

# Observation of Morphology in EPDM/Nylon Copolymer Thermoplastic Vulcanizates by Atomic Force Microscopy

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**ABSTRACT:** A thermoplastic vulcanizate (TPV) of an ethylene propylene diene terpolymer (EPDM) and nylon copolymer (PA) was prepared. Maleic anhydride-grafted EPDM (EPDM-g-MAH) and MAH-grafted EPR (EPR-g-MAH) were used as compatibilizers and sulfur was used as a curative. The phase morphology of EPDM/PA TPVs was investigated by atomic force microscopy (AFM). AFM images showed that, although there was a compatibilization reaction between EPDM-g-MAH and PA, phase inversion always existed for EPDM/EPDM-g-MAH/PA TPVs and the rubber phase could be finely dispersed in the PA matrix with an increasing compatibilizer content. For TPVs using EPR-g-MAH as a compatibilizer, three phases existed because of noncrosslinkability of EPR by sulfur. Crosslinked EPDM

particles dispersed in a comatrix of PA and EPR-g-MAH could be observed by increasing the content of EPR-g-MAH to 26 wt %. For an EPR-g-MAH content of 26 wt %, the uncrosslinked EPR-g-MAH existing in the interface between crosslinked EPDM and PA tended to coalesce and thus resulted in a morphology of large rubber regions composed of small crosslinked particles. When the dosage of EPR-g-MAH was 52 wt %, the phase morphology of the blends changed to being one of PA and crosslinked EPDM particles dispersed in the MAH-g-EPR matrix. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 1242–1248, 2003

**Key words:** atomic force microscopy (AFM)

## INTRODUCTION

Thermoplastic vulcanizates (TPVs) have become very useful as thermoplastic elastomers since their introduction in 1981. These materials have the processing characteristics of a thermoplastic and the functional performance of a conventional thermoset rubber—hence, the name “thermoplastic vulcanizates.”<sup>1</sup> The best way to prepare TPVs is through dynamic vulcanization, wherein the elastomer is preferentially vulcanized under dynamic shear to generate fine, cured rubber particles in a thermoplastic polymer matrix.

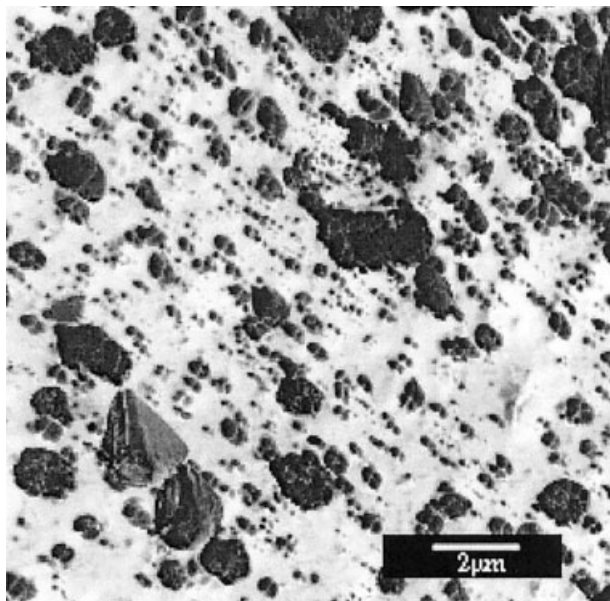
The dynamic vulcanization process was first described by Gessler and Haslett<sup>2</sup> in 1962 and then developed by Fisher<sup>3</sup> and Coran and Patel.<sup>4,5</sup> This discovery was further advanced by Abdou-Sabet and Fath through the use of preferred curatives to achieve improvement in elastomeric properties and flow characteristics,<sup>6</sup> which led to a successful commercialization of dynamic vulcanization technology. Some thermoplastic elastomers through dynamic vulcanization

have been commercialized with trade names such as Santoprene and Geolast.

In principle, there is a wide variety of commercially available rubbers and plastics that can be considered for blending and, consequently, for preparation of their TPVs. However, relatively few of them have been of technological importance, since most polymers are incompatible with each other. For TPVs, the preferred morphology is a fine and elastomeric dispersed phase and a thermoplastic continuous phase. To obtain optimum properties, the crosslinked rubber particles should be less than 2  $\mu\text{m}$  in diameter. Therefore, the interfacial tension between the components should be relatively low to achieve a good and fine dispersion of the crosslinked rubber phase. A well-known commercial example of dynamically vulcanized thermoplastic-elastomer compositions is the ethylene propylene diene terpolymer/polypropylene (EPDM/PP) TPVs.<sup>7</sup> The interfacial tension between PP and EPDM is quite low and no compatibilization is required. For polar thermoplastics, TPVs can be obtained by blending with polar rubbers, for example, TPVs of nitrile elastomer/nylon<sup>8</sup> or chlorinated polyethylene rubber/nylon.<sup>9</sup> Additionally, to prepare TPVs of a polar thermoplastic/nonpolar rubber, it is necessary to compatibilize the blend to generate a fine dispersion of the rubber phase. Compatibilization is usually achieved by the presence of a small amount of

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**Figure 1** AFM image of statically vulcanized EPDM/EPDM-g-MAH/PA (68.8/11.2/20).

a compatibilizing agent, which is a block or graft copolymer containing segments similar to each of the polymers in the blend.

Much literature is available on PP/rubber TPVs, while few publications are available concerning dynamic vulcanization of EPDM/nylon blends. Ma et al. studied the structure and properties of an EPDM/nylon copolymer high-performance elastomer<sup>10,11</sup>; however, the elastomer was prepared by static vulcanization.

The difficulty to prepare EPDM/nylon TPV is due to the high interfacial energy between the two components. By using a suitable compatibilizer and dynamic vulcanization, EPDM/nylon copolymer TPV with a high rubber fraction was successfully developed as described in our early work.<sup>12</sup> Oderkerk and Groeninckx studied the dynamic vulcanization of nylon6/EPDM blends using peroxide as a crosslinking agent and EPDM-g-MA as a compatibilizer.<sup>13</sup> It was noted in their results that the phase-inversion region could not be shifted due to the compatibilization reaction between EPDM-g-MA and nylon6. So, in their study, peroxide was premixed with the rubber before the nylon6/rubber blend was compounded. In our work, EPDM/nylon copolymer TPVs were prepared in this way. First, a nylon copolymer with a compatibilizer (EPDM-g-maleic anhydride (MAH) or EPR-g-MAH) were melt-mixed and then EPDM was melt-mixed. Several minutes later, a vulcanizing agent (sulfur) and a coagent were added to crosslink the rubber phase. Therefore, it is necessary to study the morphology of the prepared EPDM/PA TPVs and to confirm the phase inversion.

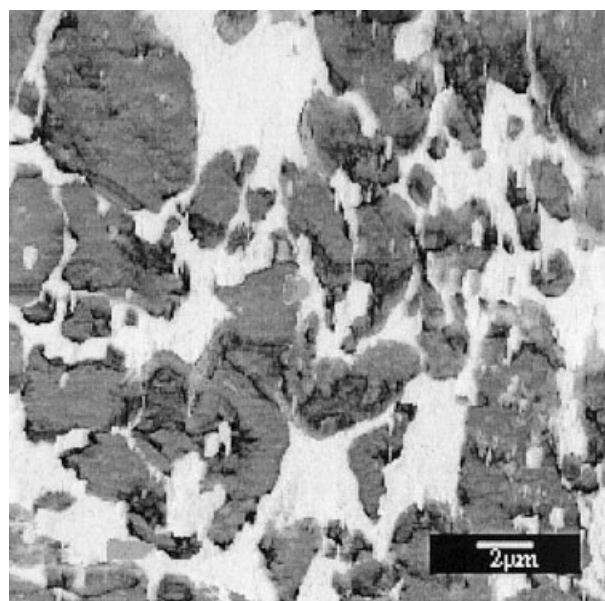
For TPVs, the phase morphology of the blends was usually examined with a transmission electron microscope (TEM).<sup>1,13</sup> Recently, atomic force microscopy (AFM) has been recognized as a powerful surface characterization technique and has been widely used to study the surface morphology of homopolymers,<sup>14,15</sup> block copolymers,<sup>16–18</sup> and polymer blends.<sup>19–24</sup> AFM does not require the staining of the sample as does TEM. Compared with contact-mode AFM, tapping-mode AFM has the advantage of lower force, less damage to soft samples imaged in air, and no scraping because of elimination of lateral force.

The purpose of the present article was to confirm the phase inversion in EPDM/PA TPVs by tapping-mode AFM. Furthermore, the effect of noncrosslinkability of the compatibilizer on the morphology of EPDM/nylon copolymer (PA) TPVs and its relationship with mechanical performance is discussed.

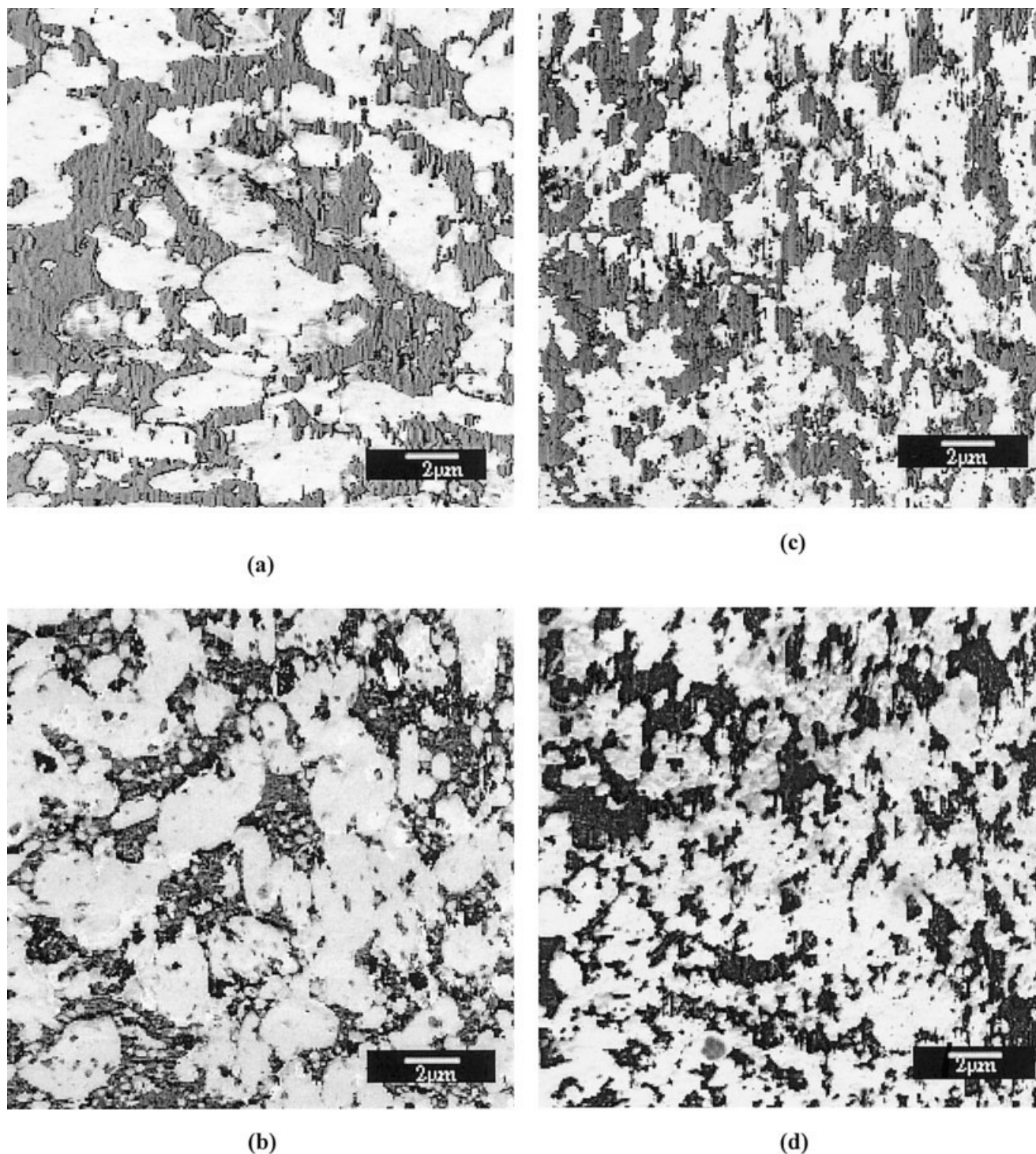
## EXPERIMENTAL

### Materials

EPDM EP4045 (ENB type) with a propylene content of 35.9 mol %,  $ML_{1+4}(100^{\circ}\text{C}) = 42$ , is a product of the Jilin Petroleum Chemical Co. Ltd. (China). A copolymer of nylon1010, 6-6, and 6 (70% nylon1010, 20% nylon6-6, 10% nylon6), with melting point of  $150^{\circ}\text{C}$ , was produced by the Shanghai Celluloid Factory (Shanghai, China). MAH-g-EPR 1801 is a product of Exxon Co. Ltd. (USA). MAH-g-EPDM (grafting degree 1.0%) was synthesized in our own laboratory. Chlorinated polyethylene (CPE) with a chlorine content of



**Figure 2** AFM image of dynamically vulcanized EPDM/PA (65/35).

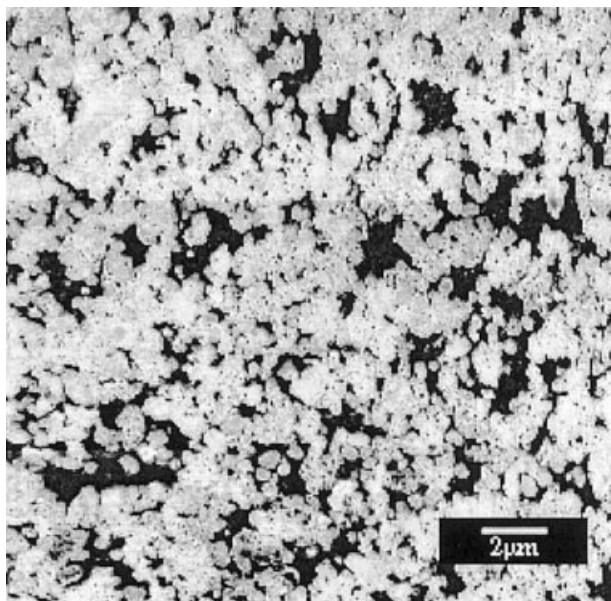


**Figure 3** AFM image of dynamically vulcanized EPDM/EPDM-g-MAH/PA: (a) 58.5/6.5/35; (b) 52/13/35; (c) 39/26/35; (d) 13/52/35; (e) 0/65/35.

36% is a product of the Jiangsu Dongtai Chemical Factory (China). Zinc oxide (ZnO), stearic acid (SA), tetramethylthiuram disulfide (TMTD), *N,N'*-*m*-phenylene bismaleimide (HVA-2), dibenzothiazyl disulfide (MBTS), dicumyl peroxide (DCP), and sulfur were used as received.

#### Preparation of EPDM/PA TPV

Prior to the melt-mixing operations, all materials were dried under a vacuum at 80°C overnight. The preparation of EPDM/PA TPV was performed at 180°C and 80 rpm in a Haake Rheocord 90 batch mixer. One



(e)

Figure 3 (Continued from the previous page)

minute after the melting of the nylon/compatibilizer blends in the mixer, EPDM was added. Four minutes later, curative and curing coagents were added while mixing. Mixing was continued for 7 min after the last ingredient was added. The batch was dumped, cut into small pieces, and remixed for an additional 3 min to ensure homogeneity. The composition was then compression-molded in a press at 180°C and cold-pressed to give samples for testing.

As indicated in our work,<sup>12</sup> sulfur was chosen to be a curative in this study after comparing the results with using phenolic resin or peroxide as a curative. The optimum content of the curative and curing coagents to ensure a suitable crosslinking degree is as follows: sulfur 2, ZnO 5, TMTD 1, MBTS 0.5, and SA 2 per 100 parts of rubber.

### AFM analysis

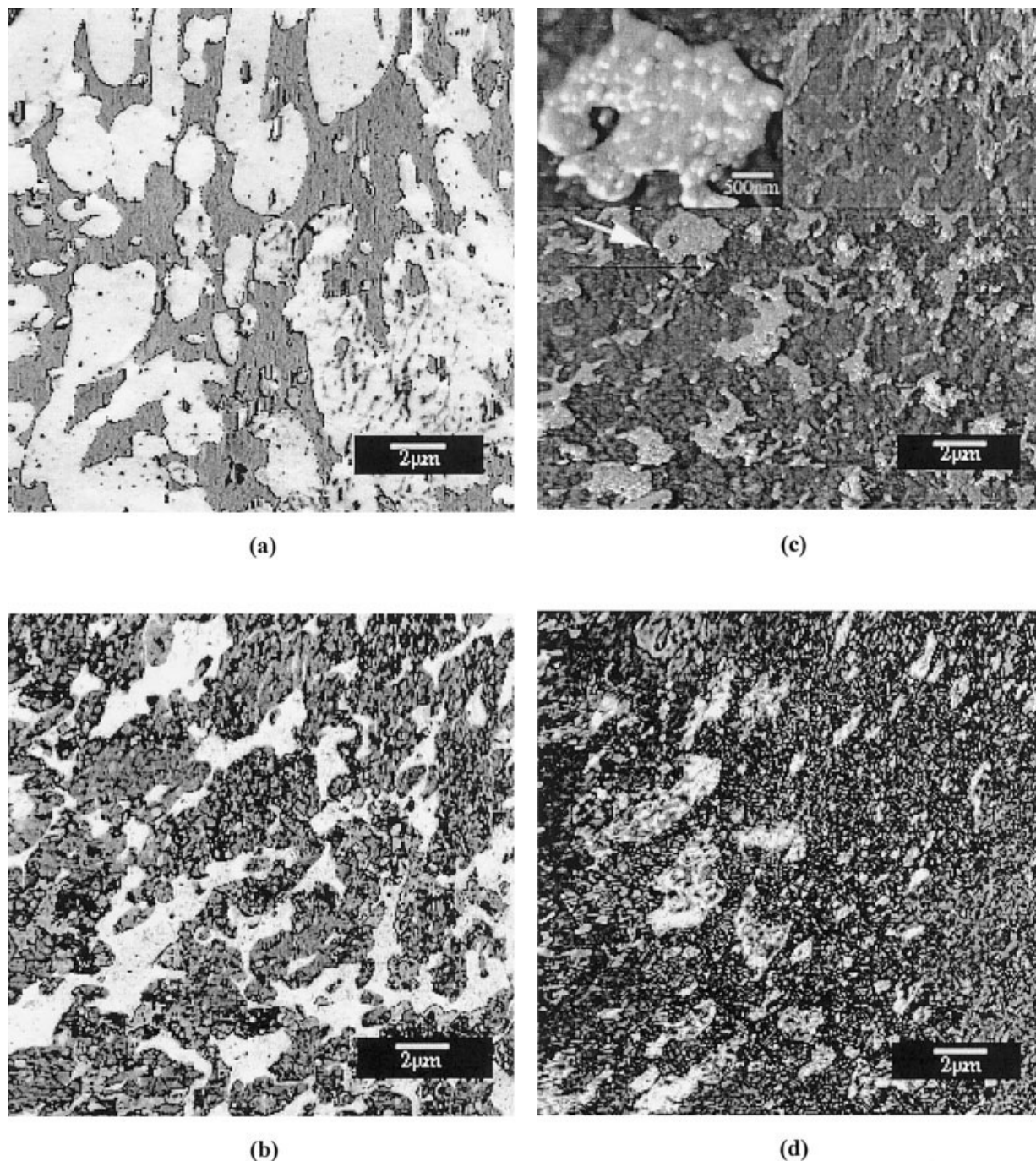
AFM images were acquired at room temperature in a noncontact mode using a JEOL JSPM-4210. The cantilevers (OMCL-AC160TS-C2, Olympus) had a spring constant of 36–66  $\text{Nm}^{-1}$  and a resonance frequency of 283–347 kHz. To get an ultrasurface, the specimen was cut with a diamond knife at  $-100^\circ\text{C}$ .

## RESULTS AND DISCUSSION

In this study, the rubber/thermoplastic ratio was chosen to be 65/35. For a 65/25 EPDM/PA composition, PA is the minor component and is the dispersed phase in an EPDM matrix. During dynamic vulcanization of such a blend, EPDM and PA have to undergo a phase

inversion to maintain the thermoplasticity of the blend. The usual way for preparing TPVs is, first, melt-mixing rubber with a thermoplastic, and a cocontinuous phase morphology is generated. Subsequently, a vulcanization agent for rubber is added to crosslink the rubber phase. Then, the rubber phase is no longer able to coalesce into a continuous phase. As the degree of crosslinking advances during mixing, the continuous rubber phase becomes elongated further and then breaks up into polymer droplets. As these droplets form, the thermoplastic becomes the continuous phase. Thus, TPVs with fine dispersed rubber particles in the thermoplastic matrix will be obtained. However, as indicated by Oderkerk and Groeninckx in their studies of the dynamic vulcanization of nylon6/EPDM blends,<sup>13</sup> the phase-inversion region could not be shifted due to the compatibilization reaction between EPDM-g-MAH and nylon6. So, in their study, peroxide was premixed with the rubber before the nylon6/rubber blend was compounded. As noted in the Experimental part, we prepared EPDM/PA TPVs in the usual way, that is, a vulcanizing agent was added after the full melt-mixing of PA with EPDM and the compatibilizer. AFM images were measured to check the occurrence of phase inversion.

Figure 1 is an AFM image of statically vulcanized EPDM/EPDM-g-MAH/PA blends, wherein the light area represents the crosslinked rubber phase and the dark area is the PA phase. It can be seen that PA droplets are dispersed in the rubber phase. Figure 2 is an AFM image of dynamically vulcanized EPDM/PA. In this micrograph, the morphology of large crosslinked EPDM particles (white) dispersed in the PA matrix (dark) can be observed, and the large rubber particles have a tendency to be cocontinuous because no compatibilizer was used. The phase morphology of EPDM/EPDM-g-MAH/PA TPVs with different dosages of the EPDM-g-MAH compatibilizer are presented in Figure 3(a–e), respectively, wherein the light area represents the crosslinked rubber phase and the dark area is the PA phase. From these AFM images, it can be seen that for a 10–100% (on total rubber dosage) EPDM-g-MAH content phase inversion always exists and the rubber phase can be finely dispersed in the PA matrix with an increasing compatibilizer content. This phenomenon shows that, although there is a compatibilization reaction between EPDM-g-MAH and PA, the phase-inversion region could be shifted. The reason for this may be that PA keeps its flow mobility in the melting state. During the dynamic vulcanization process, some PA droplets may be encapsulated by the rubber phase because of the steric stabilization effect of the EPDM-g-PA formed and the subinclusions of PA inside the rubber particles can be observed in the AFM images. However, since the crosslinking degree of the rubber phase



**Figure 4** AFM image of dynamically vulcanized EPDM/EPR-g-MAH/PA: (a) 58.5/6.5/35; (b) 52/13/35; (c) 39/26/35; (d) 13/52/35; (e) 0/65/35.

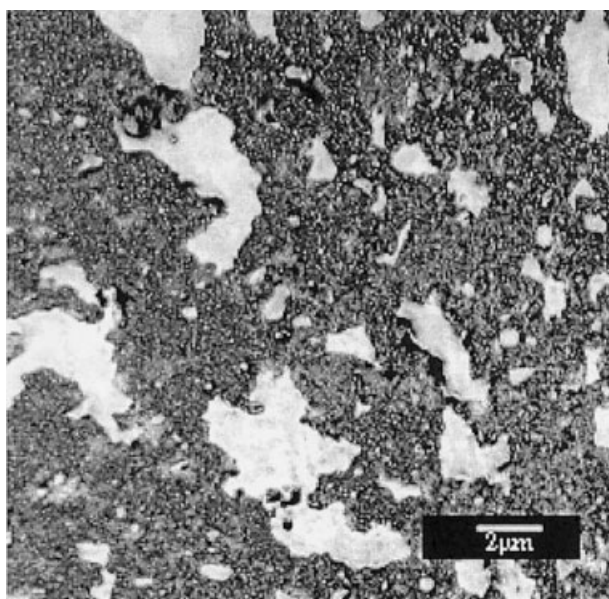
was not high enough to form a network and the PA chain keeps its flow mobility in the melting state, the PA phase tends to coalescence and can form the continuous phase. Furthermore, the size of crosslinked rubber particles decreases with an increasing dosage of EPDM-g-MAH because of the compatibilization reaction.

In our early work,<sup>12</sup> it was found that EPR-g-MAH has a better performance in compatibilizing EPDM/PA TPVs compared with EPDM-g-MAH and

that the tensile strength and the elongation at break go through a maximum value at a compatibilizer resin content (on total rubber dosage) of 20%. In the present study, the morphology of EPDM/EPR-g-MAH/PA TPVs was measured by AFM and we tried to connect the results with the mechanical properties. Figure 4(a-e) shows AFM images of EPDM/EPR-g-MAH/PA TPVs with different dosages of the EPR-g-MAH compatibilizer. Because of the noncrosslinkability of EPR by sulfur, three phases exist in these kinds



of blends. In Figure 4(a,b), it can be observed that crosslinked EPDM particles (bright regions) are dispersed in the comatrix of PA and MAH-g-EPR (dark regions). Compared with the morphology of TPVs with the same dosage of the EPDM-g-MAH compatibilizer [Fig. 3(b)], the morphology of TPVs using EPR-g-MAH as the compatibilizer shows much smaller dispersed rubber particles, which may contribute to the better mechanical performance as listed in Table I. When the content of EPR-g-MAH reached 26 wt %, it can be seen from Figure 4(c) that the particle size of the crosslinked EPDM decreases and the large bright regions seem to be composed of small particles, especially from the amplified image. This may be because, with an increasing EPR-g-MAH compatibilizer dosage, the uncrosslinked EPR-g-MAH existing in the interface between crosslinked EPDM and PA tends to coalesce. For an EPR-g-MAH dosage of 52 wt %, as uncrosslinked EPR-g-MAH becomes the continuous phase, the morphology changes to be one of the dispersion of PA and crosslinked EPDM particles (white) in the EPR-g-MAH (dark) matrix [as shown in Fig. 4(d)]. When EPDM was totally replaced by EPR-g-MAH, the system changes to be one of blends of EPR-g-MAH with PA and no dynamic vulcanization exists as EPR-g-MAH cannot be vulcanized by sulfur. So, the morphology is one of dispersed PA particles (white) in the EPR-g-MAH (dark) continuous phase [Fig. 4(e)]. The change of the morphology in the blends using EPR-g-MAH as the compatibilizer thus leads to the optimum EPR-g-MAH compatibilizer content of 13 wt % for the mechanical properties.



(e)

Figure 4 (Continued from the previous page)

**TABLE I**  
Effect of Compatibilizers on Mechanical Performance

Compatibilizer	EPR-g-MAH	EPDM-g-MAH
Hardness (Shore A)	85	86
Tensile strength (MPa)	13.3	10.1
Elongation at break (%)	295	204

Formulation: EPDM 52; compatibilizer 13; PA 35.

## CONCLUSIONS

A TPV of EPDM and PA was prepared. The phase morphology investigated by AFM indicated that phase inversion always exists for EPDM/EPDM-g-MAH/PA TPVs and the rubber phase can be finely dispersed in the PA matrix with an increasing compatibilizer content, although there is a compatibilization reaction between EPDM-g-MAH and PA. For TPVs using EPR-g-MAH as the compatibilizer, crosslinked EPDM particles dispersed in the comatrix of PA and EPR-g-MAH can be observed by increasing the content of EPR-g-MAH to 26 wt %. For an EPR-g-MAH content of 26 wt %, the uncrosslinked EPR-g-MAH existing in the interface between crosslinked EPDM and PA tends to coalesce and thus results in the morphology of large rubber regions composed of small crosslinked particles. When the dosage of EPR-g-MAH reached 52 wt %, the phase morphology of the blends changed to be one of PA and crosslinked EPDM particles dispersed in the MAH-g-EPR matrix.

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