Morphology and Mechanical Properties of Ethylene-Vinyl Acetate Rubber/Polyamide Thermoplastic Elastomers

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ABSTRACT: High performance thermoplastic elastomers based on ethylene-vinyl acetate rubber (EVM) and ternary polyamide copolymer (tPA) were prepared through a dynamic vulcanization process in the presence of dicumyl peroxide (DCP). The morphology, crystallization, and mechanical properties of the EVM/tPA blends were studied. A phase transition of EVM/tPA blend was observed at a weight ratio of 60/40. The presence of EVM increased the melting enthalpy at the high temperature of tPA, ascribing to the heterogeneous nucleating effect of EVM. The tensile strength of EVM/tPA (70/30) blends was increased up to 20.5 MPa as the DCP concentration increased to 3.5 phr, whereas the elongation at break of the blends kept decreasing as the DCP concentration increased. The addition of ethylene-acrylic acid copolymer (EAA) or maleic anhydride-grafted EVM (EVM-g-MAH) to the EVM/tPA blends both induced finer dispersion of the EVM particles in the tPA phase and improvement in the tensile strength and elongation at break of the blends, which were ascribed to the compatibilization of EAA or EVM-g-MAH. Finally, a high performance EVM/tPA (70/30) thermoplastic elastomer with Shore A hardness of 75, tensile strength of 24 MPa, elongation at break of 361%, and set at break of 20% was obtained by adding 5 wt % of EVM-g-MAH and 3.5 phr DCP. It has great potential in automotive and oil pipeline applications. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 130: 338–344, 2013

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INTRODUCTION

Dynamic vulcanization has been established as an effective method for fabrication of high performance thermoplastic elastomers (TPEs). Thermoplastic polyamide (PA)-based TPEs with nonpolar or polar rubbers as the second components, such as ethylene-propylene diene terpolymer,^{1–8} ethylene-propylene rubber,⁹ natural rubber,¹⁰ butadiene-acrylonitrile copolymer,^{11–17} hydrogenated butadiene-acrylonitrile copolymer,^{11–17} hydrogenated butadiene-acrylonitrile copolymer,^{12–24} and halogenated butyl rubber^{17,25–28} have been investigated intensively by applying dynamic vulcanization technique, and the resultant PA-based TPEs have found wide applications in sports, transport, and construction areas.

Ternary polyamide copolymer (tPA) has lower melting temperature and crystallinity than polyamide 6 (PA 6, and is generally used for modification of rubbers. Ethylene-vinyl acetate rubber (EVM) is a kind of specialty rubber with vinyl acetate content in the range of 40–80 wt %. It has been mostly used as halogen-free flame retardant, insulating, heat- or oil-resistant materials for electrical cable, construction, and automotive applications. The combination of tPA and EVM would be expected to combine the thermal stability of tPA and the oil-resistance of EVM, and producing high performance TPEs. To the best of our knowledge, there is no report on the fabrication and application of PA/EVM or tPA/EVM TPEs so far.

In this article, EVM with vinyl acetate of 40 and 60 wt % was used to blend with tPA through a dynamic vulcanization process. Ethylene-acrylic acid copolymer (EAA) or maleic anhydride-grafted EVM (EVM-g-MAH) was used as a compatibilizer for improving interfacial adhesion of the two phases. The morphology, mechanical properties, and oil-resistance of the resultant EVM/tPA TPEs were investigated systematically. The TPEs will find new applications in electrical cable, automotive, and oil pipeline areas.

EXPERIMENTAL

Materials

EVM (Levapren[®] 400HV and Levapren[®] 600HV) with 40 and 60 wt % of vinyl acetate content and Mooney viscosity $ML_{1+4}^{100^{\circ}C}$ of 20 and 27, respectively, was kindly provided by Lanxess

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Deutschland GmbH, Germany. tPA [type 150, a copolymer of polyamide 6, 66, and 1010 (10/20/70 wt %)] with the relative viscosity of 2.0 was produced by Shanghai Jiaxin Sujiao Co., Shanghai, China. Dicumyl peroxide (DCP) and MAH, analytical grade, were purchased from Sinopharm Group Chemical Reagent Co., China. EAA (EAA 1430) with 9.7 wt % acrylic acid content was purchased from Dow Chemical Co. (Midland, MI).

Sample Preparation

Preparation of EVM-g-MAH. EVM-g-MAH was prepared by melt-compounding of EVM (400 HV), MAH and DCP in a weight ratio of 100/5/0.25 at 170°C for 10 min, at a rotor speed of 50 rpm in a Haake rheometer.

Preparation of EVM/tPA/DCP TPE via a Dynamic Vulcanization Process. EVM (600 HV) was selected for preparation of EVM/tPA TPEs. DCP concentration was varied from 0 to 5 parts per hundred of EVM/tPA blends, that is, 0–5 phr based on 100 parts by weight of EVM/tPA blends. First, EVM and DCP were mixed on a two-roll mill at room temperature. tPA was separately melt-compounded at 180°C for 1 min with a rotor speed of 60 rpm using a Haake rheometer. Then, the EVM/DCP compound was added and mixed with tPA for 9 min. The resultant EVM/tPA/DCP blends were compression molded to specimens at 190°C. In comparison, EVM/tPA blends of various weight ratios were prepared following the above procedure without addition of DCP. For EVM/tPA blends with compatibilizers, EAA was used together with tPA, and EVM-g-MAH was added together with EVM.

Characterization

Tensile properties were measured following ASTM D412, by using a universal test machine (Instron 4465, Instron, Norwood, MA) at a crosshead speed of 200 mm min⁻¹. Dumbbell specimens were 75 mm in length, 1 mm in thickness, and 4 mm in width. Shore A hardness of EVM/tPA TPEs was measured according to ASTM D2240. Curing curves were recorded using a UR 2030 rheometer at 180°C. The relative curing extent was calculated by the difference between the maximal toque value (M_H) and the minimal torque value (M_L) of the curing curve ($M_H - M_L$) Swelling tests were performed according to ASTM D471, by immersing a rectangular test specimen of 25 × 25 × 1 mm³ in IRM 903 oil at 100°C for 24 h. The weights of the specimen were measured before and after the immersion, the percent changes in mass and volume were calculated following eqs. (1) and (2):

$$\Delta M = \frac{(M_2 - M_1)}{M_1} \times 100$$
 (1)

where ΔM is the change in mass (%), M_1 is the initial mass of specimen in air (g), and M_2 is the mass of specimen in air after immersion (g).

$$\Delta V = \frac{(M_2 - M_4) - (M_1 - M_3)}{(M_1 - M_3)} \times 100$$
(2)

where ΔV is the change in volume (%), M_3 is the mass of specimen in water (g), and M_4 is the mass of specimen in water after immersion (g).



Figure 1. Tensile properties of EVM/tPA blends without dynamic vulcanization. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

The phase morphology of the EVM/tPA blends was studied by observing cryogenically fractured surface of the specimens using scanning electron microscopy (S2150, HITACHI Co., Japan). The EVM/tPA blends (tPA content \leq 40 wt %) were etched with ethanol for 24 h at room temperature, and the EVM/tPA blends (tPA content > 40 wt %) were etched with acetone for 24 h at room temperature. Atomic force microscopy (AFM) images were obtained in a tapping mode on a Nano Scope III A (Digital Instrument, Plainview, NY). The cantilevers had a spring constant of 40 Nm⁻¹ and a resonance frequency of 300 kHz. Samples with ultrasmooth surface were prepared with a microtome in liquid nitrogen.

Differential scanning calorimetry (DSC) measurement was carried out by using a modulated differential scanning calorimeter (Q2000, TA Instruments, New Castle, DE). A sample of about 10 mg was dried in a vacuum oven prior to experiments. Thermograms were recorded during both heating and cooling cycle at 20° C min⁻¹ using identical setting of instrument for all the samples. The sample was heated from -60 to 250° C and held at 250° C for 1 min, then cool down to -60° C to investigate the crystallization of EVM/tPA blends during processing. Subsequently, a second identical heating cycle was performed. For the isothermal scanning to study the vulcanization reaction, a sample was quickly heated up to 180° C at 200° C min⁻¹ and kept at 180° C for 20 min. Subsequently, the sample was cooled down to -60° C then heated up to 50° C at 20° C min⁻¹.

RESULTS AND DISCUSSIONS

The morphology and mechanical properties of EVM/tPA blends were investigated, and the tensile testing results are shown in Figure 1. The tensile strength of EVM/tPA (40/60) was 25.8 MPa. It was continuously decreased to 0.8 MPa as the EVM/tPA weight ratio increased to 80/20. The value of elongation at break of EVM/tPA (40/60) was 437% and also decreased to 323% for EVM/tPA (60/40), but increased up to 913% for EVM/tPA (80/20). As shown in Figure 2, the EVM phase dispersed homogeneously in the continuous tPA matrix in the EVM/tPA(40/60) blend. As the EVM/tPA weight ratio increased





Figure 2. SEM images of cryogenically fractured surface of EVM/tPA blends. EVM/tPA: (a) 40/60; (b) 50/50; (c) 60/40; (d) 70/30; and (e) 80/20.

from 50/50 to 70/30, co-continuous phase morphology was observed. This morphology transition behavior reflects the change of elongation at break value of EVM/tPA (60/40) as observed in Figure 1.

The effect of EVM/tPA weight ratio on the crystallization behavior of tPA was studied by DSC technique (Figure 3). The glass transition temperatures of tPA and EVM were 36.3 and -29.3° C, respectively. After melt-blending process, they approached to each other, indicating a partial compatibility between tPA and EVM due to the interaction between amide groups and acetate groups attributed to the intermolecular hydrogen bonds between tPA NH groups and EVM C=O groups.²⁹ The tPA showed three melting peaks at about 54, 115, and 174°C, respectively. The melting enthalpy at 115°C was significantly decreased upon the incorporation of EVM, indicating that the EVM retarded the crystallization of tPA during the compression-molding process. While under DSC testing condition, EVM might play the role of a heterogeneous nucleating agent to facilitate the crystallization of tPA (Figure 3b). Additionally, the crystallization of tPA was sensitive to tensile stress (Table I and Figure 4), as the tensile stress induced the crystallization at high melting point region, increased the melting enthalpy and decreased the melting point. The main reason could be due to the stress induced orientation of the main chains of tPA and thus facilitated the crystallization.

The EVM/tPA (70/30) blend was chosen for preparation of EVM/tPA/DCP TPEs through a dynamic vulcanization process. EVM was the continuous phase with dispersed tPA phase in the EVM/tPA (70/30) blend (Figure 2d). After dynamic vulcanization, a phase inversion occurred (Figure 8a), which should be



Figure 3. DSC scanning curves of EVM/tPA blends. (a) First heat scanning and (b) second heat scanning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

due to the increased viscosity of EVM phase caused by the crosslinking reaction. $^{\rm 30}$

For the dynamically vulcanized EVM/tPA/DCP (70/30) TPE, the peak torque of crosslinking increased with increasing DCP loading (Figure 5). The particle size of the crosslinked EVM depended on both the crosslinking extent and the applied shear strength. During dynamical vulcanization, the rubber phase in the blends was crosslinked and immobilized, and they could be further broken down to micron-sized particles under the applied shear field.³⁰ The breakdown of particles was intrinsically inhibited with increased crosslinking,¹⁹ so excessive cross-

Table I. DSC Results of tPA Before and After Tensile

	Т _д (°С)	T _m (°C)	$\Delta H_{\rm m}$ (J/g)
tPA	36.3	54.4/115.0/173.6	2.7/19.1/0.5
tPA (after tensile)	35.8	50.8/110.2/164.9	2.4/26.7/4.3



Figure 4. DSC heat scanning curves of tPA before and after tensile test. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

linking could increase the particle size. As shown in Table II, the tensile strength increased with DCP content increasing up to 3.5 phr, where the tensile strength and elongation at break reached 20.5 MPa and 339%, respectively. With a higher DCP addition, the tensile strength and stress at 100% extension decreased, which may be due to the larger rubber particles with further increased crosslinking.

The vulcanization curves and the DSC isothermal curves were used to investigate the vulcanization reactions of EVM with different DCP addition (Figure 6). The EVM cured with 5 phr of DCP showed the highest torque, corresponding to the highest crosslink density, among other formulations.

To improve the interfacial adhesion of partially compatible PAbased blends, reactive compatibilization is one of the effective ways, which is mainly based on the reactions between amino or carboxyl end groups in PA with other active groups such as



Figure 5. Dynamic vulcanization curves of EVM/tPA (70/30) blends. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



DCP content (phr)	Tensile strength (MPa)	Elongation at break (%)	Stress at 100% extension (MPa)	Stress at 300% extension (MPa)	Set at break (%)	Shore A hardness
0	1.1 ± 0.1	663 ± 164	0.6 ± 0.2	0.8 ± 0.2	>100	40
1	11.2 ± 0.6	456 ± 26	1.6 ± 0.2	4.4 ± 0.6	60	65
1.5	13.9 ± 0.7	431 ± 20	1.3 ± 0.0	4.9 ± 0.6	50	65
2	14.5 ± 0.5	408 ± 10	1.3 ± 0.1	5.1 ± 0.6	45	64
2.5	16.7 ± 0.9	365 ± 18	3.4 ± 0.1	10.2 ± 1.5	26	66
3	16.6 ± 0.9	347 ± 25	3.4 ± 0.2	11.2 ± 1.6	23	66
3.5	20.5 ± 0.8	339 ± 11	4.9 ± 0.4	14.8 ± 1.4	23	78
4	19.4 ± 0.7	330 ± 12	2.9 ± 0.3	14.8 ± 1.3	19	75
5	18.5 ± 0.8	319 ± 7	1.9 ± 0.2	14.7 ± 1.6	15	80

Table II. Mechanical Properties of Dynamically Vulcanized EVM/tPA (70/30) Blends with Different DCP Content

succinic anhydride,³¹ MAH,^{32–34} carboxyl acid^{35–37} and oxazoline,³⁸ and so on. Here, EAA and EVM-*g*-MAH were used as compatibilizers for EVM/tPA blends. Both the tensile strength and elongation at break of EVM/tPA/compatibilizer (65/30/5) blend were increased (Table III), implying improved interfacial interaction between the two phases in the presence of the compatibilizers. EVM/tPA/EVM-*g*-MAH (65/30/5) blend had tensile strength of 24.0 MPa, elongation at break of 361%, and set at break of 20%, which were better than those of EVM/tPA/EAA blend, suggesting a better compatibilization of EVM-*g*-MAH than EAA for EVM/tPA blends.

After the compatibilizers (EAA and EVM-g-MAH) were introduced, the melting enthalpy of tPA decreased during

processing (Figure 7a), but increased during the DSC testing (Figure 7b and Table IV). There are two factors affecting the crystallization of tPA: the formation of tPA grafted copolymer (EAA-g-tPA or EVM-g-tPA) at the phase interface, which could restrict the crystallization of tPA; the decreased rubber particles caused by the compatibilization may act as nucleating agents and induce the crystallization of tPA.⁷ Additionally, the melting peak of tPA crystals with low melting point (about 82° C) disappeared after EVM-g-MAH was added, which is significant for TPE to obtain high temperature performance.

The effect of EVM-g-MAH on the phase morphology of the EVM/tPA blends was investigated by AFM. As shown in



Figure 6. The vulcanization reaction of EVM/DCP blends at 180°C. (a) vulcanization curves and (b) DSC isothermal curves. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table	III.	Mechanical	Properties	of	Compatibilized	EVM/tPA	Blends
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Sample	Tensile strength (MPa)	Elongation at break (%)	Stress at 100% extension (MPa)	Set at break (%)	Shore A hardness
EVM/tPA/DCP (70/30/3.5)	20.5 ± 0.8	339 ± 11	4.9 ± 0.4	23	78
EVM/tPA/EAA/DCP (65/30/5/3.5)	21.3 ± 1.3	366 ± 5	2.0 ± 0.1	38	78
EVM/tPA/EVM-g-MAH/DCP (65/30/5/3.5)	24.0 ± 1.6	361 ± 6	1.8 ± 0.1	20	75



Figure 7. DSC scanning curves of EVM/tPA blends after addition of compatibilizers. (a) First heat scanning and (b) second heat scanning. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table IV. D	OSC Results	of C	ompatibilized	EVM/tPA	Blends
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		First heat scanning		Second heat scanning	
Sample	T _g (°C)	T _m (°C)	$\Delta H_{\rm m}$ (J/g)	T _m (°C)	$\Delta H_{\rm m}$ (J/g)
EVM/tPA/DCP (70/30/3.5)	-22.9/33.6	54.2/119.1	1.1/5.3	128.8	0.9
EVM/tPA/EAA/DCP (65/30/5/3.5)	-23.3/34.4	82.1/123.1	0.7/3.5	82.2/129.2	1.7/1.1
EVM/tPA/EVM-g-MAH/DCP (65/30/5/3.5)	-23.7/32.1	116.7	5.2	125.8	1.6

Figure 8, the crosslinked rubber particles (white) were dispersed in the tPA matrix (dark) and the average size of EVM particles in diameter was about 1.0 and 0.5 μ m for EVM/tPA (70/30) blend and EVM/tPA/EVM-g-MAH (65/30/5) blend, respectively. The addition of EVM-g-MAH improved the distribution homogeneity of the rubber particles as well as decreased the rubber particle size.

The dispersion of EVM particles in the tPA phase was investigated by AFM. The oil-resistance of EVM/tPA blends was measured by immersing in IRM 903 oil at 100°C for 24 h. The percent change in mass and volume decreased with increasing DCP content (Figure 9), indicating an increased crosslinking density of the rubber phase. Therefore, the oil-resistance of EVM/tPA blends can be improved by dynamic vulcanization.

CONCLUSIONS

EVM and tPA are partially compatible polymers with a phase inversion point at the EVM/tPA weight ratio of about 60/40.



Figure 8. AFM phase image of (a) EVM/tPA/DCP (70/30/3.5) and (b) EVM/tPA/EVM-g-MAH/DCP (65/30/5/3.5). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



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Figure 9. Oil resistance of dynamically vulcanized EVM/tPA blends with different DCP content. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EVM/tPA (70/30) TPE were prepared through dynamic vulcanization in the presence of DCP. The tensile strength of the TPE increased with increase in DCP content up to 3.5 phr, reaching a maximum value of 20.5 MPa, and the elongation at break decreased monotonously. The oil-resistance of EVM/tPA blends was improved by dynamic vulcanization. After EVM-*g*-MAH was introduced into the TPE, the tensile strength and elongation at break of the TPEs increased, and the EVM rubber particles became smaller as observed from AFM images. A high performance EVM/tPA (70/30) thermoplastic elastomer with good mechanical properties and low hardness was obtained by adding 5 wt % EVM-*g*-MAH as the compatibilizer and 3.5 phr DCP as the curing agent.

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