Research Article

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 Conductive thermoplastic vulcanizates based on carbon black-filled bromo-isobutylene-isoprene rubber (BIIR)/polypropylene (PP)

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Abstract: Conductive elastomer materials based on carbon black (CB) filled bromo-isobutylene-isoprene rubber (BIIR)/polypropylene (PP) thermoplastic vulcanizate (TPV) were prepared by two step method and one step method. The microstructure, mechanical properties, electrical resistivity, thermal stability, electromagnetic interference shielding performance, and fracture surface morphology of composite materials were studied. The result shows the serious aggregation of CB in one-step TPV, but the uniform dispersion of CB in two-step TPV. In addition, the two-step TPV shows a higher electromagnetic interference (EMI) shielding performance and lower conductivity penetration threshold. The penetration threshold of the two-step TPV is 9.1%, and the maximum reflection loss of the two-step TPV is −29.5 dB. Therefore, this research offers an uncomplicated and scalable melt mixing approach method to manufacture conductive thermoplastic vulcanizates with excellent EMI shielding.

Keywords: CB, PP/BIIR, TPV, electrical properties, EMI

1 Introduction

Polymer blends and polymer composites are widely used in various applications due to their excellent mechanical properties [1, 2]. Adding fillers to the polymer matrix and polymer blending are effective methods to improve properties, and these properties cannot be achieved by a single component. This is an economical and environmentally friendly way to make new materials with desired characteristics [3, 4]. Traditional plastics and rubbers do not have electrical conductivity, so filling conductive fillers to improve their electrical conductivity is a simple and worthwhile method. Conductive polymer composites based on conductive fillers (such as graphene, graphite, carbon nanotubes, carbon black, etc.) and insulating polymer matrix have recently attracted great interest due to their excellent mechanical, electrical and thermal properties [5–11]. Electrically conductive elastomers with substantial elastic stretchability and good flexibility have greater potential than traditional rigid conductive polymer composites in terms of actuators, stretchable conductors and strain sensors, and can meet the growing demand for multifunctional conductive materials [12–15]. With increasingly signal interference and serious electromagnetic radiation pollution, the electrically conductive elastomers may have a large signal transmission error and low signal transmission efficiency, caused by the serious signal interference, therefore, it is necessary to prepare conductive elastomers with electromagnetic shielding interference performance [16].

Carbon black (CB) can not only be used as a reinforcing filler to enhance the mechanical properties of elastomer materials but also widely used as a conductive filler to enhance the electrical and electromagnetic shielding properties of elastomer materials [17]. The structure and specific surface area of the main aggregates of carbon black determine its difference in enhanced mechanical and electrical properties [18]. The diameter of the primary particles of CB is very small, usually less than 300 nm, which is an important feature of CB. CB is described differently as “high structure” and “low structure” related to its spatial scope, the size of the former is smaller than the latter, which is another important feature of CB. When CB reaches a certain load in polymer blends and polymer composites, it will cause the resistivity of the polymer matrix to drop rapidly and form an effective conductive network. This load value is called the percolation threshold [19]. It is generally believed that only when the conductive polymer composite material has an appropriately dense conductive network, can it cause...
good EMI shielding effectiveness and high electrical conductivity [20, 21]. However, only when the conductive percolation value of the composite material is low, which can show a high elasticity with a excellent cycle stability and high strain, which can meet the needs of practical applications [16].

Thermoplastic vulcanizate (TPV) is a kind of thermoplastic elastomer prepared by a dynamic vulcanization method, which consists of a high content cross-linked rubber phase as a diffused phase dispersed in a low content continuous thermoplastic phase to form a “sea-island structure” [22]. This structural feature gives TPV good processing properties of thermoplastics and excellent resilience of conventional vulcanized rubber [23, 24]. At the same time, TPV usually has better overall mechanical properties and lower processing costs than traditional rubber and elastomers [25]. In recent years, due to increasing attention to environmental issues, TPV constitutes the fastest growing elastomer market. In addition, many efforts have been made in the development of conductive TPV materials to enlarge the practical applications of TPVs [26–29]. Ma et al. [30] studied the distribution behavior and electrical properties of multi-wall carbon nanotubes (MWCNTs) in PP/EPDM TPV, and found that MWCNTs are mainly distributed in the polypropylene plastic matrix, and MWCNTs are more evenly distributed in the two-step method to obtain a lower percolation threshold. Dey et al. [31] filled CB into NR/EOC TPV and found that as the amount of carbon black increases, the mechanical properties of TPV decrease while the electrical properties increase.

In this work, conductive elastomer materials based on CB filled bromo-isobutylene-isoprene rubber (BIIR)/polypropylene (PP) thermoplastic vulcanizate were prepared by two step method and one step method, to obtain composite materials with lower percolation threshold, good mechanical properties and EMI shielding effectiveness, to adapt to the actual low-cost industrial production process. With the increase of the CB content, the conductivity and thermal properties of two-step TPV and one-step TPV have been continuously enhanced. Both the two-step method and the one-step method TPV exhibit good electrical properties when the CB content is 20%, but the two-step method TPV has a lower conductivity percolation threshold and better electromagnetic shielding performance.

2 Experimental

2.1 Experimental materials and preparation methods

The random copolymer PP (K4912, density = 0.905 g/cm³, MFR = 12 g/10 min at 2.16 kg load and 230°C) was purchased from Yanshan Petroleum Chemical Co., Ltd., China. A commercial grade BIIR (CHAMBROAD BIIR 2828) was from Chambroad Petrochemicals, Shandong, China, with a halogen content of 2.0±0.2 wt.% and a Mooney viscosity ML (1+8/125°C) 32+4 MU. Super conductive carbon black (CB F900A), DBP absorption value is 450 ml/g, specific surface area is 750-1100 m²/kg, diameter is 30-100 nm, from Tianjin Ebo rubber Chemical Co., Ltd., China. Phenolic resin (PF, SP1045), used as curing agent, was obtained from SI Group-Shanghai Co., Ltd., China. Both zinc oxide (ZnO) and antioxidant IRGANOX 1010 (pentaerythritol tetrakys 3-(3,5-ditert-butyl-4-hydroxyphenyl) propionate) are commercially available.

The melt-reactive blending process for preparing TPV/CB composites was carried out in a SU-70B internal mixer (Changzhou Suyan Technol. Co., Ltd, China) at the rotor speed of 50 rpm. Two different processing procedures are designed to prepare TPV/CB composite elastomers, namely one-step method and two-step method. For the one-step method, first mix BIIR and PP in a mixer at 180°C; 3 min later, add ZnO, PF and antioxidants to the mixing chamber, continue to melt reaction and mix for 5 min; finally add CB and mix for 10 min, then take out the mixture and chopped. About the two-step method, BIIR/PF master batches and PP/CB were firstly prepared in the mixer at 50°C for 8 min and 180°C for 5 min, respectively. Then, the two pre-mixed batches were melt-mixed at 180°C for 5 min.

The sample preparation procedures are shown in Figure 1.

For all the samples, the weight ratio of BIIR to PP was kept at 7:0:30. The content of ZnO was 1 wt.% (to the weight
of the blends). The content of PF was 2 wt.% (to the weight of the blends). The content of antioxidant was 0.5 wt.% (to the weight of the blends). For ease of understanding, the sample is expressed as one-step-TPVx and two-step-TPVx, where x represents the content of CB.

2.2 Characterization

2.2.1 Tensile

Using CMT4104 universal material testing machine to test the samples at a cross head speed of 500 mm/min. Measure each sample at least five times and take the average value as the test result. The dumbbell-shaped sample was injection molded at 180°C and 0.5 MPa in the injection molding machine (WZS10D, Shanghai Xinshuo Precision Machinery Co., Ltd.).

2.2.2 Electrical

When the volume resistivity was lower than $10^5$ Ω·cm, the conductivity of the sample was measured by the four-probe method (RTS-9, Guangzhou Four-Probe Technology Co., Ltd. China). Using a high resistivity meter (ZC36, Shanghai Precision Instrument Co., Ltd. China) tested samples with a volume resistivity over $10^5$ Ω·cm. The sample size for high volume resistivity measurement is $2 \times 100 \times 100$ mm$^3$, and the sample size for low volume resistivity measurement is $2 \times 100 \times 100$ mm$^3$.

2.2.3 Scanning electron microscope (SEM)

A scanning electron microscope (TecnaiG220 FEI) was used to characterize the surface morphology of the material.

2.2.4 Thermogravimetric analysis (TGA)

Under a nitrogen atmosphere, the thermal stability of the composites was measured using a thermogravimetry (STA449C/6/G, NETZSCH, Germany). The samples were heated from room temperature up to 600°C at a heating rate of 20°C/min. Approximately 10 mg of samples were used for each thermogravimetric analysis (ASTM E 1131).

2.2.5 Differential scanning calorimetry (DSC)

A differential scanning calorimeter (DSC214, NETZSCH, Germany) was used to measure the melting and crystallization of the composite in nitrogen atmosphere. For each test, in order to eliminate the previous thermal history, a 10 mg sample was first heated to 250°C at a rate of 10°C /min, and then kept at this temperature for 5 minutes. Then the sample was cooled to room temperature at a cooling rate of 10°C/min and secondly reheated to 250°C at the same heating rate (ASTM D 3418).

2.2.6 Electromagnetic interference shielding measurements

Ceyear3656D vector network analyzer was used to measure the electromagnetic interference shielding performance of the samples in the frequency range of 1~7 GHz. Before testing, all samples were cut into rings with an outer diameter of 7 mm and an inner diameter of 3.04 mm and a thickness of 3.0 mm. According to transmission line theory, the electromagnetic wave absorption capacity of a material is expressed by reflectance (RL), and the formula is shown below [32–34]:

$$RL (dB) = 20 \log \left( \frac{|Z - Z_0|}{|Z + Z_0|} \right)$$

where,

$$Z = Z_0 \left( \frac{\mu_r}{\varepsilon_r} \right)^{\frac{1}{2}} \tanh \left\{ j \left[ \frac{2\pi f d (\mu_r \varepsilon_r)}{c} \right]^{\frac{1}{2}} \right\}$$

$$Z_0 = \sqrt{\frac{\mu_0}{\varepsilon_0}}$$

$\mu_0$ is the permeability of free space, $\varepsilon_0$ is the permittivity of free space, $\mu_r$ is the permeability of free space, $\varepsilon_r$ is the permittivity of free space, $\mu_r = \mu' - j\mu''$ is the relative complex permeability constant of the absorbing material, $\varepsilon_r = \varepsilon' - j\varepsilon''$ is the relative complex permittivity of the absorbing material, $f$ is the frequency of the incident electromagnetic wave, and $d$ is the thickness of the absorbing layer, $c$ is the speed of light, $\mu'$ is the real part of the relative complex permeability constant of the absorbing material, and $\mu''$ is the imaginary part of the relative complex permeability constant of the absorbing material, $\varepsilon'$ is the real part of the relative complex permittivity of the absorbing material, and $\varepsilon''$ is the imaginary part of the relative permittivity of the absorbing material.

The reflection loss (RL) value usually indicates the microwave absorbing ability of the material. The larger the RL value, the better the wave absorbing performance of the
material. According to the international electromagnetic protection standards, when the RL value is less than $-10$ dB, it means that 90% of the electromagnetic waves can be absorbed; if the RL value is less than $-20$ dB, it means that 99% of the electromagnetic waves can be absorbed [35, 36].

3 Results and discussion

3.1 Morphology observation

The morphology of TPV and TPV/CB composites was observed by SEM to reveal the dispersion state of CB in the composite matrix. Figure 2(a) shows the morphologies of one-step-TPV0. It can be seen from the figure that BIIR rubber particles are dispersed in the continuous PP phase to form a “sea-island” structure. Figure 2(d) shows the morphologies of two-step-TPV0, which also forms a “sea-island” structure similar to one-step-TPV0. Further observation, compared with the BIIR particle size of the one-step TPV0, the phase size of the BIIR particles of the two-step TPV0 is smaller. The BIIR particle size of one-step-TPV0 is about 5 µm, while in two-step-TPV0 it is about 2 µm. It may be due to the reason that a large number of BIIR nano-droplets were cross-linked in-situ into BIIR particles in the two-step-TPV0, while in the one-step-TPV0, the nano-droplets were first melted and then cross-linked to form BIIR particles of larger size [37]. Figure 2(b) and 2(c) show the morphology of one-step-TPV16 observed at different scales, we can see that CB particles are not uniformly dispersed and there is some of CB aggregates. The morphology of two-step-TPV16 observed at different scales was shown in Figure 2(e) and 2(f). The CB particle distribution is more uniform compared with one-step TPV, since the dispersion of CB and the in-situ crosslinking of BIIR nanodroplets occur simultaneously in the two-step method, this facilitates the dispersion of CB in the composite material, while the larger BIIR particles in the one-step method hinder the dispersion of CB. Further observations revealed that the CB of the two TPV composites is almost completely located in the PP phase. This is because the cured BIIR has a higher viscosity ratio than PP, these phenomena are consistent with Wu et al.’s report on the preferential position of CB in the PP matrix in TPV composites [38].

3.2 Mechanical performance analysis

Figure 3 shows the typical stress-strain curves of TPV. For the two TPV0 samples, the strain-stress curves have no obvious stress yield, showing rubber-like behavior. The tensile strength of the two-step TPV0 is 12.6 MPa, which is 3.5 MPa higher than the 9.1 MPa of the one-step-TPV0, and the elongation at break of the two-step-TPV0 is 160%, which is slightly lower than the elongation at break of the one-step-TPV0 of 182%. According to Boyce et al. [39], larger rubber particles result in a thicker PP matrix layer, when the PP matrix layer near the rubber particles is thicker, the plastic deformation of the PP matrix layer is reduced, causes a pseudo continuous rubber phase, and TPV exhibits elastomer-like behavior during stretching, such as a smaller tensile strength and higher elongation at break. Therefore, the size of the dispersed BIIR particles caused the difference in mechanical properties between the two TPV0 samples. This is consistent with the morphological results we have observed, and a reasonable conclusion can be drawn, the BIIR particle size of TPV can be successfully controlled by different processing methods.

![Figure 2: SEM micrographs of (a) one-step-TPV0, (b) and (c) one-step-TPV16, (d) two-step-TPV0, (e) and (f) two-step-TPV16.](image1)

![Figure 3: Tensile stress-strain curves of one-step-TPV0 and two-step-TPV0.](image2)
3.3 Analysis of electrical properties

Figure 4 shows the curves of log (Resistivity) versus CB content of BIIR/PP TPV via two different processing procedures. As seen from the figure that the volume resistivity of the composite material decreases with the increase of CB content, and then drops sharply at the critical concentration of CB particles, indicates that the conductive network has initially formed [39]. Before percolation, the resistivity of the composite material decreases with the increase of CB content, which indicates that carbon black has an impact on the electrical properties of the blend, and after percolation, when the content of CB higher than 16 wt.% that the blend’s resistivity reaches to a plateau form which it means that the resistivity does not change. Compared with the conductive percolation threshold of the one-step TPV of 12.7 wt.%, the conductive percolation threshold of the two-step TPV is lower at 9.1 wt.%, the conductive percolation threshold of two-step TPV is also lower than previous studies on conductive TPV [40, 41]. According to Li et al. [42], the key factors that determine the percolation threshold of the polymer/CNT nanocomposites include the aspect ratio of MWCNT and the dispersibility of MWCNT agglomerates. Therefore, it can be inferred that the conductive seepage threshold of CB filled BIIR/PP TPV is mainly due to the dispersion of CB in the composite material. Because of the similar processing temperature, shear rate and time, blending ratio, same kind of materials, the results clearly show that the difference in the electrical properties of the composite materials were caused by different processing procedures [30]. So, the significantly different percolation thresholds of the two kinds of elastomeric composites are mainly from the dispersion states of CB caused by the different TPV phase structures: because the dispersion of CB and the in-situ crosslinking of BIIR nanodroplets occur simultaneously in the two-step method. This facilitates the dispersion of CB in the composite material, while the larger BIIR particles in the one-step method hinder the dispersion of CB. Clearly, the two-step-TPV is more suitable for preparing conductive elastomer materials with relatively low CB content.

3.4 TGA

In a nitrogen atmosphere, the thermal stability of the two-step dynamic vulcanized CB filled BIIR and PP composites was evaluated by TGA. Table 1 and Figure 5 respectively show thermal degradation data and the thermogravimetric curve of the two-step-TPV with different content of CB. It can be seen from Figure 5 that all composite materials have undergone a single-step degradation in the range of 350-480°C under nitrogen atmosphere. The initiation of degradation (T_{10\%}) in the BIIR/PP TPV without CB occurred at around 372.7°C. The initial decomposition temperature of the two-step TPV16 is 382.7°C, which is higher than that of SIR/TPU/10phr SiO\textsubscript{2}/2 wt.% CNTs by Pan et al. [43].

| Sample          | Temperatures at 10% weight loss (°C) | Mass of residual (%) |
|-----------------|--------------------------------------|----------------------|
| Two-step-TPV0   | 372.7                                | 0.8                  |
| Two-step-TPV4   | 378.3                                | 5.3                  |
| Two-step-TPV8   | 379.2                                | 8.1                  |
| Two-step-TPV12  | 380.1                                | 10.5                 |
| Two-step-TPV16  | 382.7                                | 14.1                 |

Table 1: TGA parameters for two-step-TPV with different content of CB.
initial degradation temperature and residual mass increase with the increase of CB content. This may be due to the interaction between the CB particles and the polymer matrix through good dispersion and the high thermal stability of CB. CB particles cover these inserted polymer chains, this prevents the chains from being directly exposed to heat.

3.5 DSC

Figure 6 shows the melting curves of the two-step-TPV with different content of CB at a heating rate of 10°C/min. The melting temperature of CB filled BIIR/PP TPV composites slightly increases due to CB loading. Because part of the heat is absorbed by the CB, the heating system requires more energy, and the melting temperature rises eventually. Figure 7 shows the non-isothermal crystallization curves.

![Figure 6: Melting curves of two-step-TPV with different content of CB.](image1)

![Figure 7: Cooling curves of two-step-TPV with different content of CB.](image2)
and behaviors of the two-step-TPV with different content of CB. The crystallization peak became sharper, indicating that the heterogeneous nucleation of CB is effective. This finding is consistent with the reported result [41]. The crystallization temperature of CB filled BIIR/PP TPV composites slightly increases with increasing CB content. Because well-dispersed carbon black can provide more nucleation sites and help increase the crystallization temperature of the composites.

### 3.6 Electromagnetic interference shielding properties

In order to study the electromagnetic interference shielding performance of TPV, we selected typical samples for testing by Cyear3656D vector network analyzer in the frequency range of 1–7 GHz. Figure 8 shows the curve of reflection loss for one-step-TPV and two-step-TPV with 0 and 16 content of CB. There is almost no difference in reflection loss between one-step TPV and two-step TPV without CB, which indicates that the structure of TPV has no effect on the reflection loss, but is related to the filler and the dispersion state of the filler. When the content of CB is 16, the reflection loss of the one-step TPV and two-step TPV are significantly enhanced compared to 0 parts of carbon black, indicating that when CB is blended with TPV as a conductive filler, the electromagnetic shielding performance of the composite can be enhanced. The maximum reflection loss of the two-step TPV16 is $-29.5$ dB, which is $50.5\%$ lower than the maximum reflection loss of the one-step TPV16 of $-19.6$ dB, this is similar to the average shielding effectiveness value of

![Figure 8: Reflection loss of frequency in 1–7 GHz for typical samples.](image)

![Figure 9: Schematic showing shielding mechanism of one-step-TPV16 and Two-step-TPV16.](image)

![Figure 10: Frequency dependence of (a) complex permittivity and (b) complex permeability of one-step-TPV16 and two-step-TPV16.](image)
Ma et al.’s MWCNTs filled EPDM/PP TPV of 29.8 dB [16]. And the effective absorption frequency range of two-step TPV is 2.5–5.5 GHz (reflection loss value is less than −10 dB), which is wider than the effective absorption range of one-step TPV 2.6–4.9 GHz, owing to the smaller domain size of BIIR particles offers more opportunity for electromagnetic waves to interact with CB network to realize the wave attenuation. Additionally, CB is more evenly dispersed in two-step TPV than one-step TPV, and the network structure formed is more compact. In order to illustrate this point more clearly, Figure 9 shows a sketch of the shielding mechanism of these two composite systems.

Figure 10 shows the electromagnetic parameters of one-step-TPV16 and two-step-TPV16 in the frequency range of 1–7 GHz. It can be seen that the $e'$ of the two-step-TPV16 is higher than that of the one-step-TPV16, and the $e''$ of the two-step-TPV16 is slightly lower than that of the one-step method. Because of the better dispersion of CB in the two-step method, the composite material has better dielectric properties. The $\mu'$ of the two-step-TPV16 is lower than that of the one-step-TPV16, and $\mu''$ is higher than that of the one-step-TPV16, which may also be caused by the dispersion state of CB. The variation trend of complex permittivity and complex permeability of one-step-TPV16 and two-step-TPV16 with frequency is the same, indicating that the composite materials prepared by different methods will not affect the variation of electromagnetic parameters with frequency.

4 Conclusions

Conductive elastomer materials based on carbon black (CB) filled bromo-isobutylene-isoprene rubber (BIIR)/polypropylene (PP) thermoplastic vulcanizate were prepared by two step method and one step method. The mechanical, morphology, electrical, thermal and electromagnetic shielding properties of two-step-TPV and one-step-TPV are studied. Under the same CB load, two-step TPV has higher conductivity and good electromagnetic interference shielding performance. The reason is that CB is more uniformly dispersed in the two-step TPV than the one-step TPV by observing morphology. When the filling amount of CB is 16 wt.%, both the two-step TPV and the one-step TPV show good conductivity. But the two-step TPV has a lower conductivity percolation threshold. This work offers an uncomplicated and scalable melt mixing approach method to manufacture conductive thermoplastic vulcanizates with excellent EMI shielding.

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