

Study on the microstructure and properties of bromobutyl rubber (BIIR)/polyamide-12 (PA12) thermoplastic vulcanizates (TPVs)

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ABSTRACT: In this study, polyamide-12 (PA12)/brominated isobutylene-isoprene (BIIR) TPVs with good mechanical properties and low gas permeability were prepared by dynamic vulcanization in a twin-screw extruder. The effects of three kinds of compatibilizers on the microstructure and properties of BIIR/PA12 TPV were studied. The compatibility between BIIR and PA12 was improved when maleated hydrocarbon polymeric compatibilizer is added. The reaction between maleic anhydride and amine in polyamide leads to the *in situ* formation of hydrocarbon polymer grafted polyamide which subsequently can be used to lower the interfacial tension between BIIR and polyamide. The compatibilizing effect of maleic anhydride modified polypropylene (PP-g-MAH) on BIIR/PA12 blends is the best among these compatibilizers because the surface energy of PP-g-MAH is very close to that of BIIR. The dispersed rubber phase of the blend compatibilized by PP-g-MAH shows the smallest size and more uniform size distribution, and the resulting TPVs show the best mechanical properties. The effects of fillers on the properties of BIIR/PA12 TPV were also investigated. The size of the BIIR phase increases with the increase in the content of CaCO₃. The modulus and tensile strength of TPVs increased with the increase in the content of CaCO₃ because of the reinforcing effect of CaCO₃ on TPVs. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2016, 133, 43043.

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INTRODUCTION

Thermoplastic vulcanizate (TPV) is a kind of typical green polymer material produced by dynamic vulcanization, which consists of a high content of crosslinked rubber as the dispersed phase and a low content of thermoplastics as the continuous phase.^{1–7} TPVs combine the excellent resilience of ordinary vulcanized rubbers, and the high processability and recyclability of thermoplastics, and thus have been widely used in industries such as automotive, building, and electronics in recent years.^{8,9} Nowadays, TPVs are becoming one of the fastest growing polymer materials owing to the requirement of environmental protection and resource saving.¹⁰

Since the first commercialization of “Santoprene,” a TPV based on ethylene-propylene diene monomer (EPDM) and polypropylene (PP), was produced by Monsanto in 1981, up to now, most commercial TPVs were based on EPDM and PP because of their structural compatibility. Nowadays more and more

studies have been focused on acrylonitrile-butadiene rubber/PP TPVs, butyl rubber/PP and polyamides (PA)/isobutylene-isoprene (IIR) TPVs because of their good oil resistance, good sealability and good barrier characteristic. Among these TPVs, brominated isobutylene-isoprene (BIIR)/PA12 TPVs have great potentials in such applications as innerliner of tire treads and refrigeration hoses, etc.^{11–13} because both PA 12 and BIIR have good barrier characteristics and thus they have attracted much attention in recent years. In this study, PA12 was used as the plastics because of its excellent solvent and oil resistance, low water absorption and relatively low melting point, which is very close to the vulcanization temperature of BIIR. BIIR instead of IIR was used as rubber because BIIR have better compatibility with PA12 than IIR.¹⁴

The properties of TPVs are affected by many factors such as the physical and chemical characteristics of rubber and thermoplastics, the phase morphology, the blend ratio, the compatibility between rubber and thermoplastics. Of these factors, the

Table I. Characteristics of Materials Used

	Trade mark	MFI ^a (g/10 min)	T_m (°C)	Br content (wt %)	Mooney viscosity (ML(1 + 4) 125°C)
PA12	3030 JI5	4	173	-	-
BIIR	2030	-	-	1.8	32

^a At 230°C and 2.16 kg.

MFI = melt flow index; T_m = melting point.

compatibility between the rubber and plastics matrix plays a very important role in the properties of the TPVs. The big difference in the solubility parameter between the polar PA12 and the nonpolar BIIR leads to poor compatibility between PA12 and BIIR. Previous study reported that a reaction between PA12 and BIIR could occur during blending, resulting in the *in situ* formation of compatibilizer.¹⁵ Nevertheless, the compatibility between PA12 and BIIR is very poor without the addition of compatibilizer because little compatibilizer can be formed by the *in situ* reaction between PA12 and BIIR owing to the severe phase separation. It has been reported that maleic anhydride (-MA) containing polymers can be used as compatibilizers of PA and IIR, because the MA groups can react with the amide groups of PA.^{16–20}

Up to now, most of the studies^{14,21–24} on IIR/PA TPV were based on the TPVs without fillers and prepared in Haake rheometer or internal mixer for easily controlling the process of dynamic vulcanization. However, the commercial TPVs always contain complicated compositions such as fillers, which are typically used to control the hardness, modulus, and processability of TPV. In addition, the fillers have an obvious effect on the final morphology of TPV. On the other hand, the commercial TPVs are preferably produced by using twin-screw extruder for continuous and large-scale processing with high outputs and high efficiency. Compared with Haake rheometer or internal mixer, it is harder to control the morphology during dynamic vulcanization by using a twin-screw extruder. In addition, the strong shear stress by increasing rotate rate of the screws and short dynamic vulcanization time (generally less than 90 s) by using twin-screw extruder can have an obvious effect on the final microstructure of TPVs, which has seldom reported.

Thus, in this study, a group of dynamically vulcanized BIIR/PA12 TPV were prepared by using a co-rotating twin-screw extruder. The effect of the compatibilizers, and the fillers on the phase morphology and properties of BIIR/PA12 TPVs were carefully studied. Our goal is to provide guidance for the large scale production of high performance BIIR/PA12 TPVs for the application as innerliner of tire treads and refrigeration hoses.

EXPERIMENTAL

Materials

Table I lists the characteristics of the PA12 and BIIR, which were bought from Ube Ltd. (Japan) and Lanxess Chemical (Canada), respectively.

Table II. Composition of Premixes without Fillers

Ingredient	Content of the ingredients (phr)
BIIR	100
PA12	54-X
Compatibilizers	X(5,10,20)
Anti-oxidant 1010	1
ZnO	3.5
Stearic acid (SA)	2
HVA-2	4

For 100 phr BIIR, the total amount of PA12 and compatibilizers is 54 phr.

Phr = per hundred rubber; HVA-2 is the abbreviation of *N,N'*-*m*-phenylene dimaleimide.

Maleic anhydride modified polypropylene (PP-g-MAH) was obtained from Dupont with the trade mark 353D. Maleic anhydride Modified Ethylene-Octane Copolymer (POE-g-MAH) was obtained from Ningbo Nengzhiguang Company with the trade mark N410. Styrene-Ethylene-Butylene-Styrene grafted by maleic anhydride (SEBS-g-MAH) was obtained from Kraton Performance Polymers Inc. with the trade mark FG 1901X. The grafting degree of the compatibilizing agents is shown in Table III. Pentaerythritol tetrakis 3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate (Irganox 1010) was used as an antioxidant. The crosslinking agents were composed of zinc oxide (ZnO) and *N,N'*-*m*-phenylene dimaleimide (HVA-2). The calcium carbonate, provided by Henankeli New Material Co., Ltd., China, has a average particle size of 1.3 μm and an apparent density of 1.13 g/cm³. The surface of CaCO₃ was not modified. Irganox 1010, SA, ZnO, HVA-2 are commercially available.

Preparation of BIIR/PA 12 TPV

To ensure BIIR fully vulcanized, the static curing characteristics of the different amount of ZnO/HVA-2 was determined before preparing BIIR/PA TPV. The curing system (ZnO 3.5 phr, HVA-2 4 phr) used in this study was chosen because the crosslink density is high enough and the T_{90} is 100 s at 180°C and T_{90} is \sim 82 s at 200°C.

Table III. Size and Size Distribution of Rubber Particles of TPVs

Compatibilizers or additives	d_n (μm) ^a	d_v (μm) ^b	PDI
None	3.69	7.67	2.08
SEBS-g-MAH	2.50	4.81	1.92
POE-g-MAH	2.60	5.09	1.96
5 phr PP-g-MAH	2.64	4.87	1.84
10 phr PP-g-MAH	2.26	4.10	1.81
20 phr PP-g-MAH	Phase inversion unoccurred		
10 phr CaCO ₃	2.65	4.45	1.68
30 phr CaCO ₃	4.14	7.18	1.73

^a Standard deviation of \pm 3.2%.

^b Standard deviation of \pm 3.6%.

BIIR/PA12 TPV was prepared in a intermeshing co-rotating twin-screw extruder (HTS-40, Nanjing Xiangsu Factory, China) with L/D of 52 with temperature of each zone controlled. The premix of the BIIR/PA12 blend was prepared by using the two-roll mill as follows. PA 12 was first dried in an oven at 80°C for 8 h to prevent the PA from hydrolysis. The BIIR rubber and PA12 were fed into the two-roll mill in the required mass ratio (65:35) at 190°C for 3 min, resulting in continuous rubber phase. Meanwhile the antioxidant was added to prevent the degradation of PA12 at high temperature. The compatibilizers were also added in this process. Subsequently, the homogeneous blend was transferred to another two-roll mill at room temperature, and the crosslinking agents and fillers were added. The basic composition of the premix for dynamic vulcanization without compatibilizers and fillers is given in Table II. The blends needed to be pelletized for feed to the twin-screw extruder mentioned above. The temperature of each zone from the feeding zone to the die in the extruder is set between 180°C and 200°C, meanwhile the rotor speed used is 450 rpm. During dynamic vulcanization, the BIIR phase in the blends transfers from continuous phase to dispersed phase (see below).

Characterization

Morphological Analysis. An S-4700 scanning electron microscope (SEM) purchased from Hitachi Co. (Japan) was used to observe the morphologies of the TPVs. The mode of back scattered electron (BSE) imaging was used. Before the observations, the samples were polished at -130°C by using a cryo-ultramicrotome (Leica EM UC7; Germany).

The particle size distribution was determined with the 2D area measurement software of SEM image analysis (Image-Pro Plus 4.5). To obtain a representative result, three SEM-BSE graphs and more than 100 particles were examined. The number-average diameter (d_n), the volume-average diameter (d_v), and the polydispersity index (PDI) were calculated according to:

$$d_n = \frac{\sum_i n_i d_{n_i}}{\sum_i n_i} \quad (1)$$

$$d_v = \frac{\sum_i n_i d_{n_i}^4}{\sum_i n_i d_{n_i}^3} \quad (2)$$

$$\text{PDI} = \frac{d_v}{d_n} \quad (3)$$

Mechanical Properties. To prepare test specimens, all TPVs and PA12 were put into a specially designed mold and warmed for 8 min at 200°C in an electrically heated press and then pressure was applied for 2 min, after which the mold was moved to another press immediately and pressed at room temperature for 3 min to make the samples cool down to keep the shape. The BIIR rubber was crosslinked with the same crosslinking agents by static vulcanization at 180°C.

The tensile properties of TPVs and BIIR were measured according to ASTM D 412 on a CMT 4104 testing machine, MTS systems corporation (Shenzhen, China) with dumbbell-shaped samples (25 × 6 × 2 mm) at a crosshead speed of 500 mm/min at 23°C. The tensile properties of PA12 was measured with dumbbell-shaped samples (20 × 4 × 0.5 mm) at a crosshead

speed of 50 mm/min at 23°C. For each measurement, five specimens were tested.

Surface Energy Measurement. The surface energy γ and its associated dispersion component γ^d and polar component γ^p of the film samples were evaluated by contact angle measurements using a Kruss DSA 100 instrument from Germany. γ , γ^d , and γ^p has the relationship as follows:

$$\gamma = \gamma^d + \gamma^p \quad (4)$$

The PA 12 and compatibilizer film were compression molded at 200°C and 100 bar to a thickness of 0.5 mm, and the BIIR films were static vulcanized and compression molded to a thickness of 1 mm at 180°C and 100 bar.

The static contact angle θ between film samples and drops of two different liquids (water and ethylene glycol) was measured separately. Then the γ , γ^d , and γ^p of the samples were calculated according to the Young's equation [eq. (5)] and Owens-Wendt-Rabel-Kaelble (OWRK) method [eq. (6)]²⁵:

$$\gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \theta \quad (5)$$

$$\gamma_{sl} = \gamma_{sg} + \gamma_{lg} 2 \left(\sqrt{\gamma_{sg}^d \gamma_{lg}^d} + \sqrt{\gamma_{sg}^p \gamma_{lg}^p} \right) \quad (6)$$

where γ_{sg} is the interfacial energy between the substrate and the gas, γ_{sl} is the interfacial energy between the solid and liquid phases, γ_{lg} is the interfacial energy between the liquid and gas phases.

Rheological Properties. The rheological properties of the samples were studied using a capillary rheometer (model RH 2000, Malvern instruments Ltd.). Measurements were carried out at 200°C under Double-bore experiment mode. The L/D ratio of the capillaries were 16/1 and 0, respectively. Each flow curve was generated from data collected at seven different shear rates ranging from 20 s⁻¹ to 2000 s⁻¹. The results were processed by the software afforded by Malvern Instrument, and all the rheological data obtained were subjected to Bagley and Rabinowitch calibration.

Gas Permeability Measurements. Nitrogen permeation tests were conducted at 40°C according to the ISO 2782 differential-pressure method with a home-made apparatus. The pressure on one face of the sample sheet was kept at 0.57 MPa with pure nitrogen gas, and the other face at 0.1 MPa with a carrier gas (pure hydrogen). The rate of transmission of nitrogen was determined by gas chromatography from which the nitrogen permeability was calculated.

RESULTS AND DISCUSSION

Effect of Compatibilizers on the Microstructure and Mechanical Properties of TPV

Types of Compatibilizers. Three kinds of compatibilizers namely PP-g-MAH, POE-g-MAH and SEBS-g-MAH were used to increase the compatibility between PA 12 and BIIR. The effect of these compatibilizers on the phase morphology and mechanical properties of TPV were studied. The backbone of these compatibilizers are compatible with BIIR, and physical entanglement of the molecular chains of these compatibilizers and BIIR can occur. On the other hand, MAH group can have

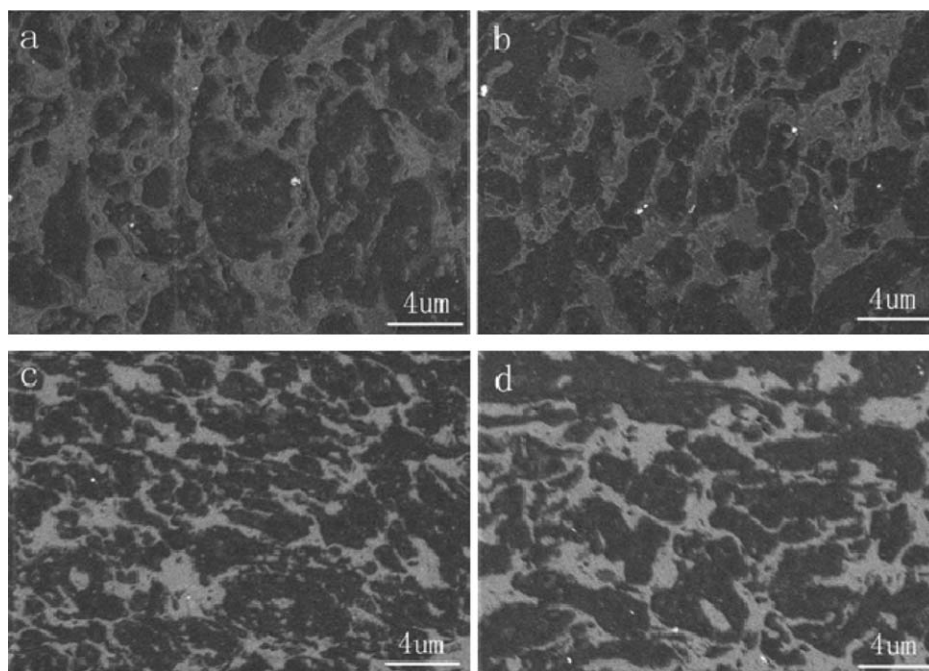


Figure 1. Phase morphology of BIIR/PA12 TPV with different kinds of compatibilizers by using SEM-BSE: (a) without compatibilizer; (b) with 10 phr PP-*g*-MAH; (c) with 10 phr POE-*g*-MAH; (d) with 10 phr SEBS-*g*-MAH.

chemical reactions with terminal amino group of PA12, thus improving the compatibility between BIIR and PA12.

Figure 1 shows SEM-BSE micrographs of TPVs with the same content but different kinds of compatibilizers. The lighter regions represent the PA12 phase and the darker regions represent the cross-linked BIIR phase. As the rubber phase is dynamically crosslinked during mixing, phase inversion occurs even for dynamically vulcanized BIIR/PA12 blends with the blend ratio of 65/35, resulting in the formation of a large content of BIIR phase dispersed in a small content of continuous PA12 phase. The rubber particle size and its distribution was measured by the Image-pro Plus 4.5, and the results were summarized in Table III. For the blend without compatibilizers, the d_n , d_v and the particle size distribution (PDI) reaches 3.69 μm , 7.67 μm , and 2.08, respectively. This is ascribed to the high interfacial tension between BIIR and PA 12 caused by the apparently different surface energy of BIIR and PA12 (see Table IV). The d_n , d_v , and PDI of all the blends with various kinds of compatibilizers reduces, indicating more smaller particle size and more uniform particle size distribution, as shown in Figure 1. Among these blends with different kinds of compatibilizers, the d_n , d_v and PDI of the blend with PP-*g*-MAH is the smallest, indicating the best compatibility between BIIR and PA12. The surface energy of BIIR, PA 12 and various kinds of compatibilizer are summarized in Table IV. Obviously, the surface energy of PP-*g*-MAH (24.8 mN/m) is very close to that of BIIR (25.1 mN/m), suggesting better compatibility between BIIR and PP-*g*-MAH.²⁶ Thus, chain entanglement between BIIR and PP-*g*-MAH occur more easily. Meanwhile, the graft degree of PP-*g*-MAH on PA12 is the highest among these compatibilizers, which indicates that more chemical reactions between PP-*g*-MAH and amide groups of PA12 have occurred. As a result,

PP-*g*-MAH shows the best compatibilizing effect on BIIR and PA 12. That is why TPVs prepared with PP-*g*-MAH as the compatibilizer possesses the best mechanical properties (see below).

To study the effect of compatibilizers on the mechanical properties of BIIR/PA12 TPVs, the stress–strain curves of TPVs with different compatibilizers were studied and the results are shown in Figure 2. As expected, pure PA12 shows high tensile strength, high tensile modulus and typical yielding behavior of plastic [see Figure 2(a)], whereas pure BIIR shows low tensile strength and low modulus [see Figure 2(b)]. The stress–strain behavior of BIIR/PA TPV is obviously different from that of pure PA and pure BIIR. The stress–strain curves of TPV show plastic-like stress–strain behavior in the low strain, because the high modulus PA12 as the continuous phase deforms immediately under the applied stress. In this case, the interface between PA and BIIR determines the load transfer efficiency from the PA matrix to the rubber particles. Without the addition of the compatibilizing agent, the high interfacial tension and poor interfacial

Table IV. MAH Content of Compatibilizers and Surface Energy of Materials Used

Materials	MAH content (%)	Surface energy (mN/m) ^a
PA 12	–	42.1
BIIR	–	25.1
PP- <i>g</i> -MAH	1.8	24.8
POE- <i>g</i> -MAH	0.8	19.6
SEBS- <i>g</i> -MAH	1.5	23.2

^a Standard deviation of $\pm 5\%$.

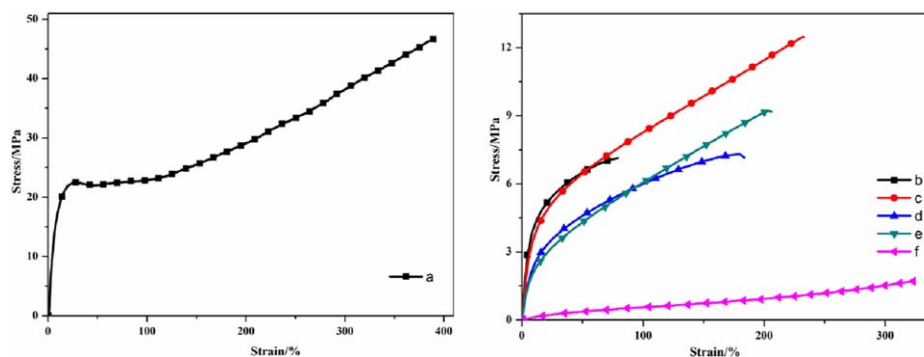


Figure 2. Stress–strain curves: (a) PA12; (b) BIIR/PA12 TPV without compatibilizer; (c) BIIR/PA12 TPV with 10 phr PP-g-MAH; (d) BIIR/PA12 TPV with 10 phr POE-g-MAH; (e) BIIR/PA12 TPV with 10 phr SEBS-g-MAH; (f) BIIR. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

interaction between PA and BIIR leads to the fracture of the material at the elongation at break less than 100% (see Figure 2). In this case, the TPV cannot be used as an elastomer. After the addition of various kinds of compatibilizers, the interfacial adhesion between PA and BIIR increases, leading to the obvious increase in the elongation at break. Among these compatibilizers, the blend compatibilized by PP-g-MAH shows the higher tensile strength, the higher elastic modulus and the larger elongation at break (270%), ascribed to the best compatibilizing effect of PP-g-MAH on BIIR/PA12 blend. The elastic modulus of the blends compatibilized by POE-g-MAH and SEBS-g-MAH is slightly lower than that of the blend without compatibilizer. This is ascribed to the much lower elastic modulus of POE-g-MAH and SEBS-g-MAH themselves (2–10 MPa) than that of PA 12 (~9000 MPa). In a word, PP-g-MAH is an efficient compatibilizer for BIIR/PA12 blends.

Contents of PP-g-MAH. The effects of the contents of PP-g-MAH on the phase morphology and mechanical properties of BIIR/PA12 blends were also investigated. The SEM-BSE micrographs of the vulcanized blends with various contents of PP-g-MAH as compatibilizers are shown in Figure 3, and the corresponding values of d_n , d_v and PDI are shown in Table III. Obviously, the BIIR phase in BIIR/PA12 blends with 5 phr or 10 phr of PP-g-MAH is dispersed in continuous PA12 phase [see Figure 3(a,b)], indicating that phase inversion of BIIR from continuous phase to dispersed phase in TPV has occurred. With the increase in the content of PP-g-MAH from 5 phr to 10 phr, d_n , d_v , and PDI all become smaller. And this is ascribed to the more sufficient chemical reaction between amide group and MAH group. With the further increase in the content of PP-g-MAH to 20 phr, the BIIR phase in the blend exhibits continuous phase, and the phase morphology of PA 12 can be

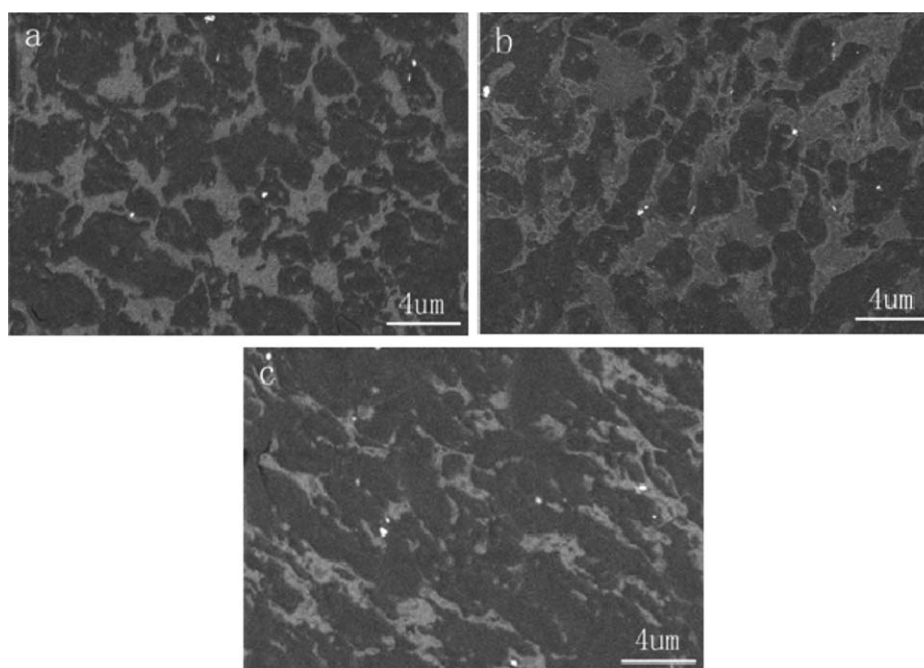


Figure 3. Phase morphology of BIIR/PA12 TPV with various amounts of PP-g-MAH as compatibilizers: (a) 5 phr PP-g-MAH; (b) 10 phr PP-g-MAH; (c) 20 phr PP-g-MAH.

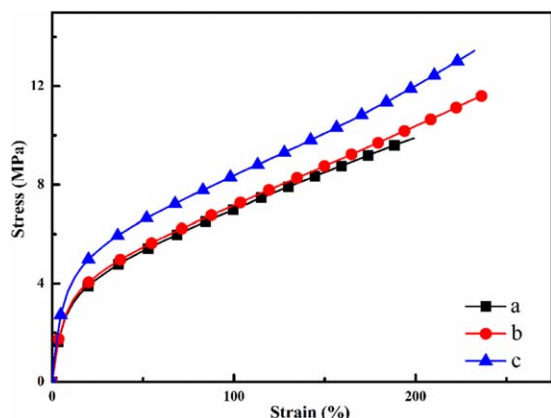


Figure 4. Stress–strain curves of BIIR/PA12 TPV with various amounts of PP-g-MAH as compatibilizers: (a) 5 phr PP-g-MAH; (b) 10 phr PP-g-MAH; (c) 20 phr PP-g-MAH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

continuous phase or dispersed phase. In this case, the phase inversion of BIIR from continuous phase to dispersed phase does not occur during dynamic vulcanization [see Figure 3(c)]. Meanwhile, the blends with 20 phr of PP-g-MAH do not show the reprocessability, again demonstrating that the phase inversion does not occur in the vulcanized BIIR/PA blends with 20 phr of PP-g-MAH. Thus, the blend with 20 phr of PP-g-MAH is not TPV. The reason is that the addition of too many compatibilizers decreases the content of PA12 (see Table II). Less content of plastic phase (with 20 phr of PP-g-MAH) is not favorable for phase inversion.

The stress–strain curves of the blends with various contents of PP-g-MAH are shown in Figure 4 and the corresponding mechanical properties are summarized in Table V. Obviously, both the tensile strength and elastic modulus increase with the increase in the content of PP-g-MAH, and the blend with 20 phr of PP-g-MAH shows the highest tensile strength and elastic modulus, demonstrating that the phase morphology of the blend with 20 phr of PP-g-MAH is a co-continuous morphology. If the PA 12 phase is a dispersed phase, the tensile strength and elastic modulus of the blend with BIIR as a continuous phase will be much lower, similar to that of pure BIIR. Although phase inversion does not occur, more PP-g-MAH increases the interaction between amide group in PA12 and

MAH group, resulting in stronger interfacial adhesion. So, the blend with 20 phr of PP-g-MAH shows the highest mechanical strength. In addition, the elongation at break of TPVs increases with the increase in the content of PP-g-MAH. Considering both the mechanical properties and the phase morphology, the best content of PP-g-MAH used to improve the compatibility is 10 phr.

Effect of Fillers on the Microstructure and Mechanical Properties of TPV

Calcium carbonate (CaCO_3) has been widely used as white filler in the rubber industry. The addition of CaCO_3 in TPV was used to reduce the cost and to improve the mechanical properties.

The SEM-BSE micrographs of TPVs with various contents of CaCO_3 added are shown in Figure 5. We can observe that most of the CaCO_3 are located in the BIIR phase for both blends with 10 phr and 30 phr of CaCO_3 . The reason is that the thermoplastics crystallize during cooling after blending with BIIR. The inorganic filler CaCO_3 was added into the blend at room temperature, and so the fillers can only disperse in the BIIR phase instead of the PA phase. It is clearly seen in the micrograph (Figure 5) that CaCO_3 (white particles) are preferentially dispersed into the rubber phases, resulting in the increase in the viscosity and modulus. With the increase in the content of CaCO_3 from 10 phr to 30 phr, both d_n and d_v of the TPVs composites increase, whereas the PDI of all the three samples are almost the same, as shown in Figure 5 and Table III. This can be ascribed to the increase in the viscosity and modulus (see Figure 7), which is not favorable for the breakdown of the rubber phase during dynamic vulcanization. So the size of the BIIR phase increases with the increase in the content of CaCO_3 .

The stress–strain curves of TPVs and TPV composites with 10 phr and 30 phr of CaCO_3 are shown in Figure 6, and the corresponding mechanical properties are summarized in Table V. The strength at the same strain obviously increases with the increase in the content of CaCO_3 , whereas the elongation at break slightly decreases. Since the same content of PP-g-MAH was added in the TPVs, the obvious increase in the strength at the same strain is ascribed to the reinforcing effect of CaCO_3 on TPVs.

Table V. Mechanical Properties of Various Kinds of BIIR/PA12 TPVs

Compatibilizers or fillers	Tensile strength/MPa	Elongation at break/%	Tensile stress at elongation of 100%/MPa
None	7.1 ± 0.2	79 ± 9	–
SEBS-g-MAH	7.2 ± 0.3	184 ± 15	6.0 ± 0.2
POE-g-MAH	9.2 ± 0.2	206 ± 16	6.1 ± 0.3
5 phr PP-g-MAH	9.9 ± 0.2	199 ± 13	7.0 ± 0.2
10 phr PP-g-MAH	11.6 ± 0.3	270 ± 18	7.2 ± 0.3
20 phr PP-g-MAH	13.4 ± 0.3	232 ± 13	8.3 ± 0.4
10 phr CaCO_3	12.6 ± 0.4	242 ± 14	8.0 ± 0.3
30 phr CaCO_3	13.0 ± 0.3	194 ± 12	10.2 ± 0.3

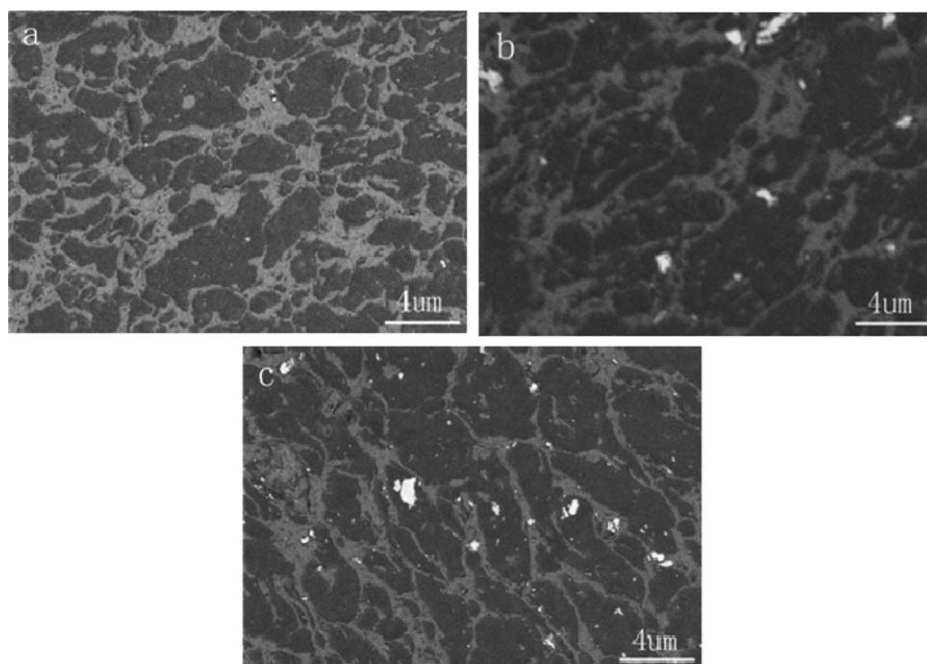


Figure 5. Morphology of BIIR/PA 12 TPV with various amounts of fillers: (a) TPV without fillers; (b) TPV with 10 phr CaCO_3 ; (c) TPV with 30 phr CaCO_3 .

Capillary rheometry, as a widely used technique for the determination of the rheology behavior of various materials with Newtonian behavior or non-Newtonian behavior, was used to determine the rheology of BIIR/PA12 TPVs with different content of CaCO_3 , and the results are shown in Figure 7. We can see that all the samples show pseudoplastic flow behavior in the studied range of shear rates. The melt viscosity at the same shear rate for TPVs filled with 10 phr of CaCO_3 is almost the same as that of TPVs without the addition of CaCO_3 . With the content of CaCO_3 increasing to 30 phr, the melt viscosity at the same shear rate are only slightly increased. The reason is that most of the CaCO_3 are located in BIIR phase during mixing at room temperature. The slight increase in the melt viscosity at the same shear rate is

mainly attributed to the increase in the shear viscosity caused by the addition of large content of CaCO_3 .

The gas permeability of polymers has been extensively studied because of their technological importance in industrial applications. The gas permeability of the dynamically vulcanized BIIR/PA12 blends and the TPV composites with CaCO_3 are shown in Figure 8. For comparison purpose, a commercially available innerliner material made from BIIR was also tested under the same condition. We can observe that the dynamically vulcanized BIIR/PA12 blends we prepared possesses much lower permeability than that of the commercially available innerliners. The reason is that compared with BIIR, it is more difficult for gas to

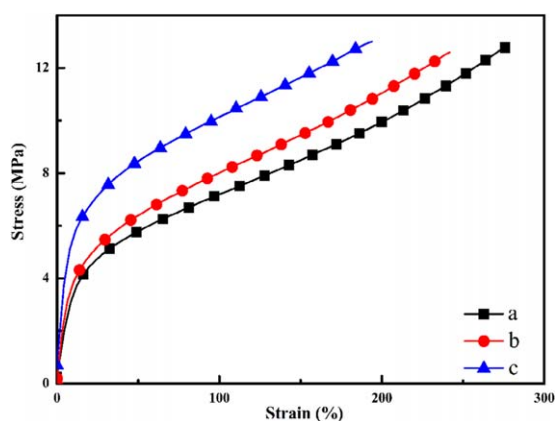


Figure 6. Stress–strain curves of BIIR/PA 12 TPV with various amounts of fillers. (a) TPV without fillers; (b) TPV with 10 phr CaCO_3 ; (c) TPV with 30 phr CaCO_3 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

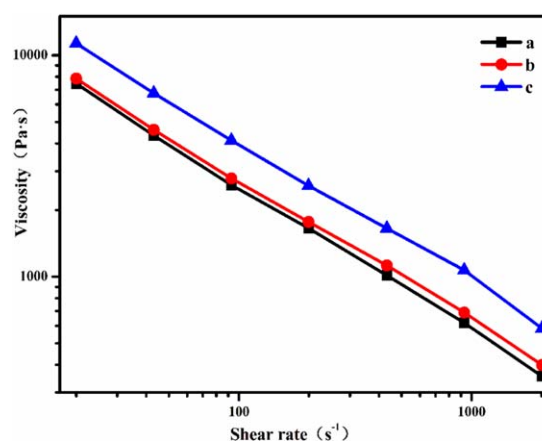


Figure 7. Melt viscosity as a function of shear rate for dynamically vulcanized BIIR/PA12/filler composites: (a) TPV without fillers; (b) TPV with 10 phr CaCO_3 ; (c) TPV with 30 phr CaCO_3 . [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

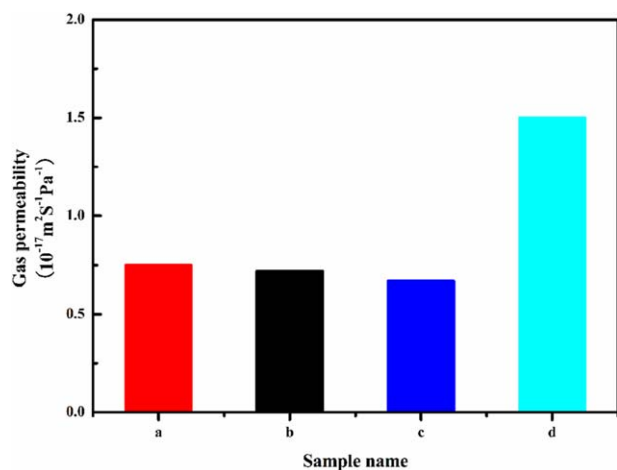


Figure 8. The gas permeability results: (a) TPV without fillers; (b) TPV with 10 phr CaCO_3 ; (c) TPV with 30 phr CaCO_3 ; (d) innerliners commercial available. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

diffuse and permeate through PA 12 because of the crystallization in PA12, leading to the better gas barrier properties for PA12 than BIIR. The addition of CaCO_3 can slightly decrease the gas permeability of BIIR/PA12 TPV, thus can slightly increase the gas barrier properties, but not as good as that of the composites with layered fillers such as graphene sheets or layered silicates, as reported in previous studies.²⁷ The better gas barrier properties of TPV/ CaCO_3 composites than that of BIIR/PA12 TPV is ascribed to the better gas barrier properties of CaCO_3 with compact microstructure than that of polymer with bigger free volume.

CONCLUSIONS

A novel BIIR/PA12 TPVs with good mechanical properties and gas permeability was prepared by dynamic vulcanization in a twin-screw extruder. The compatibility between BIIR and PA12 was significantly improved by the reaction of amide group of BIIR and maleic anhydride of three kinds of compatibilizers. The compatibilizing effect of PP-g-MAH on BIIR/PA12 blends is the best among these compatibilizers because the surface energy of PP-g-MAH is very close to that of BIIR. The dispersed rubber phase of the blend compatibilized by PP-g-MAH shows the smallest size and more uniform size distribution, and the as-obtained TPVs show the best mechanical properties. The size of the BIIR phase increases with the increase in the content of CaCO_3 because most of the CaCO_3 are located in the BIIR phase. The addition of CaCO_3 can obviously increase the modulus and tensile strength of TPVs because of the reinforcing effect of CaCO_3 on TPVs. The resulting TPV shows much better gas barrier property than that of the commercially available innerliners. The TPVs we prepared with good mechanical properties and gas barrier property can be used as innerliners to replace the traditional thermoset rubber. Meanwhile, BIIR/PA12 TPV can be recycled and can reduce the thickness of innerliners, and thus can save energy and protect environment.

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