Influence of different pendant vinyl contents in polybutadiene on the properties of peroxide cured EPDM/SBS/PB composite

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Abstract
A series of ethylene–propylene–dicyclopentadiene copolymer (EPDM)/styrene–butadiene–styrene copolymer (SBS)/polybutadiene (PB) composites were prepared to investigate the relationship between the pendant vinyl contents in PB and the properties of the composites. In this article, EPDM/SBS/PB ternary composites were prepared using initiators in solution and then curing in a vacuum oven. The PB containing pendant vinyl can be used as co-agent for curing composites, whereas the peroxide initiator can generate free radicals, which avail the crosslinking interaction. The resulting composites have been characterised by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM), testing of gel content and swelling ratio and mechanical test. DSC and TGA results indicated that the addition of 1, 2-vinyl in PB improved the reactivity and thermal stability of the composites, respectively. The results on gel content and swelling ratio revealed that the composites featured a crosslinked structure and high solvent resistance by increasing the 1, 2-vinyl content in PB. The FESEM result shows that the composites presented good compatibility with increasing pendant vinyl content in PB. The EPDM/SBS/PB (the PB containing 90% 1, 2-vinyl) composite outperforms the PB containing 1% 1, 2-vinyl in terms of mechanical properties (about 473% increase of tensile strength). This work demonstrates that use high vinyl PB to fabricate the ternary composites with excellent comprehensive performances exhibited potential for substrate materials application.

Abbreviations

PB polybutadiene
PCB printed circuit board
BIPB bis(tert–butyldioxyisopropyl)benzene
PP polypropylene
EPDM ethylene–propylene–dicyclopentadiene copolymer
EOC ethylene octene copolymer
LDPE low density polyethylene
SBS styrene–butadiene–styrene copolymer
NR natural rubber
TPVs thermoplastic vulcanizates
PLA-b-PFS poly(lactic acid)–block-poly(2,5-furandimethylene succinate)
VTMs vinyltrimethoxysilane
pbw parts–by–weight
PTFE poly tetra fluoro ethylene

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1. Introduction

Polybutadiene (PB), ethylene–propylene–dicyclopentadiene copolymer (EPDM) and styrene–butadiene–styrene copolymer (SBS) blends are widely used in high–frequency printed circuit board (PCB) due to their desirable electrical properties, such as low dielectric constant and loss at high frequency, which ensure the quality of signal transmission [1]. PCB materials also require excellent thermal and mechanical properties. The properties of ternary blends are closely related to the compatibility and degree of crosslinking. Therefore, this paper discusses in detail the effect of different pendant vinyl contents in PB on the properties of cured EPDM/SBS/PB composites. PB with considerably amount of pendant vinyl groups can undergo cross-linking curing reaction in which the pendant vinyl double bonds disappear in the presence of a suitable cross-linking agent [2–4]. EPDM and SBS, which contain unsaturated functional groups, can co-cure with PB. The above compounds are referred to as free radical-curable polymers.

There are many strategies to improve compatibility and crosslinking density of polymer blends, including grafting initiated by catalyst [5] or gamma radiation [6] and modifying with functional-polyers as reaction agents [7–9]. Herein, to accelerate the polyene curing reaction with olefin-reactive sites, crosslinking agents are an ideal choice [10–12]. Among these crosslinking agents, organic peroxide initiators have attracted attentions because they are capable of curing standard unsaturated polymers. Different initiators feature varying mechanisms for inducing reactions on polyene polymers [13]. In this study, blends based on EPDM, SBS and PB were prepared using initiators in solution followed by curing [14]. The organic peroxide of bis(tert-butyl)oxyisopropyl)benzene (BIPB) can be used as an effective initiator to induce a crosslinked structure of an unsaturated polymers. Numerous investigations into advantages of crosslinked structure have been published. For example, the crosslinked LDPE exhibited good thermal stability [15]; VTM-crosslinked PP/EPDM had excellent compatibility and resistance to solvent attack [16] and the crosslinked PLA-b-PES possessed excellent mechanical properties [17].

To increase the compatibility and crosslinking degree of EPDM/SBS/PB composites, according to Ziaee et al [18] and Dluzneski [19] researches, another feasible approach involves the use of PB containing 1, 2-vinyl group as co-agent in the presence of peroxide initiator. Naskar et al [20] studied PB with high amounts of 1, 2-vinyl as crosslinking co-agent in peroxide cured PP/EOC TPVS system, whereas Jiao et al [21] comprehensively studied the crosslinking behavior of PB/NR blends by using gamma radiation. However, the effect of vinyl content in PB on the crosslinking density of EPDM/SBS/PB composites has been rarely studied. Besides, only a few papers have been reported to address the EPDM/SBS/PB comprehensive performance and the related application. In this investigation, we focused on improving crosslinking density and compatibility from the point of PB molecular structure. As a result, five kinds of PB with different content of 1, 2-vinyl was used. In addition, the content of side groups in the main chain of the PB backbone influenced the inter-reaction with EPDM and SBS polymers, and this influence is reflected in the reactivity, thermal stability and mechanical properties of the cured composites. This research will be beneficial in manufacturing electrical substrate materials.

2. Experimental

2.1. Materials

EPDM (Trilene® 65) was purchased from Uniroyal Chemical Co. SBS (Kraton® D1118) was purchased from Kraton Co. BIPB, antioxidant 697 and xylene were purchased from Wengjiang Reagent Co., Qingdao jade new material technology Co. and ChengDu Kelong Chemicals Co., respectively. Table 1 presents the parameters of low molecular weight PB with 1%, 28%, 40%, 70% and 90% 1, 2-vinyl.

| N₂ | nitrogen |
| DSC | differential scanning calorimetry |
| TGA | thermogravimetric analysis |
| FESEM | field emission scanning electron microscopy |

2.2. Sample preparation

A 10 parts–by–weight (pbw) SBS, 20 pbw EPDM and 70 pbw PB were completely dissolved in xylene (polymer blend and solvent ratio of 1:1 by weight) and stirred at 90 °C until a homogeneous mixture was formed. Then, 1.7 pbw BIPB and 1 pbw antioxidant 697 were added to the mixture and stirred for another 120 min. Table 2 shows the compositions of EPDM/SBS/PB blends employed in this work. The number following PB represents
the 1, 2-vinyl content in PB. For example, composite PB40 contains 40% 1, 2-vinyl. After mixing, the blends were poured onto a PTFE plate to form a uniform film. The film was dried and cured in vacuum oven at 50 °C/1 h, 100 °C/1 h, 120 °C/4 h and 170 °C/2 h. Finally, the samples were gradually cooled down at room temperature and then removed from the oven.

2.3. Characterisation

Differential scanning calorimetry (DSC) (Model DSC − Q100, USA) was carried out in a TA instrument. The DSC temperature ranged from room temperature to 240 °C at a heating rate of 10 °C min⁻¹ under N₂ atmosphere and nitrogen flow rate of 50 ml min⁻¹.

Thermogravimetric analysis (TGA) (Model TGA − Q50) was performed in a TA instrument at a heating rate of 20 °C min⁻¹ and nitrogen flow rate of 40 ml min⁻¹. During the measurements, sample of about 3—10 mg was heated from room temperature to 600 °C under nitrogen atmosphere.

Gel content analysis was conducted by a Soxhlet extraction set using xylene as solvent. The samples (about 2 g) were extracted for 24 h in boiling xylene, and the sample residues were dried in a vacuum oven at 70 °C until constant weight. The gel content was determined using the following relation (1):

\[
\text{Gel Content(%) } = \frac{W_{G1}}{W_{G2}} \times 100\%
\]

where \(W_{G1}\) and \(W_{G2}\) refer to weights of samples before and after extraction, respectively.

The swelling ratio of samples was determined by soaking a sample in xylene for 72 h at room temperature. The original weight of the sample was represented by \(W_{S1}\), and excess xylene was removed from the swollen sample surface and then weighed immediately (\(W_{S2}\)). Swelling ratio was obtained using the following relation (2):

\[
\text{Swelling ratio } = \frac{W_{S2}}{W_{S1}}
\]

Mechanical tests on the films were carried out with SAN CMT6104 series desktop electromechanical universal testing machine at room temperature and according to ASTM D 412—98 A standard test method [20]. The sample had a length of 100 mm, a width of 10 mm and a thickness of 1.5 mm, and a cross-head speed of 500 mm min⁻¹.

Hardness tests were conducted using Shore A hardness tester according to ASTM D2240—97 [4]. Each sample type was tested five times, and the average value was obtained.

Table 1. Typical properties of different polybutadiene.

| Product      | 1, 2-vinyl (%) | Molecular weight (Mn, g mol⁻¹) | Specific gravity @ 25 °C | Source       |
|--------------|----------------|--------------------------------|--------------------------|--------------|
| Polyol 130   | 1              | 3000                           | 0.90                     | Evonik Degussa Co. |
| Ricon® 130   | 28             | 2500                           | 0.89                     | Cray Valley Co. |
| Ricon® 138   | 40             | 2000                           | 0.89                     |              |
| Ricon® 157   | 70             | 1800                           | 0.89                     |              |
| Ricon® 154   | 90             | 5200                           | 0.89                     |              |

* Datasheet from supplied companies.

Table 2. Formulation of polymers compounds (All Values in pbw).

| Component/Composite no. | PB1 | PB28 | PB40 | PB70 | PB90 |
|-------------------------|-----|------|------|------|------|
| EPDM                    | 10  | 10   | 10   | 10   | 10   |
| SBS                     | 20  | 20   | 20   | 20   | 20   |
| 1% 1, 2-vinyl PB        | 70  | —    | —    | —    | —    |
| 28% 1, 2-vinyl PB       | —   | 70   | —    | —    | —    |
| 40% 1, 2-vinyl PB       | —   | —    | 70   | —    | —    |
| 70% 1, 2-vinyl PB       | —   | —    | —    | 70   | —    |
| 90% 1, 2-vinyl PB       | —   | —    | —    | —    | 70   |
| BIPB                    | 1.7 | 1.7  | 1.7  | 1.7  | 1.7  |
| Antioxidant 697         | 1   | 1    | 1    | 1    | 1    |

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The morphologies of EPDM/SBS/PB composites were studied using field emission scanning electron microscopy (FESEM) (FEI Co, USA). The FESEM samples were fractured in liquid nitrogen, and thin film gold was vacuum-deposited onto the fresh fractured surface prior to analysis.

### 3. Results and discussion

#### 3.1. Differential scanning calorimetry

The exothermic peak temperature \( T_p \), which closely related to cross-linking process, was measured by DSC. During the cross-linking process, \( T_p \) appears at low temperature may be attributed to the superior reactivity of the reactants. Figure 1 shows the heating curves of five different composite systems. The temperature peaks were related to multiple parameters, including initiator or co-agent type, microstructure or molecular weight of the polymer and the composite ratio \(^22-26\). Herein, the value of \( T_p \) depends on the content of 1, 2-vinyl in polybutadiene, specifically, the \( T_p \) decreased with increasing 1, 2-vinyl content in PB. Composites PB90 and PB1 yielded \( T_p \) values of 175.71 °C and 198.17 °C, respectively. Moreover, the PB90 composite (about 175.71 °C) outperform polyene polymer have been reported \(^27\) (about 200 °C) in terms of crosslinking temperature. According to Wilkie et al cis or trans 1, 4- and vinyl 1, 2-PB in the presence of initiator undergo different cross-linking mechanisms \(^27\). In this study, the BIPB initiator caused the radical-curable polymers to generate free radicals, thereby forming ternary crosslinked blends via a combination of free radical on polymer chains. Scheme 1 presents the possible cross-linking mechanism. Given the presence of 1, 2-vinyl in PB, crosslinking was dominated the process, that is, the hanging vinyl of a chain reacted more efficiently than the cis or trans isomer of vinyl. In composite PB90 the probability of reacting pendent 1, 2-vinyl is higher. On the other hand,
the DSC test results showed that the composite PB90 first undergoes a vigorous cross-linking reaction as the curing temperature increases. Hence, composite PB90 exhibited superior reactivity [28].

3.2. Thermogravimetric analysis

Figure 2 shows the comparison of the thermal decomposition temperatures of EPDM/SBS/PB (five types of PB with different 1, 2-vinyl contents) composites. Table 3 lists the temperatures corresponding to different weight losses, 5 wt% ($T_5$), 10 wt% ($T_{10}$), 50 wt% ($T_{50}$), and 90 wt% ($T_{90}$), for the composites. The decomposition temperature at which the mass loss of polymer reaches 5 wt% ($T_5$) is generally used as a criterion for thermal stability [29]. As observed in figure 2, composites PB1 and PB90 showed a $T_5$ of 362.28 °C and 434.56 °C, respectively. When the 1, 2-vinyl content of PB increased to 90%, $T_{10}$ shifted to a high value, which was 22 °C higher than that of 1% 1, 2-vinyl content. Furthermore, addition of different 1, 2-vinyl contents in PB resulted in minimal effect on improving the decomposition temperatures at $T_{50}$ and $T_{90}$. The thermal stability of a polymer is closely related to crosslinking density, that is, a high crosslinking density leads to a good thermal stability [16, 22]. Increasing the 1, 2-vinyl content in PB provided the EPDM/SBS/PB composite with more chance to form a crosslinked network structure. This trend could be illustrated that the high concentration of 1, 2-vinyl in PB has a positive effect on the thermal stability of the composites, because of the higher reaction probability than that of PB containing low 1, 2-vinyl. Thus, 1, 2-vinyl groups play an important role in improving thermal stability of composites.

3.3. Gel content and swelling ratio of the composites

The gel content and swelling ratio of a polymer are used to characterise the degree of crosslinking [30]. Figure 3 shows the gel content and swelling ratio of five types of EPDM/SBS/PB composites. The figure also shows that with increasing pendant vinyl content in PB, the gel content increased steadily, whereas the swelling ratio decreased. Considering the relatively high reactivity of high-vinyl-content PB, 1, 2-vinyl in PB acts as an excellent co-agent in elevating the degree of crosslinking. The EPDM/SBS/PB composites exhibited a crosslinked structure, indicating a relative high solvent resistance. During curing, the 1, 2-vinyl groups in PB possibly improved the crosslinking structure due to the pendent vinyl groups are more active than cis or trans structure (scheme 1). A co-agent augments crosslinking — by network enhancement through the crosslinking of co-agent between polymer chains [21]. Ultimately, composite PB90 showed the highest crosslinking density and
best solvent resistance. These results correspond to the thermal stability of the EPDM/SBS/PB composites studied by TGA (figure 2) due to the thermal stability is related to crosslinking density.

3.4. Mechanical properties of the composites
With increasing 1, 2-vinyl content in PB, the tensile strength and hardness of EPDM/SBS/PB composites increased, whereas the elongation of break notably decreased (figure 4). From figure 4, the tensile strength of EPDM/SBS/PB90 reached 8.88 MPa, which is much higher than that of composite PB1 (1.55 MPa). The trend reveals the stable and strong interfacial linkage between polymers with high 1, 2-vinyl PB content. These phenomena can be attributed to the presence of 1, 2-vinyl fragments. The pendant vinyl group is more likely to form free radicals than the vinylidene group, thereby causing a crosslinking reaction (presented in scheme 1). The formation of strong interphases indicates the superior mechanical properties of the composites. The reduction of C=C double bond rendered the cured composites less flexible. The improved mechanical properties indicate that addition of 1, 2-vinyl group in PB may effectively reinforce the degree of crosslinking of the composites [31, 32]. The better compatibility of composite reinforces the mechanical properties, and such condition is mainly due to the increase in the degree of crosslinking and enhancement of interfacial linkage.

3.5. Morphology
To gain insights into the compatibility if addition of PB containing 1, 2-vinyl as co-agent in EPDM/SBS/PB composites, we investigated the morphologies of PB1, PB40 and PB90 composites by FESEM, and the experimental results are shown in figure 5. The micrographs of EPDM/SBS/PB composite show that the incompatible particle sizes gradually reduced (figures 5(a)–(c)). Specially, PB90 showed uniformly dispersed
particles on the surface, and these particles were markedly smaller in size compared with those of PB1. This phenomenon indicates that sample homogeneity increased with increasing 1, 2-vinyl content in PB. Thus, the 1, 2-vinyl sections in PB can be used as effective co-agents to increase the compatibility of ternary components. Figures 6(a)–(c) show the tensile fractured surface photomicrographs of PB1, PB40 and PB90 composites, respectively. Several black hollows, which were generated from the removed incompatible particles, were observed from the images. The increasing 1, 2-vinyl content of the composites and the decreasing number and size of black hollows indicate the increasing interfacial adhesion of the composites. A wide and deep crack appeared on the surface as 1, 2-vinyl content increased, and manifested a brittle surface morphology [33]. The SEM investigations were in-line with the observed mechanical properties. The enhanced compatibility of the composites reinforced their mechanical properties (figure 4).

4. Conclusion

The content of 1, 2-vinyl group in PB can remarkably affect the crosslinking density and properties of BIPB peroxide cured EPDM/SBS/PB composites. Hence, the PB containing more pendant vinyl groups can generate more free radicals in the presence of BIPB peroxide initiator, thus contributing to crosslinking among the three polymers. In this study, the EPDM/SBS/PB composite showed excellent reactivity and thermal stability by incorporating PB containing 90% 1, 2-vinyl. A considerable number of pendant vinyl groups in PB participated in the curing reaction of EPDM/SBS/PB composites, resulting in a crosslinked structure and high solvent resistance. Considering the studied mechanical properties and SEM micrographs, increasing the 1, 2-vinyl content in PB benefitted the formation interfacial adhesion of the composites and enhancement of compatibility. Taking the advantages of 1, 2-vinyl in PB, EPDM/SBS/PB (containing 90% 1, 2-vinyl or more) ternary system exhibited great potential to be an electronic substrate materials, where excellent thermal stability and mechanical property standards are all required.

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