# The Morphology and Property of Ultra-Fine Full-Vulcanized Acrylonitrile Butadiene Rubber Particles/EPDM Blends

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**ABSTRACT:** A novel UFNBRP/EPDM blend was prepared by compounding ultra-fine full-vulcanized acrylonitrile butadiene rubber particles (UFNBRP) with ethylene–propylene–diene monomer (EPDM) matrix. The morphology, dynamic property, and curing property of the blend were discussed in detail. TEM and SEM observations showed that, no matter how high the blend ratio of UFNBRP to EPDM matrix was, UFNBRP particles always kept being in the dispersion phase because of its extremely high viscosity resulting from self-crosslinking, but were not dispersed as nanosize units, as expected. Dynamic properties, illustrated by DMTA, further demonstrated that two phases exhibited two separate glass transition temperatures, indi-cating distinct phase separation and weak phase interaction. Rubber processing analyzer results showed that inorganic filler as well as UFNBRP particles in EPDM matrix formed a network and blocked the flow properties of the compound. At the same time, the introduction of UFNBRP particles evidently affected the vulcanization of EPDM, when sulfur was used as a vulcanizing agent, and improved the mechanical properties of EPDM. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3673–3679, 2006

**Key words:** rubber; blend; crosslinked particles; morphology

## INTRODUCTION

Two technological means are often used to improve the properties of current rubber materials. One is to change the chemical compositions and molecular structure by polymerization; the other is to blend with different types of rubbers. Commercially, the second method is the most cost-efficient and widely used method, to overcome the drawbacks of single rubber. Ethylene–propylene–diene monomer (EPDM) is a kind of rubber with very low C=C content and nonpolar molecules, and possesses balanced heat stability, aging-resistance, elasticity, especially at very low temperature, and water-resistance, and therefore, it is now widely applied in many rubber products, substituting for natural rubber, styrene–butadiene rubber, butadiene rubber, etc. Unfortunately, the application of EPDM is restricted because of its poor solvent-resistance and adhesion property. Blending EPDM with acrylonitrile–butadiene rubber (NBR) can improve the aforementioned disadvantages of EPDM, because NBR with strong polar molecules exhibits excellent solvent-resistance and adhesion properties. There are lots of literatures involving it.[1–4] It is the fact that the morphology of the polymer/polymer blend depends on the blend ratio, the viscosity, surface property of each component, and mixing process.[5,6] When NBR is dispersed in the EPDM matrix, the dispersion domain is larger, with very wide size distribution, and the interphase adhesion is very weak, resulting in a blend with poor mechanical properties. It is explained that they are incompatible and have different vulcanization rates. Therefore, the grafted copolymer of EPDM and maleic anhydride or allyl glycidyl ether is used to improve the morphology and mechanical properties of EPDM/NBR blend.[2–4]

Qiao and coworkers have successfully prepared a series of new ultra-fine full-vulcanized rubber powder (UFRP) by crosslinking the rubber latex using irradiation-curing method, including styrene butadiene rubber powder (UFSBRP), carboxylic styrene butadiene rubber powder, acrylonitrile butadiene rubber powder (UFNBRP), carboxylic acrylonitrile butadiene rubber powder, and silicon rubber powder.[7–9] These UFRP has a size distribution of 50–150 nm.[9,10] As we know, conventional rubber powder is a kind of un-

cured rubber, and is often used as the matrix as well as the bulk rubber. However, UFRP can hardly flow, owing to full vulcanization, and hence is only used as a kind of special filler. For example, UFRP is used as a toughening modifier by incorporating a small amount of UFRP into brittle resin, or to prepare thermoplastic elastomer (TPE) by blending a great amount of UFRP into thermoplastic resin.[7–12] It was found that as toughening modifier, UFSBRP offered polypropylene (PP) balanced toughness, strength, and heat stability.[7,13] The improvement in toughness attributed to the fine dispersion and the excellent elasticity of UFRP, and at the same time, the increase in strength and heat stability was the reason that the crystallization of PP was strengthened because of UFRP's nucleation effect.[7,13] It is also true for PA6/UFRP blend.[14] For such UFRP/thermoplastic resin blends, the transition between toughened resin and TPE only depends on the UFRP loading amount, because they have the same preparation process. However, few researches focused on the UFRP/rubber blend. In the present work, novel UFRP/EPDM compounds were prepared by directly blending UFNBRP into the EPDM matrix. Meanwhile, the morphology, dynamic property, and curing property of the blends were discussed as well. As expected, transmission electron microscope (TEM) and scanning electron microscope (SEM) observations showed that, no matter how high the blend ratio of UFRP to rubber matrix was, UFRP kept being in the dispersion phase because of its extremely high viscosity resulting from self-crosslinking, and exhibited the reinforcement for EPDM. At the same time, the aggregation of UFRP particles in the rubber matrix was also observed.

## EXPERIMENTAL

### Materials

UFNBRP, Narpow™ VP-401(single particle size distribution, 100–150 nm; ACN content, 26 wt %), was manufactured by Beijing BHY Chemical Industry New Technology Company, China. EPDM, 4045 (ethylene content, 52 wt %; ENB content, 7.7 wt %, $ML^{100°C}_{1 + 4}$, 45), was commercially produced by a synthetic rubber factory of Jinlin Petroleum Company, China. NBR, N240S (ACN content, 26 wt %, $ML^{100°C}_{1 + 4}$, 56) was bought from JSR Co., Japan. Other chemicals were available from the store.

### Blends preparation

UFNBRP/EPDM blends were prepared on a two-roll mill. Adjust two rolls of mill to the closest distance when EPDM becomes fluidic, and UFRP was added into EPDM (step by step) to ensure good dispersion, and then, vulcanizing agent and accelerator, based on the EPDM matrix, were introduced (as shown in Table

**TABLE I**
**The Compositions of the UFNBRP/EPDM Blend**

| Mixing ratio | 0/100 | 10/90 | 20/80 | 30/70 | 40/60 | 50/50 | 60/40 |
|---|---|---|---|---|---|---|---|
| EPDM4045 | 100 | 90 | 80 | 70 | 60 | 50 | 40 |
| VP-401 | | 10 | 20 | 30 | 40 | 50 | 60 |
| DCP | 5.0 | 4.5 | 4 | 3.5 | 3 | 2.5 | 2.0 |
| TAIC | 2.0 | 1.8 | 1.6 | 1.4 | 1.2 | 1.0 | 0.8 |

I) to get the compound. Curing characteristics (scorch time, $t_{10}$; cure time, $t_{90}$; minimum torque, $M_L$; maximum torque, $M_H$) were determined by disc oscillating rheometer, and the compound was vulcanized at platen press, with 15 MPa pressure. Test specimens were obtained by tailoring the vulcanized compound (blend). The vulcanization temperature was set as 160°C.

NBR/EPDM blends were also prepared by compounding EPDM with bulk NBR through the aforementioned preparation process.

### Test and characterization

#### TEM and SEM

The morphology structure of the blend was observed by TEM. The ultrathin sections were cut from the sample in liquid nitrogen, and were stained with osmium tetraoxide ($OsO_4$) to obtain sufficient contrast. This was an exception to the UFNBRP/EPDM blend. A Hitachi (Japan) H-800 TEM, with an acceleration voltage of 100 kV, was used to observe the ultrathin sections. The morphology of the tensile fracture surface for the blend was observed with a Cambridge (British) S-250MK3 SEM. The fracture surfaces were vacuum-plated with gold–platinum for electrical conduction.

#### DMTA

A PE7 dynamic mechanical thermal analyzer (DMTA), manufactured by PE company of USA, was used to evaluate the dependence of dynamic elastic modulus (E') and loss factor (tan δ) of the sample on the temperature. The DMTA experimental setup was based on the single tensile cantilever bend geometry. The frequency was selected as 10 Hz, and the strain used was 0.5%. The temperature was set from −95 to 120°C, at an elevation rate of 3°C/min, to obtain the glass transition temperature.

#### Rubber processing analysis

Dependence of the storage modulus on the shear strain for the compounds was measured by rubber processing analyzer (RPA) 2000 from Alpha Com-

pany, USA. The test temperature was 60°C, and the test frequency was 1 Hz.

## Mooney viscosity

The compound was preheated for 1 min at 100°C on Monsanto Mooney viscosity tester, and then the rotor was rotated for 4 min at the speed of 2 rpm, and at that time, the torque value was recorded as Mooney viscosity of the compound. The average of two measurements for each sample was reported.

## Mechanical properties

Tensile test, tear test, and hardness of the blends were carried out according to ASTM D 412, ASTM D 624, and ASTM D 2240, respectively. During tensile test and tear test, five specimens were tested to give the average. During the hardness test, the hardness of three different spots of the sample was measured to give the average.

## RESULTS AND DISCUSSION

### Morphology

TEM micrographs of UFNBRP/EPDM and NBR/EPDM blends are shown in Figure 1(a)–1(g). As for the UFNBRP/EPDM blends without extra staining treatment, the two-phase morphology in Figure 1(a)–1(e), i.e., "sea-island" morphology is visible in the blends with different UFNBRP/EPDM blend ratios, in which the deep gray spherical dispersed phase is UFNBRP, the gray continuous phase is EPDM, and those with many dark particles, with the sizes of less than 200 nm, is a kind of the inorganic filler as separator for UFNBRP. It was evident that UFNBRP was unevenly dispersed in EPDM, with particle sizes of 1–5 $\mu$m, which are much larger than the original size of UFNBRP. As the blend ratio of UFNBRP/EPDM increased to 30/70, the larger dispersed UFNBRP particles were observed. It was implied that UFNBRP occurred to aggregate during mixing. As we expected, UFNBRP always kept being in the dispersion phase even when the blend ratio of UFNBRP/EPDM reached 60/40. As for NBR/EPDM blends, it is necessary to stain the sections with $OsO_4$, to clearly observe their two-phase morphologies. As shown in Figure 1(f) and 1(g), the white domain refers to the EPDM phase, while the dark domain is the NBR phase. It could be observed that NBR was dispersed as round-like particles, with the sizes less than 4 $\mu$m, in EPDM when NBR/EPDM ratio was 20/80, whereas the morphology of the blend was similar to the co-continuous phase at the NBR/EPDM ratio of 60/40, where the two domains had very large sizes.
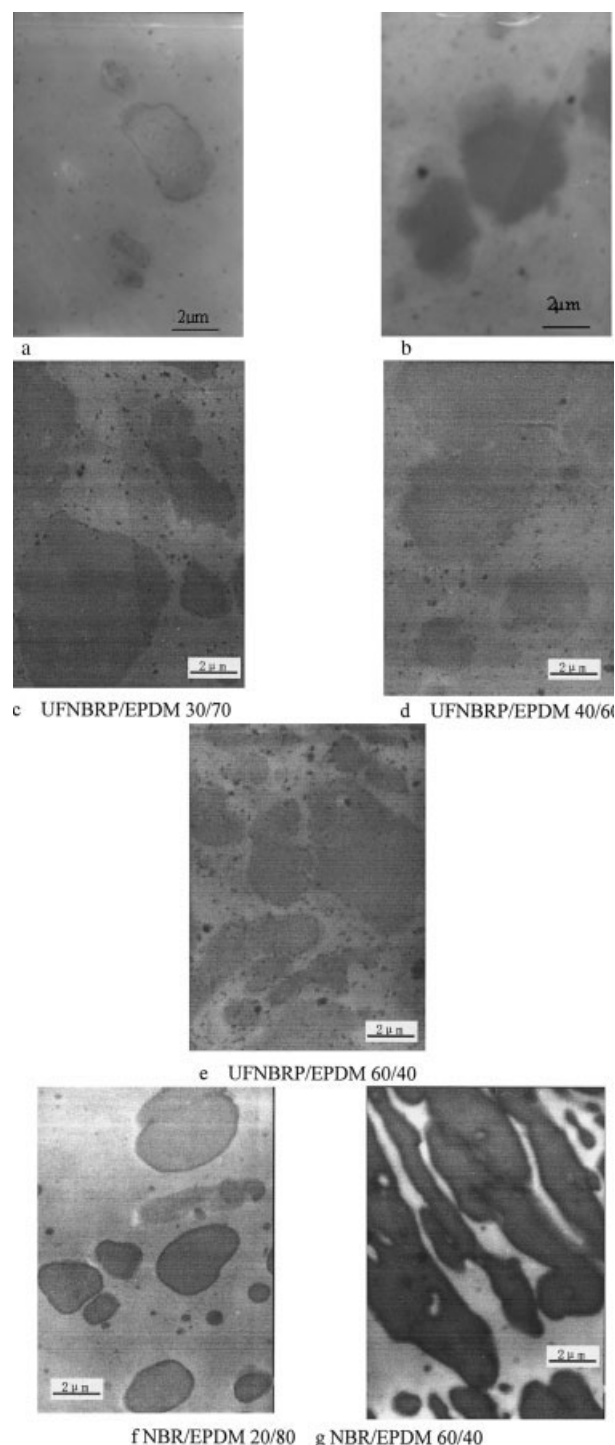


**Figure 1** TEM observations of cut sections of UFNBRP/EPDM and NBR/EPDM blends.

It is well known that the phase structure of the blend is influenced by several factors, including the surface characteristics, blend ratio, the viscosity of each component, and compounding process.[5,6] As discussed earlier, the phase morphology of the NBR/EPDM blend evolved from the sea-island morphology, with NBR as the dispersion phase into the cocon-
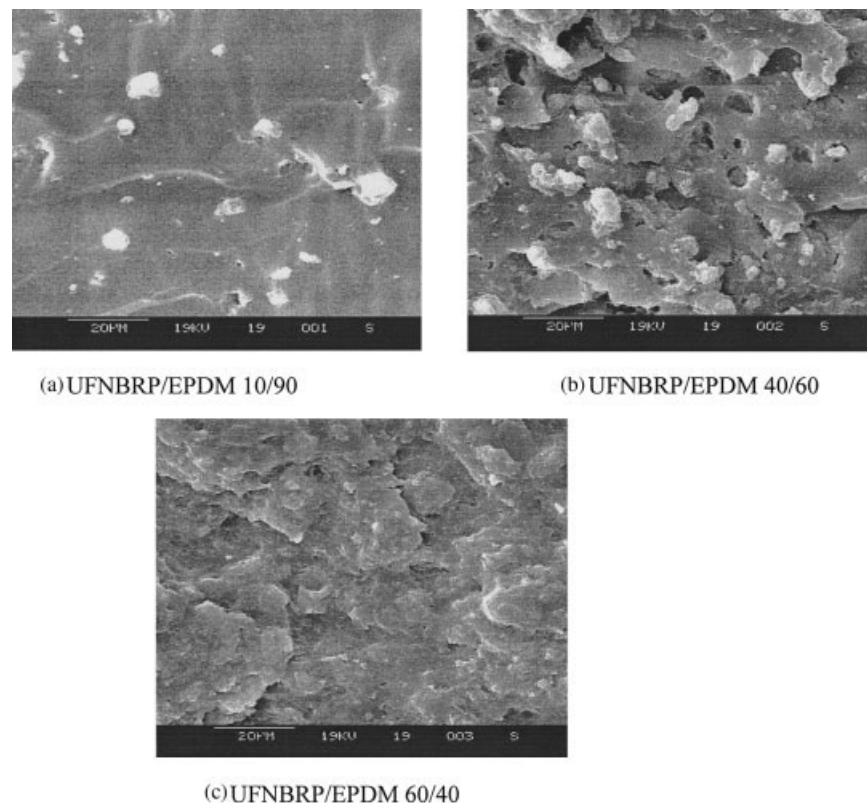
**Figure 2** SEM observations of tensile fracture surfaces of UFNBRP/EPDM blends.

tinuous phase, as the NBR/EPDM ratio increased. NBR with strong molecular polarity has higher surface tension than EPDM, resulting in incompatibility between them. When NBR/EPDM ratio was 20/80, NBR with higher viscosity inclined to form the dispersion phase, so that it could be dispersed as round particles with the lowest surface energy. As the NBR content increased, it became more difficult for NBR to be dispersed in EPDM. On the contrary, as to UFN-BRP/EPDM system, UFNBRP has extremely high viscosity resulting from self-crosslinking, compared with uncured EPDM, and so it is always kept in the dispersion phase in the blend independent of blend ratio. As well as the nanofiller, UFNBRP, with particle sizes of 50–150 nm, inclined to aggregate because of its large surface area/volume ratio. Moreover, the aggregation of UFNBRP was intensified by adhering to each other, which resulted from its deformation during mixing. Obviously, the rise in the number of UFNBRP particles increased the chance of the aggregation, causing the dispersion phase with larger sizes.

Figure 2(a)–2(c) shows SEM observations of tensile fracture surfaces of UFNBRP/EPDM blends. There existed some exposed UFNBRP particles and holes on the tensile fracture surface of the blend, when the UFNBRP/EPDM ratio was not more than 40/60. Some very tiny inorganic filler could also be observed. These holes were ascribed to pull-out of UFNBRP particles

from EPDM matrix. This further demonstrated that the interphase adhesion between UFNBRP and EPDM was very weak. Besides their poor compatibility, they could not make good use of large surface area/volume of nanoparticles to improve the interphase adhesion, because UFNBRP were not dispersed as nanosized units as we expected. Unexpectedly, it is difficult for the blend with the UFNBRP/EPDM ratio of 60/40 to observe dispersed UFNBRP particles, except several holes. It might be thought that many UFNBRP particles adhered each other together.

## DMTA analysis

DMTA is used to evaluate the homogeneity of the blend. Figure 3 displays the temperature dependence of loss factor (tan δ) and storage modulus (E') of UFNBRP/EPDM blends. The temperature corresponding to the peak of loss factor (tan δ) may be regarded as the glass transition temperature ($T_g$) of the polymer. Seen from Figure 3(a), $T_g$ of EPDM is about −50°C, while $T_g$ of UFNBRP is close to −10°C. It could be observed that only the peak of tan δ at −50°C appeared, when the blend ratio of UFNBRP/EPDM was not more than 30/70; thereafter, the peak of tan δ at −10°C began to appear. As the UFNBRP/EPDM ratio increased, the first peak at −50°C remarkably declined, and at the same time, the second peak at
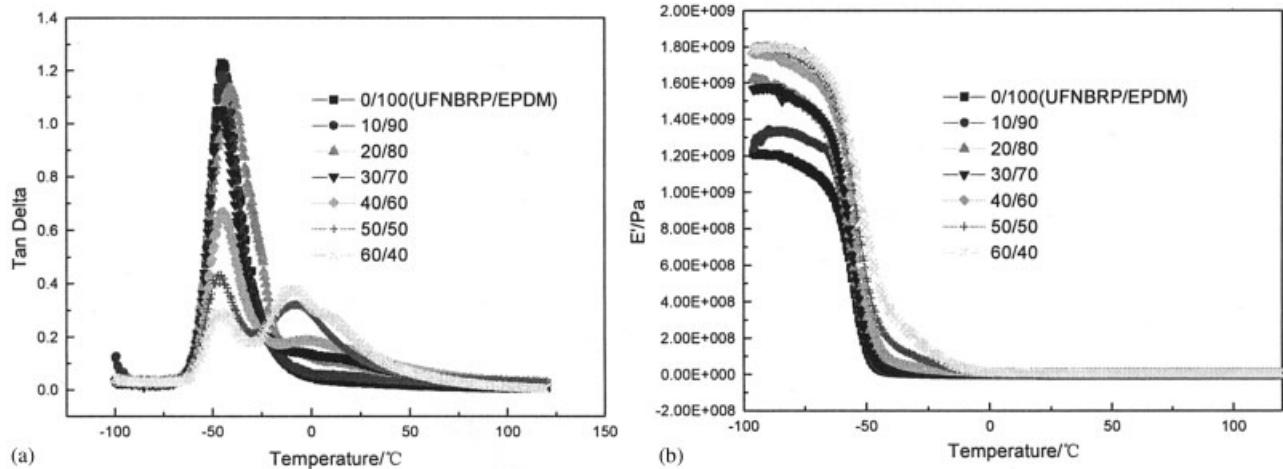
**Figure 3** The temperature dependence of loss factor (tan δ) and storage modulus (E') of UFNBRP/EPDM blends.

−10°C rose up. It was worth noting that the second peak somewhat moved toward low temperature, but the first peak did little as the UFNBRP content increased, which attributed to the cure reactions between UFNBRP particle and EPDM, as discussed hereafter. Seen from Figure 3(b), storage modulus (E') of the blend increased with the increasing UFNBRP content, especially at the temperature lower than the $T_g$ of EPDM and between the $T_g$ of EPDM and UFNBRP. When the temperature was lower than the $T_g$ of EPDM, both rubbers were glassy, and so the macromolecular chains could not move. However, UFNBRP has higher stiffness due to stronger molecular interactions; therefore, E' of the blend dramatically ascended with UFNBRP loading. When the temperature was between the $T_g$ of EPDM and UFNBRP, rubber macromolecular chains began to motion, resulting in the marked reduction of E'. Even so, E' of the blend was

higher with higher UFNBRP content, in which EPDM macromolecular chains began to motion earlier than that of UFNBRP.

## RPA analysis

RPA is often used to evaluate the processing properties of the rubber compound at the different strain and temperature. Dependence of storage modulus (G') of the compound on shear strain is shown in Figure 4. From Figure 4, at very low strain, the plateau (initial) storage modulus of the compound mounted up with the increasing UFNBRP/EPDM ratio. In case of the compound containing only 10 wt % UFNBRP, the initial storage modulus was much higher than that of EPDM. The dominating reason was that UFNBRP had been vulcanized while EPDM was not uncured in the compound. Moreover, G' rapidly decreased until it
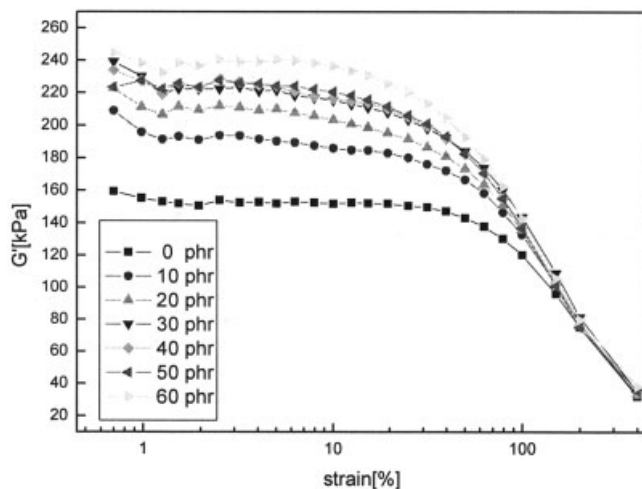


**Figure 4** Dependence of storage modulus (G') of the compound containing different UFNBRP content on shear strain.
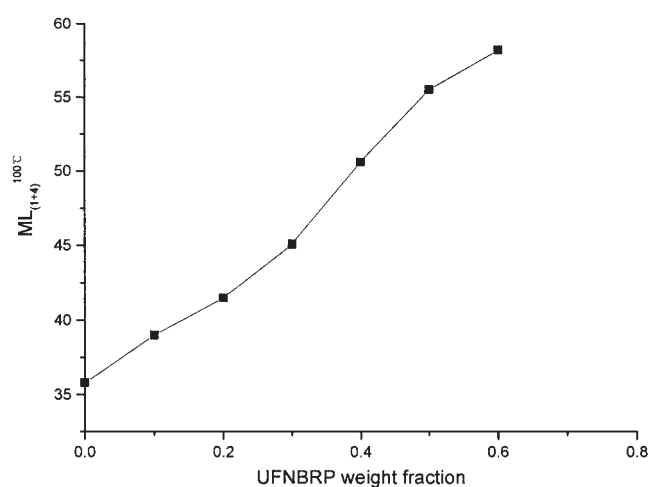


**Figure 5** Dependence of Mooney viscosity of the compound on UFNBRP weight fraction.

TABLE II
The Cure Characteristics of UFNBRP/EPDM Compounds

| UFNBRP/EPDM blend ratio | 0/100[a] | 10/90[a] | 100/0[a] | 0/100[b] | 10/90[b] | 60/40[b] | 100/0[b] |
|---|---|---|---|---|---|---|---|
| Maximum torque, $M_H$/N m | 32.85 | 13.26 | 30.96 | 59.15 | 56.47 | 58.25 | 30.96 |
| Minimum torque, $M_L$/N m | 4.14 | 3.85 | 13.72 | 4.96 | 5.55 | 8.62 | 13.72 |
| $M_H$–$M_L$/N m | 28.71 | 9.41 | 17.24 | 54.19 | 50.92 | 49.63 | 17.24 |
| Scorch time, $t_{10}$/min | – | – | – | 2.7 | 2.8 | 2.5 | 2.3 |
| Cure time, $t_{90}$/min | – | – | – | 32.2 | 25.8 | 20 | 30 |

[a] Sulfur vulcanizing system.
[b] Peroxide vulcanizing system.

converged at a very high strain, when the shear strain increased to more than 10%. It was evident that G′ for the compound with the higher UFNBRP loading began to decline at the lower shear strain. It was explained that the network formed by UFNBRP particles existed in the compound similar to inorganic particles filled rubber compound.[15–18] The blend with higher UFNBRP loading had a stronger network, and so G′ began to decline at the lower shear strain and decreased more rapidly because of the collapse of the network. In contrast with inorganic particles filled rubber compound, the plateau stage for UFNBRP/EPDM compound was longer even when the UFNBRP/EPDM ratio reached 60/40. It was thought that UFNBRP particles could be deformed under shear strain. The higher plateau G′ indicated that the compound showed poorer flow property. Figure 5 shows the dependence of Mooney viscosity of the compound on blend ratio. Mooney viscosity reflects the flow property of the compound at the fixed low shear rate. From Figure 5, Mooney viscosity of the compound rose up straight with the increasing UFNBRP/EPDM ratio. This is because the crosslinked rubber particles greatly blocked the flow of the compound because of the extremely high viscosity. This further confirmed the aforementioned result.

## Curing characteristics

Table II reveals the cure characteristics of UFNBRP/EPDM compound. It was found that the torque difference ($M_H$–$M_L$) of the compound, even containing 10 wt % UFNBRP, was much smaller than that of EPDM when sulfur was used as a vulcanizing agent. The surface of the cured compound was also observed to be sticky. It is the fact that ($M_H$–$M_L$) can reflect the crosslinking degree of the compound. This implied that the UFNBRP/EPDM compound did not reach the full vulcanization, even if sulfur and accelerator were further increased. Therefore, scorch time and cure time of the compound was not given here. Surprisingly, UFNBRP could also continue curing because ($M_H$–$M_L$) reached 17.2 N m, but lower than ($M_H$–$M_L$) value of EPDM, indicating that UFNBRP has not reached the true full vulcanization. It was also proved

that UFNBRP particles could agglomerate during storing. As well as NBR, UFNBRP particles have faster cure rate to waste accelerator and sulfur, leading to the insufficient vulcanization of EPDM matrix. However, UFNBRP is a kind of vulcanized rubber particle after all, and so accelerator and sulfur could not be dispersed inside them, and only be absorbed on the surfaces of these particles. Hence, it was thought that a small amount of cure reaction might occur between the surfaces of UFNBRP particles rather than between UFNBRP particles and EPDM.

When peroxide was used as vulcanizing agent, $t_{10}$ and ($M_H$–$M_L$) of UFNBRP/EPDM had no marked change close to that of EPDM matrix, but cure time was evidently shortened with the increasing UFNBRP content. It is suggested that peroxide could be preferentially used as vulcanizing agent for UFNBRP/EPDM compound. The rise in $M_L$ was due to the block effect of UFNBRP particles as mentioned earlier. Similarly, UFNBRP also occurred to vulcanize somewhat. It is true that EPDM and NBR have the close cure rate in peroxide vulcanizing system.[19] At the moment, a small amount of cure reactions was thought to occur between UFNBRP particles as well as between them and EPDM. The cure reactions between interphase might result in a little improvement in the interfacial adhesion, on the other hand, it might be unfavorable that the adhering of UFNBRP cannot be separated any more if the chemical bonding exists between UFNBRP particles, owing to their second vulcanization. Therefore, it is suggested that the compatilizer could be introduced during mixing to improve the fine dispersion of UFNBRP particles as well as NBR in EPDM matrix.

## Mechanical properties

Seen from Figure 6, as UFNBRP/EPDM ratio increased, the blend exhibited a little enhancement in hardness and tensile strength, but tear strength of the blend appeared at a maximum value at the UFNBRP/EPDM ratio of 30/70. Obviously, the reinforcing effect of UFNBRP is not as good as conventional nanofiller, such as silica and carbon black. This mainly attributed to the very low modulus of UFNBRP, besides its poor
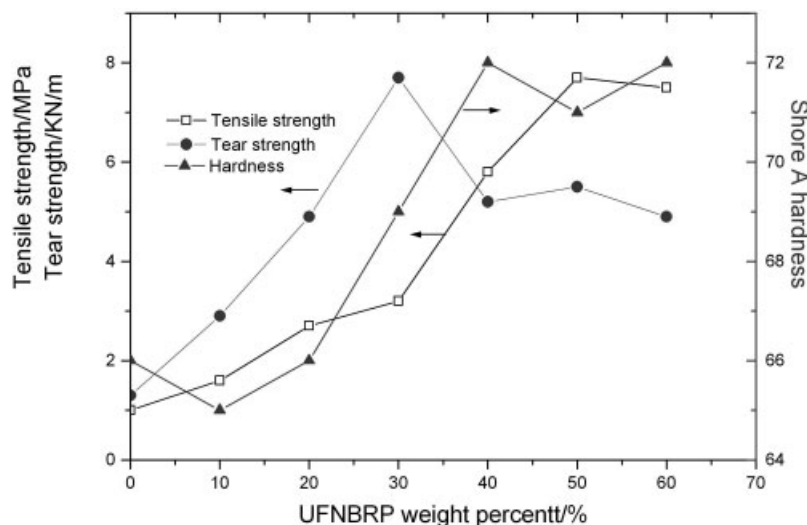
**Figure 6** Mechanical properties of UFNBRP/EPDM blends.

dispersion and interphase adhesion, as mentioned earlier. Nevertheless, it is expected that the elasticity of rubber could be improved by incorporating UFNBRP particles into the rubber matrix, without the expense of strength and modulus.

## CONCLUSIONS

A novel UFNBRP/EPDM blend was prepared by compounding UFNBRP particles into the EPDM matrix. No matter how high the blend ratio of UFNBRP to EPDM matrix was, UFNBRP particles always kept being in the dispersion phase due to its extremely high viscosity resulting from self-crosslinking, but were not dispersed as nanosize units, as expected. The two phases exhibited two separate glass transition temperatures, indicating distinct phase separation and weak phase interaction. As well as inorganic filler, UFNBRP particles in rubber matrix formed a network and blocked the flow properties of the blend. At the same time, the introduction of UFNBRP particles evidently affected the vulcanization of EPDM, when sulfur was used as a vulcanizing agent, and improved the mechanical properties of EPDM.

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