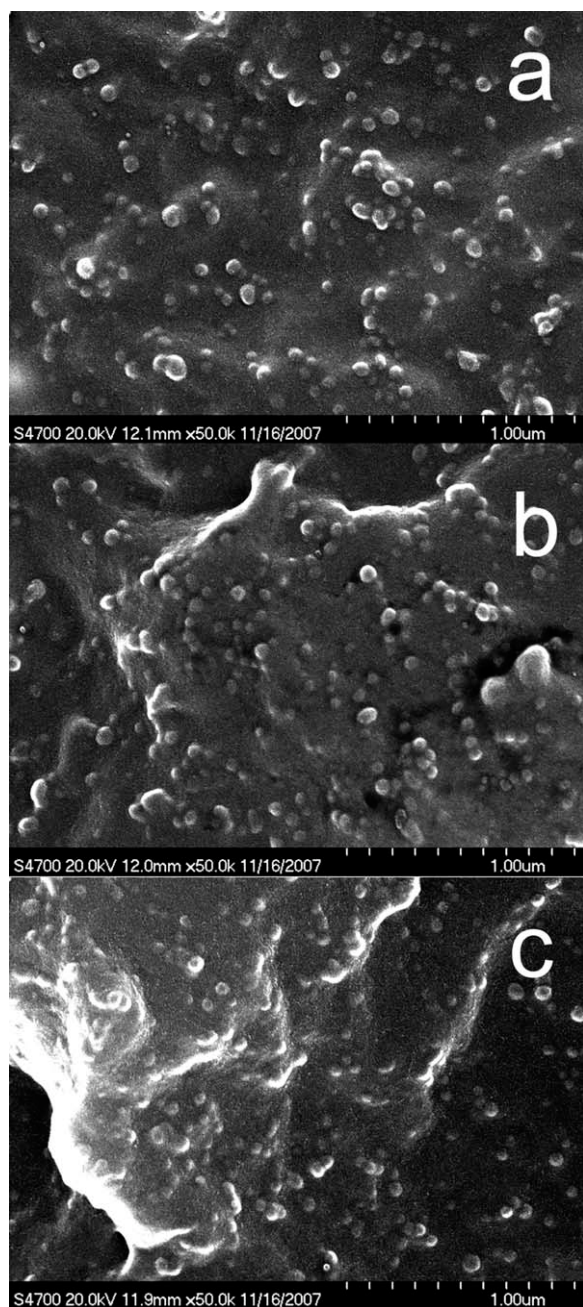


Figure 7 Morphologies of the MStAN-filled NBR composites before and after the heat treatment (a, b, c are the SEM images for the sample with no heat treatment and the samples heat treated at 100 and 140°C, respectively).

effective and efficient in elastomer reinforcement. The MStAN-filled SBR and NBR composites exhibited dramatic enhancement in mechanical perform-

ances, compared with the neat elastomer matrices. In the MStAN-filled NR composites, because the stretch-induced crystallization of the NR molecular chains had been restricted, there were only improvements in the stress at elongation and tear strength, not in the tensile strength.

Heat treatment to the filled composites made it a way for further enhancing the performances of the nano-composites. Compared with the effect of the heat treatment to MStAN/NBR composites, which naturally possessed a good dispersion of the MStAN particles, heat treatment resulted in much more dramatic effects in the MStAN/SBR composites.

References

1. Wang, M. J. *Rubber Chem Technol* 1998, 71, 520.
2. Hamed, G. R. *Rubber Chem Technol* 2007, 80, 533.
3. Allen, G. *Plast Rubber* 1976, 1, 38.
4. Payne, A. R.; Whittaker, R. E. *Composites* 1970, 1, 203.
5. Bokobza, L. *Macromol Mater Eng* 2004, 289, 607.
6. Zhang, L. Q.; Jia, D. M. *Symposium of International Rubber Conference, Beijing, 2004*; p46.
7. Boonstra, B. B. *Polymer* 1979, 20, 691.
8. Mark, J. E.; Abou-Hussein, R.; Sen, T. Z.; Kloczkowski, A. *Polymer* 2005, 46, 8894.
9. Mullins, L. *Rubber Chem Technol* 1969, 42, 339.
10. Gary, R. H. *Rubber Chem Technol* 2000, 73, 524.
11. Zhang, L. Q. *Invited Lecture for 9th International Conference on Frontiers of Polymers and Advanced Materials (ICFPAM), Poland, 2007*.
12. Kraus, G.; Rollmann, K. W.; Gruver, J. T. *Macromolecules* 1970, 3, 92.
13. Morton, M.; Healy, J. C. *Appl Polym Symp* 1968, 7, 155.
14. Morton, M. *Adv Chem Ser* 1971, 99, 490.
15. Cai, J. J.; Salovey, R. *J Mater Sci* 1999, 34, 4719.
16. Cai, J. J.; Salovey, R. *J Mater Sci* 2001, 36, 3947.
17. Zheng, L.; Xie, A. F.; Lean, J. T. *Macromolecules* 2004, 37, 9954.
18. Wang, X. R.; Hall, J. E.; Warren, S.; Krom, J.; Magistrelli, J. M.; Rackaitis, M.; Bohm, G. G. A. *Macromolecules* 2007, 40, 499.
19. Gauthier, M.; Munam, A. *Polymer* 2009, 50, 6032.
20. Zhang, L. Q.; Wang, Y. Z.; Wang, Y. Q.; Yuan, S.; Yu, D. S. *J Appl Polym Sci* 2000, 78, 1873.
21. Wu, Y. P.; Wang, Y. Q.; Zhang, H. F.; Wang, Y. Z.; Yu, D. S.; Zhang, L. Q.; Yang, J. *Compos Sci Technol* 2005, 65, 1195.
22. Wang, Y. Q.; Wu, Y. P.; Zhang, H. F.; Zhang, L. Q.; Wang, B.; Wang, Z. F. *Macromol Rapid Commun* 2004, 25, 1973.
23. Ma, J.; Xiang, P.; Mai, Y. W.; Zhang, L. Q. *Macromol Rapid Commun* 2004, 25, 1692.