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Design and preparation of cross-linked α-methylstyrene acrylonitrile copolymer nanoparticles and their interfacial investigation with rubber

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ABSTRACT: Cross-linked α-methylstyrene and acrylonitrile (MStAN) copolymer particles in a latex form were synthesized by free radical emulsion polymerization. The particles showed a narrow size distribution and an average diameter of 65 nm. The amount of the vinyl groups at the surface of the (MStAN) copolymer particles resulted from varied amount of the initiator (APS) and the cross-linking agent (DVB) was detected by iodine titration method. When filled into ethylene propylene rubber (EPR), the MStAN nanoparticles exhibited excellent reinforcing capabilities, and with the increase of the vinyl groups at the surface of MStAN particles, the tensile stress of MStAN/EPR increased. Results demonstrated that the vinyl groups at the surface of the (MStAN) copolymer particles provided certain chemical interactions between the filler particles and the macromolecular chains of rubber matrix. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41914.

INTRODUCTION

Commercial rubbers are often filled with fillers, either to enhance their mechanical properties or to reduce cost.[1] Reinforcing by nanoparticles is an effective way to enhance the performances of the elastomeric polymers; the properties of the nanoparticles filled rubber depend primarily on the interactions between the matrix and the filler particles, although interparticle interactions are also important.[2] Strong interactions between the matrix polymer and the filler particles can increase the viscosity and the dynamic moduli, for example, certain chemical interaction between the matrix polymer and the filler particles can result in the increased cross-linking density of the composite,[3] formation of the bound rubber,[4,5] constrained of the molecular chain around the surface of fillers.[6–9]

Because of the incompatibility with the rubber matrix, many efforts have been devoted to investigate the influence of filler surface treatment on the filler-rubber interactions. In most studies commercial fillers such as carbon black, silica[10] are used. Filler-to-filler and filler-to-rubber interactions were characterized by TEM and SEM. The dispersion of the fillers in the rubber matrix verified the filler-to-rubber interaction indirectly. The complex viscosity and dynamic modulus of the composites were measured also to reveal the filler-to-rubber interaction.[11–13] However, these methods still did not characterize the active points on the surface of the fillers directly. Recently, rubber industry also started to show some interests in developing novel elastomer reinforcing agents from polymeric fillers. The polymeric fillers (usually some rigid emulsion particles like polystyrene nanoparticles) have lower densities than conventional fillers, the influence on dynamic moduli of model crosslinked polystyrene fillers has been investigated by simple dispersion of the particles in different matrices,[14–17] by incorporating the particles into the matrix network through covalent bonding, and by adding a shell to enhance filler compatibility with the matrix.[18–20]

We had raised a concept of the ideal fillers for elastomer reinforcement.[21,22] In our earlier work, cross-linked polystyrene (PS) particles and cross-linked α-methylstyrene acrylonitrile (MStAN) copolymer particles in a latex form were synthesized by free radical emulsion polymerization. Styrene-butadiene rubber (SBR) filled with cross-linked polystyrene (PS) particles, and nitrile-butadiene rubber (NBR) filled with cross-linked α-methylstyrene acrylonitrile (MStAN) copolymer particles were prepared. The PS and MStAN nanoparticles exhibited excellent reinforcing capabilities.[23–25] However, we have not yet discussed and analyzed the amount of the chemical activity at the surface of nanoparticles. Comparing the two kinds of particles, glasstransition temperature of the MStAN copolymer particles is higher than that of the PS particles, which can meet some high

Table I. Main Formula of Polymerization with α-MS and AN

Ingredients	Loading (wt %)
AN	30
α-MS	60
SDS/OP-10	3
APS	0.5–2
DVB	5–30
NaHCO$_3$	0.2
H$_2$O	150

Table II. Recipe for EPR Composites

	Loading (phr[a])			
Ingredients	I	II	III	IV
EPR	100	100	100	100
MStAN	30	30	0	0
DCP	2	0.2	0.2	2
TAIC	0.65	0	0	0.65

[a] Parts per hundred rubber parts in weight.

temperature vulcanization process requirements. Therefore, following study focused on the reinforcement of the MStAN spherical nano-particles to the elastomer matrices, and the influence of the quantity of chemical active spots at the surface on the chemical interaction between the rubber matrix and the filler.

In this work, polymeric fillers of MStAN nanoparticles were designed and prepared for elastomer reinforcement. The quantity of unreacted vinyl groups at the particle surface was analyzed. The nanoparticles were filled into the EPR matrix to prepare the filled rubber compound, and the influence from the vinyl groups of the nanoparticles on the filler-rubber interactions was investigated.

EXPERIMENTAL

Materials
Alpha-methylstyrene [α-St, Alfa Aesar China (Tianjin)], acrylonitrile [AN, Alfa Aesar China (Tianjin)], divinyl benzene [DVB, Jinke Fine Chemical Agent (Tianjin), China], ammonium persulfate (APS, Beijing Chemical Agent, China), polyoxyethylene octylphenol ether[emulsifier OP-10, Vason Chemical Agent (Tianjin), China], and sodium dodecyl sulfonate (SDS, Beijing Yili Fine Chemical, China) were used as received. EPR Rubber was purchase from Jilin Petro-Chemical. The dicumyl peroxide (DCP) (AkzoNoble Chemicals, Nanjing, China) and triallyl isocyanurate (TAIC) (Wah Sing Chemical, Jiangsu, China) were commercial products. All other chemicals for rubber com-

pounds 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, was first charged with appropriate amount of emulsifier SDS/OP-10 and deionized water. The stirrer was started 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-St, AN, and DVB at a predetermined ratio. The formulation for the polymerization was shown in Table I. Following another 30 min emulsification, the batch was heated to 75°C. When temperature was stable, polymerization was initiated by adding APS aqueous solution. NaHCO$_3$ aqueous solution was added to adjust the pH value of the latex to 7. The solution temperature was maintained at 75°C during the polymerization process. Remaining monomers were added by dripping after 30 min since the initiation. After 5 h, the emulsion polymerization reaction was stopped. And the cross-linked α-methyl styrene-acrylonitrile copolymer (MStAN) latex was obtained.

MStAN latex was demulsified by 5 wt % CaCl$_2$ aqueous solution and washed several times by deionized water. After dried under vacuum, the MStAN solid powder fillers were obtained.

Preparation of the MStAN-Filled Elastomer Composites
According to the formulation shown in Table II, MStAN nanoparticles, dicumyl peroxide (DCP), and TAIC were mixed into the EPR in a six-inch two-roll mill. The compound was
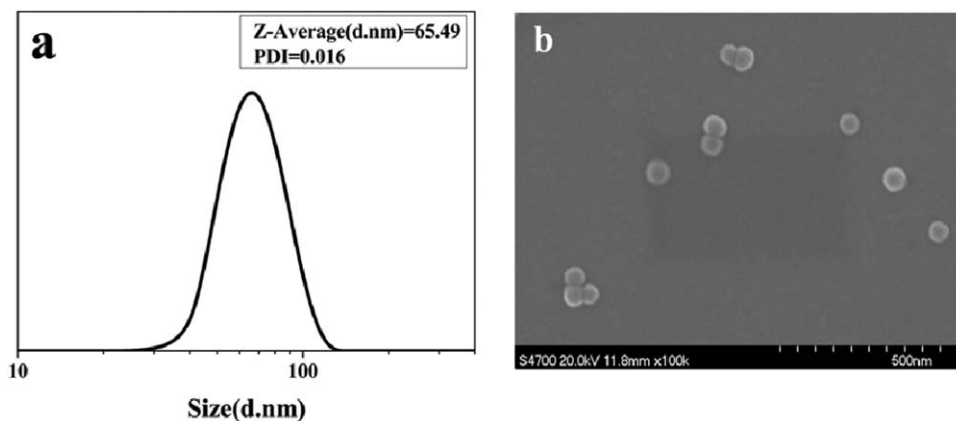
Figure 1. Morphology, size, and size distribution of cross-linked MStAN nanoparticles. (a) The result of the same sample from the DLS test and (b) the SEM image of MStAN nanoparticles particles with DVB consumption of 20 wt % of copolymer monomer loading.
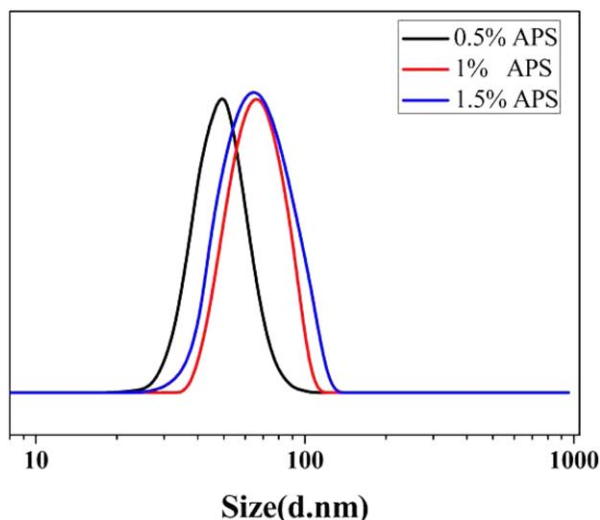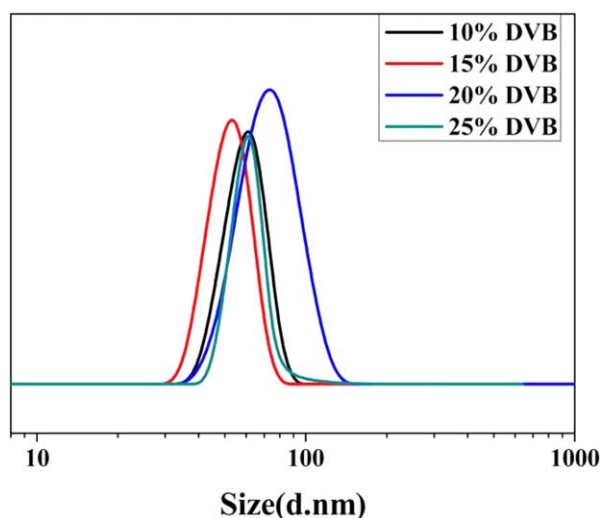
Figure 2. Effect of the content of the imitator (APS) on DLS of the MStAN nanoparticles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
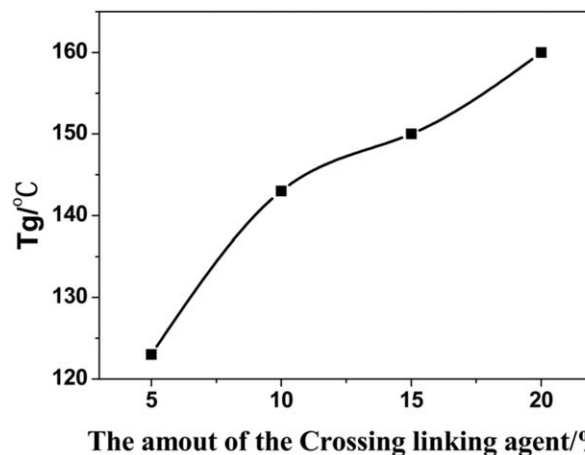
compression molded in a hot press at 160°C for the optimum curing time of T_{90}.

Characterization Techniques

The particle size and the particle size distribution were measured by Zeta sizer Nano ZS particle analyzer (UK Malvern Instruments) in the means of dynamic light scattering (DLS). The SEM images were obtained by S-4700 Scanning Electron Microscope (Japan Hitachi) performed at an accelerating voltage of 20 kV. DSC tests were carried out with DSC-2C differential scanning calorimeter (US Perkin-Elmer) in N_2 gas flow with a heating rate of 10°C/min. Tensor 27 Fourier transform infrared spectrometer(FTIR, German Bruker Optik Gmbh) was employed to detect the MStAN particles and the composition of the MStAN filled EPR, the scan range was 4000 to 400 cm^{-1} with a resolution of 0.5 cm^{-1}.

Figure 4. Tg of the MStAN nanoparticles with varied DVB concentration from DSC.

Vinyl groups in MStAN nanoparticles were determined by iodometry. A flask was charged with 0.5 g of prepared MStAN powder and 100 mL of chloroform; and some other flasks were prepared in the same way. The flasks were placed on the oscillation device for 2 h at 25°C. After oscillation at the speed of 200 r/min for 2 h, the MStAN was swelled and a uniform dispersion of chloroform solvent was formed. After that, 25 mL ICl solution was added to each flask, and then these flasks were kept for different periods of time of 4, 16, 36, 64, and 81 min. At the end of each period of time, the KI solution (KI, 10 g/L) was added into the flask and the solution was vibrated by ultrasonic for 30 min, in order to make the vinyl groups of the MStAN nanoparticles and ICl fully reacted. The samples were titrated by 0.1 mol/L $Na_2S_2O_3$ standard solution to calculate the content of the vinyl groups. The content of vinyl groups (Av) in the MStAN nanoparticles was calculated from the cost volume of $Na_2S_2O_3$.

Vulcanization kinetic characteristic curves of rubber compounds were determined on a curometer (Beihua Huanfeng, China) at
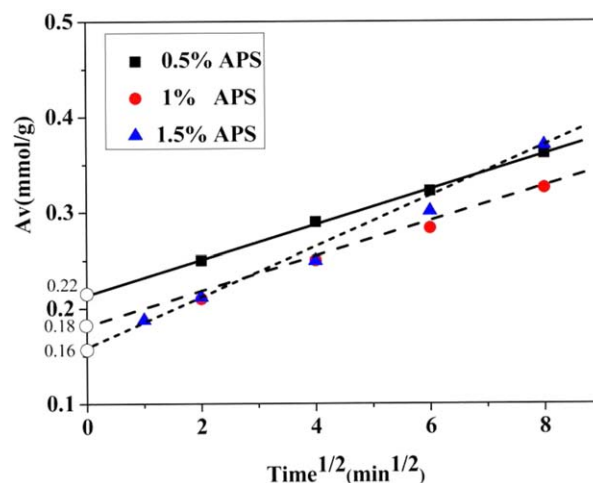

Figure 3. Particle size and distribution of the MStAN nanoparticles with varied DVB. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 5. The effect of APS concentration on the amount of vinyl groups on the surface of MStAN nanoparticles determined by extrapolation. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. The Total Amount of the Vinyl Groups and Its on the Surface of the MStAN Nanoparticles with DVB Concentration

DVB/ total monomer	10%	15%	20%	25%	30%
The amount of the vinyl groups on the surface of nanoparticles (mmol/g)	0.18 ± 0.10	0.35 ± 0.13	0.47 ± 0.12	0.38 ± 0.10	0.37 ± 0.11

the temperature of 160°C with set amplitude of 0.5° and vibration frequency of 100 cpm (1.66 Hz). Tensile tests were performed on a CTM 4104 tensile tester (SANS, Shenzhen, China) at a cross-head speed of 500 mm/min and a temperature of 23 ± 2°C according to ASTM D412. Shore A hardness of the vulcanizes were measured according to ASTM D2240, using a XY-1 type A durometer (No. 4 Chemical Machinery Plant of Shanghai Chemical Equipment, Shanghai, China), and three different spots of the sample (over 6 mm in thickness) were measured to give the average value.

RESULTS AND DISCUSSION

Particle Size, Morphology and Vinyl Groups on the Surface of the MStAN Nanoparticles

Particle Size, Morphology of MStAN Particles. With α-St, AN, and DVB at varied ratio, the cross-linked MStAN spherical nanoparticles were prepared by radical emulsion polymerization. The particle size of the as-prepared MStAN nanoparticles was analyzed with Zetasizer Nano ZS particle analyzer. The morphology of the nanoparticles was observed by SEM. The results showed that the MStAN nanoparticles took a spherical shape in the size of 50–70 nm with a narrow distribution, as seen in Figure 1.

Figure 2 shows DLS of MStAN particles which were prepared by seeded emulsion polymerization at different weight ratios of initiator (APS) with the content of the DVB kept 10 wt % of the monomers. With APS content increasing, the size of the particles changed slightly while and the size distribution became wider. From the emulsion polymerization mechanism, the more initiators were decomposed more radicals to form emulsion

micellars and the possibility of collisions between micellars increased, a part of the collided micellars were formed bigger size particles, which resulted the particle size distribution became wider.

MStAN nanoparticles with different cross-linking densities were prepared by varying the consumption of DVB at 5, 10, 15, and 20 wt % of the copolymer monomer loading with the content of the initiator (APS) kept 1 wt %. As shown in the Figure 3, the size and distribution of the MStAN copolymer changed slightly with the increasing content of DVB in monomers.

As seen in Figure 4, the glass-transition temperature of the MStAN particles increased with DVB concentration. Result indicated that the mobility of the MStAN nanoparticles molecules decreased. The glass-transition temperature of the cross-linked MStAN nanoparticles increased, thus the particles achieved higher modulus. The outcome above could make the cross-linked MStAN particles more competent when it was in high temperature environment applications.

Vinyl Groups on the Surface of the MStAN Nanoparticles. Divinyl benzene (DVB) is used as a cross-linking agent in the polymerization reaction, which has two reactive vinyl groups. When one vinyl group of the DVB reacted, the activity of the other vinyl group reduced obviously. Thus a part of the vinyl groups were left during the copolymerization reaction, which formed the rest vinyl groups of the MStAN nanoparticles. A part of these vinyl groups distributed inside the particles and some others were on the surface of the MStAN nanoparticles.[26] Given that the different content of the initiator (APS) and
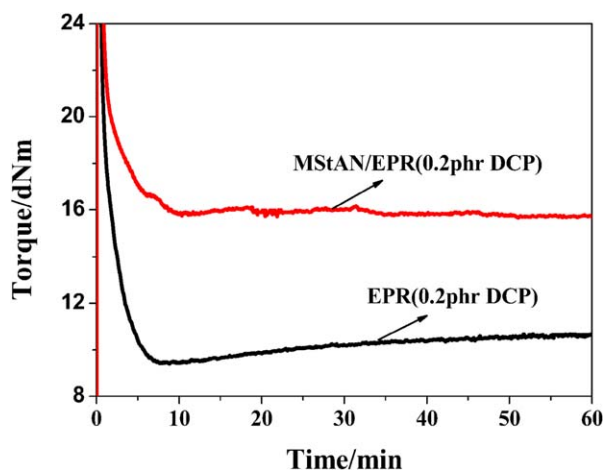
Figure 6. Curing kinetics of MStAN/EPR matrix and EPR matrix. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
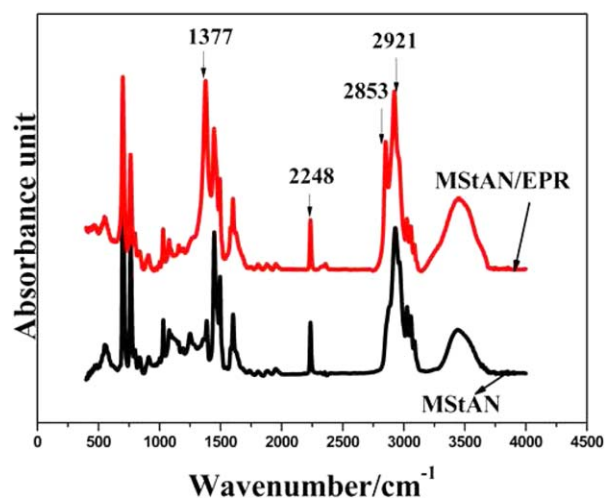
Figure 7. IR of the extraction MStAN/EPR composite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. Mechanical Properties of the MStAN-Filled EPR 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})
Pure EPR	43 ± 2	0.8 ± 0.2	0.9 ± 0.3	1.1 ± 0.3	516 ± 34	24 ± 3	6 ± 1
MStAN (30 phr)/EPR	62 ± 1	1.4 ± 0.1	2.4 ± 0.2	12.4 ± 0.5	761 ± 22	40 ± 5	25 ± 3

cross-linking agent (DVB) had little influence on the particle size as shown in the Figures 2 and 3, the amount of the vinyl groups on the surface of the MStAN nanoparticles was detected by means of the iodometry. It was found that the amount of the vinyl groups (Av) had a linear benefice relationship with the square root of the reaction time when the reaction time was above about 1 min.[27] It could be explained by staged diffusion process of ICl molecules. ICl molecules firstly reacted with vinyl groups which distributed on the surface of particles within extremely short time when the ICl solution was added to the flask, and then the reaction was a rate-determining stage which depended on diffusion process time. With the reaction time increase, the detected Av value increased, and a linear relationship was established between the Av value and the square root of reaction time in a specific range. If the rate-determining step of the detection of the vinyl groups is the diffusion process of ICl into the MStAN nanoparticles, the amount of vinyl groups detected should be proportional to the square root of the reaction time, assuming that the vinyl groups distribute homogeneously in the reacted layer. In present work, the amount of the vinyl groups at the surface of the MStAN particles could be estimated by extrapolating the straight part to 0 min as shown in the Figure 5.

The effect of the DVB concentration and the initiator (APS) concentration on the amount of surface vinyl groups of the MStAN nanoparticles was studied. Figure 5 shown that with the increase of initiator (APS) concentration in monomers, the amount of vinyl groups at the surface of MStAN nanoparticles decreased.
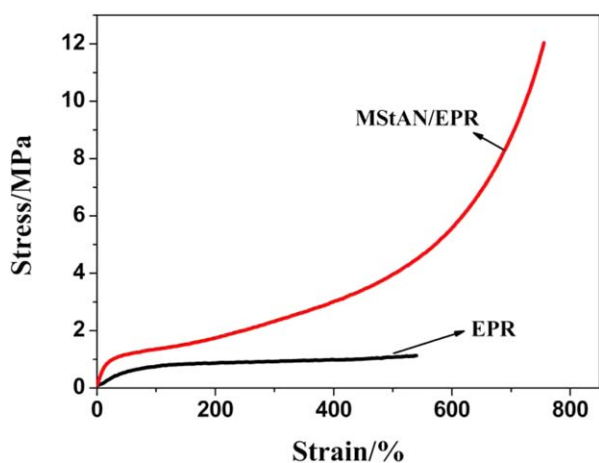
The amount of the vinyl groups on the surface of the MStAN nanoparticles was estimated by extrapolating the straight part in the figure to 0 min, as shown in Figure 5. Vinyl groups on the surface of the MStAN particles decreased with the increasing ratios of initiator in the copolymerization, because of the increasing of free radicals led to an increasing polymerization degree.

As shown in Table III, the amount of the vinyl groups of the MStAN nanoparticles increased and the content of the vinyl groups on the surface of the MStAN nanoparticles increased firstly and then decreased. In fact, as we prepared the MStAN nanoparticles by radical emulsion polymerization, it was found when the amount of the DVB increased up to 20% wt of the monomers, some gel was produced, and when the amount of DVB further increased, the gel also increased. This was probably because the vinyl groups on the surface reacted between the particles, which resulted the agglomeration between particles.[25] Based on the above experimental phenomena, when the amount of DVB was lower than 20% wt, with the increase of DVB, the vinyl groups on the surface increased. However, as the amount of DVB increased to higher than 20%, the vinyl groups on the surface were reacted between particles. In other words, this could attribute to the cross-linking between the latex particles, the cross-linking between the particles will consume the vinyl groups on the surface of the nanoparticles; therefore, the vinyl groups on the surface of the particles decreased.

The Chemical Interaction Between the Filler and the Matrix
As revealed in Figure 6, since trace amount of 0.2 phr DCP was added into the EPR, the formula as shown in Table II (III), the
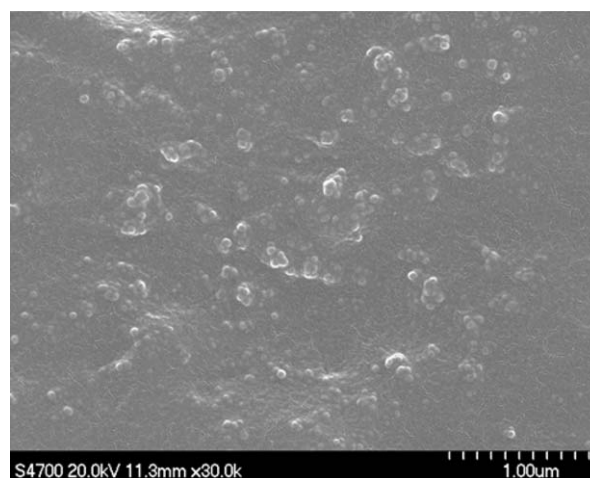

Figure 8. Reinforcing behavior of the MStAN-filled EPR composites with a loading of 30 phr. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 9. Morphology of the MStAN particles in EPR elastomeric matrix.

Table V. Mechanical Properties of the MStAN-Filled NBR Composites at Varied Vinyl Groups on the Particles Surface

| Samples	Shore A hardness/(°)	Stress at 100% elongation/(MPa)	Stress at 300% elongation/(MPa)	Tensile strength /(MPa)	Elongation at break/(%)	Permanent set/(%)
MStAN$_3$ (0.22 mmol/g)/EPR	62 ± 1	1.4 ± 0.1	2.5 ± 0.1	10.2 ± 0.1	622 ± 25	10 ± 5
MStAN$_2$ (0.18 mmol/g)/EPR	65 ± 2	1.4 ± 0. 1	2.4 ± 0.1	9.3 ± 0.2	665 ± 16	20 ± 4
MStAN$_1$ (0.16 mmol/g)/EPR	68 ± 2	1.4 ± 0.1	2.2 ± 0.1	4.5 ± 0.2	623 ± 27	32 ± 7

EPR curing curve was uptrend slightly during the rubber vulcanization process. It indicated that a small quantity of cross-linking network of vulcanized rubber matrix was formed. While in the MStAN nanoparticles filled EPR composites, though same amount of 0.2 phr DCP was added into the compound, the formula as shown in Table II (II), torque of the filled composites did not increase during the rubber vulcanization time. This was probably due to the vinyl groups on the surface of the MStAN filler consumed the 0.2 phr DCP. In the process of the vulcanization, the DCP decomposed to free radicals, then the vinyl groups on the surface of the MStAN particles firstly reacted with the free radicals, and the monomer radicals further reacted with EPR molecular chain. As for 0.2 phr DCP was quite a small amount, the MStAN particles was only linked to the EPR molecular chain, but no crosslinking network formed between the EPR molecular chains.

About 0.2 phr DCP was added into the MStAN (30 phr) filled EPR compound, the formula as shown in Table II (II), and the compound was vulcanized at 160°C for a period time of 40 min. The vulcanizate was further extracted with toluene in the flask. The weight of the vulcanizate was found reduced with the extension of the time. After 72 h, the weight of the vulcanizate went constant. By doing this, the free rubber chains was extracted by the toluene, while those macromolecules chain which was reacted with the vinyl groups would not be extracted by toluene, and was kept in the flask. After the extraction by toluene, the resulted compound was washed by acetone and dried, and then the extracted compound was tested by infrared spectroscopy. Certain chemical interaction between the filler and the matrix provided by the vinyl groups on the surface was confirmed by FTIR spectra as shown in Figure 7. As seen in Figure 7, the band at 1377 cm^{-1} was attributed to the symmetric distortion vibration of –CH$_3$, the bands at 2921 cm^{-1} was attributed to the symmetrical stretching vibration of –CH$_2$, and the bands at 2858 cm^{-1} was attributed to the stretching vibration of –CH$_2$. Both the MStAN copolymer particles and the extracted compound exhibited a peak at 2248 cm^{-1}, which correspond to the -CN stretching vibration of saturated aliphatic nitrile. After normalization by the -CN peak at 2248 cm^{-1}, compared with those of the MStAN copolymer particles, symmetrical stretching vibration of –CH$_2$ observed at 2921 cm^{-1}, the stretching vibration of –CH$_2$ observed at 2853 cm^{-1} and symmetric distortion vibration of –CH$_3$ observed at 1377 cm^{-1} of the extracted compound was obviously stronger, which demonstrated that the covalent bonding between the vinyl groups on the surface of MStAN nanoparticles and the macromolecular chain of EPR rubber matrix was formed.

Reinforcement to Elastomer Matrix

Cross-linked MStAN spherical nanoparticles, prepared with α-St at 60% wt, AN at 30 wt %, DVB at 15% wt and the initiator APS at 1% wt, were mixed in ERP with a loading of 30 phr. The formula of MStAN nanoparticles-filled EPR was shown in Table II (I). Mechanical performances of EPR nanocomposites filled with the MStAN particles were presented in Table IV. There were significant improvements in mechanical properties
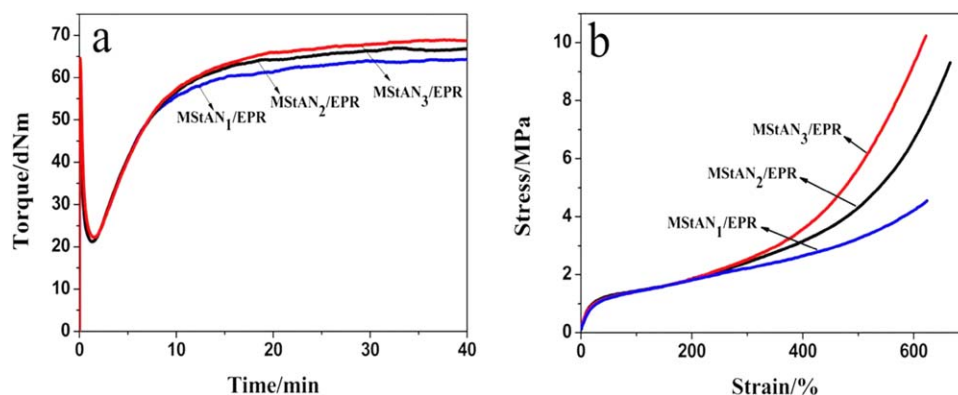
Figure 10. Mechanical properties and curing behaviors of the MStAN nanoparticles filled EPR composites. (a) The curing kinetics of the MStAN /EPR compound and (b) the stress–strain performances of the MStAN /EPR nanocomposites). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of the MStAN-filled EPR nanocomposites, compared with those of the neat EPR.

The nano-sized spherical shape was beneficial to the reinforcement of the elastomer matrix. The high surface area of the particles provided sufficient interphase for the filler-rubber interactions.[28] As shown in Figure 8, with vinyl groups at the surface provide certain chemical interaction between the filler and the macromolecular chain of rubber matrix, the tensile strength increased rapidly.[28–31] The MStAN nanoparticles achieved almost fine dispersion in the EPR matrix as seen in Figure 9, but slight agglomeration was also observed due to the poor compatibility between the MStAN polymeric fillers and the EPR elastomer matrix.

MStAN-Filled EPR Composites with Varied Content of Vinyl Groups on the Surface of MStAN Particles

As demonstrated above, the vinyl groups on the surface of MStAN particles exhibited dramatic influence on the mechanical properties of the MStAN filled elastomer composites due to the enhanced filler-rubber interactions.

In order to further investigate the influence from the filler-rubber interactions, $MStAN_1$, $MStAN_2$, and $MStAN_3$ with varied content of the vinyl groups on the surface of 0.16, 0.18, and 0.22 mmol/g respectively, were prepared by the formula that employed 10% wt DVB and 1.5, 1.0, and 0.5% wt APS of the monomers. The mechanical properties of the composites with varied vinyl groups' content on the filler surface were investigated under the same filler loading of 30 phr, the formula as shown in Table II (I). Results were listed in Table V, the curing kinetics of the compounds were shown in Figure 10(a), and the stress–strain performances of the nanocomposites were shown in Figure 10(b).

As indicated in Table V, with the increasing of the content of vinyl groups content on filler surface, stress at 300% elongation and tensile strength increased, and while permanent set decreased. And the Shore A hardness and the elongation at break changed slightly. Increasing vinyl groups on the surface of the MStAN particles could improve the mechanical performance due to enhanced filler-rubber interactions. The more interactions indicated that the recovery of the EPR macromolecular chain was easier after the deformation, which resulted in permanent set decrease.

Figure 10(a) shows the curing kinetics of MStAN/EPR compound. With the increasing of amount of vinyl groups on the surface, the cross-linking density of rubber matrix changed little while still increased. This could be mainly attributing to the vinyl groups on the surface of MStAN nanoparticles improved the filler-rubber interactions, the more vinyl groups on the surface of MStAN nanoparticles the more chemical point for the EPR macromolecular chain, which provided the larger cross-linking density of the rubber matrix. In the process of stretching, rubber molecules were slowly stretched from random coil, and the rubber macromolecular chain between the particles orientated, the more vinyl groups on the surface of the particles, the more rubber macromolecular chain grafted on the particles which resulted in higher tensile stress and elongation.[28–31]

In Figure 10(b), the stress–strain curves of $MStAN_1$ (0.16 mmol/g), $MStAN_2$ (0.18 mmol/g) and $MStAN_3$ (0.22 mmol/g) nanoparticles filled EPR vulcanizes were plotted. It could be found that with the vinyl groups on filler surface increased, the stress increased abruptly under large deformation. With the help of vinyl groups, the chemical bonding between EPR matrix and MStAN nanoparticles were built up and enhanced, thus the stress of nanocomposites got improved with higher vinyl content.

CONCLUSIONS

A cross-linked copolymer of α-methyl styrene acrylonitrile particles was successfully synthesized by radical emulsion polymerization. The vinyl groups on the surface of MStAN copolymer were detected by iodine titration method. The vinyl groups on the surface of the MStAN nanoparticles can be modified by controlling the DVB content and the initiator (APS) content.

Vulcanization kinetic characterization results and the FTIR spectra demonstrated that the vinyl groups at the surface of the (MStAN) copolymer particles provided certain chemical interaction between the filler and the macromolecular chain of rubber matrix. Mechanical performances of the MStAN filled EPR nanocomposites were significant improved compared with those of the neat EPR. With higher amount of vinyl groups on the surface, the MStAN filled EPR nanocomposites showed better mechanical performances.

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