Performance tuning of EPDM/HDPE thermoplastic dynamic vulcanizate: synergistic effect of rubber-plastic ratio and crosslinking agent

Wang Xinyu, Wang Shulin, Wang Xuanlun*

(Chongqing University of Technology, Chongqing 400054, China)

Abstract: This paper employs a dynamic vulcanization two-step extrusion process to prepare ethylene propylene diene monomer (EPDM)/high-density polyethylene (HDPE) thermoplastic vulcanizate (TPV). It investigates the influence of different rubber-plastic ratios on the mechanical properties and microstructure of EPDM/HDPE-based TPV, and analyzes the impact of varying amounts of crosslinking agents on the processing properties of EPDM/HDPE blends. The results indicate that as the resin content decreases, the tensile strength and elongation at break of the TPV show a significant decreasing trend. When the rubber-plastic ratio is 60/40, it exhibits superior mechanical properties and a distinct "sea-island" structure in its microstructure, which is superior to other rubber-plastic ratios upon comprehensive comparison. As the amount of crosslinking agent increases, the crosslinking rate gradually accelerates. However, an excessively high crosslinking rate makes it difficult to achieve the requirements of phase inversion and fine rubber crushing. When the amount of crosslinking agent is 0.3 parts, the crosslinking rate is moderate, resulting in a TPV product with good surface smoothness and uniform texture distribution.

Key words: dynamic vulcanization; thermoplastic dynamic vulcanized rubber; rubber-plastic ratio; crosslinking agent; phase inversion

Classification number: TQ330.46 **Article number:** 1009-797X(2026)06-0027-06

Document code: B **DOI:** 10.13520/j.cnki.rpte.2026.06.009

Thermoplastic vulcanizate (TPV) is a kind of environmentally friendly and low-carbon composite material that possesses both rubber characteristics and plastic processing properties. Compared to traditional vulcanized rubber, its preparation process is simpler, does not require specialized vulcanization, consumes less energy during processing, produces less pollution, and allows for the reuse of scrap materials. Compared to traditional rubber production processes, its production process is shortened by 1/4, energy consumption is reduced by 25% to 70%, processing efficiency is increased by 10~ to 20 times, and costs are reduced by approximately 10%.

TPV typically features a high content of rubber as the dispersed phase and a low content of resin as the continuous phase. The key to successfully preparing TPV lies in phase inversion, where the high content of rubber transitions from the continuous phase to the dispersed phase. To accomplish this transition of rubber from the continuous phase to the dispersed phase during the blending process, a special technique—dynamic vulcanization technology—is required. The crux of TPV preparation lies in dynamic vulcanization, which mainly involves crosslinking the rubber phase while the resin is melted and blended, ultimately forming an "island-in-the-sea" structure. This unique microstructure endows TPV with both the mechanical properties of vulcanized rubber and the processing characteristics of thermoplastic.

In this paper, EPDM was selected as the rubber phase and HDPE as the resin phase, employing a peroxide vulcanization

Biography: Wang Xinyu (1999-), a master's student, mainly focuses on the research of preparation process and properties of thermoplastic elastomers.

system. The vulcanizing agent was di-tert-butyl peroxy isopropyl benzene (BIBP), and the co-vulcanizing agent was triallyl isocyanurate (TAIC). A twin-screw extruder was used for dynamic vulcanization to prepare EPDM/HDPE-based TPV. The study investigated the impact of different crosslinking agent dosages on processing torque, as well as the influence of varying rubber-resin ratios on the tensile properties and microstructure of TPV.

1 Experimental part

1.1 Experimental materials and experimental formulas

High-density polyethylene, grade 5000S, Sinopec Lanzhou Petrochemical Co., Ltd.; ethylene-propylene-diene monomer rubber, grade 3092PM, Sinopec Mitsui & Co., Ltd.; high-density polyethylene grafted with maleic anhydride, grade W1H, Xiamen Kaisi Plastic Technology Co., Ltd.; BIBP, TAIC, and antioxidants are all commercially available.

Table 1 Formula of EPDM/HDPE/HDPE-g-MAH blend system

Sample Number	EPDM/portion	HDPE/portion	HDPE-g-MAH/portion
1#	0	100	0
2#	50	50	3
3#	60	40	3
4#	70	30	3
5#	80	20	3
6#	100	0	0

Note: The following reagents are calculated based on 100 phr of EPDM. BIBP: 0.3 phr, TAIC: 0.5 phr, antioxidant: 0.5 phr.

1.2 Experimental equipment and instruments

Electric Heated Blast Drying Oven, BPG-9070A, Shanghai Yiheng Scientific Instrument Co., Ltd.; Twin-Screw Extrusion Granulator, TSE-30A/500-11-40, Nanjing Ruiyafusite Polymer Equipment Co., Ltd.; Movable Parallel Twin-Screw Extrusion Platform, SJSP-20×25, Harbin Hapu Electrical Technology Co., Ltd.; High-Speed Mixer, SHR-10, Jiangsu Baixiong Co., Ltd.; Mixing Torque Rheometer, Mix-60, Harbin Hapu Electrical Technology Co., Ltd.; Electronic Universal Tensile Testing Machine, CMT-2503, Zhuhai Sansi Taijie Electrical Equipment Co., Ltd.; Scanning Electron Microscope (SEM), JCM-7000, JEOL Ltd.; Electronic Balance, LQ-6, Rui'an Ante Weighing Equipment Co., Ltd.

1.3 Sample preparation

First, EPDM and HDPE were placed in a 60°C electric constant temperature forced-air drying oven for 4 hours to fully remove moisture. Then, the dried EPDM and HDPE were added to a high-speed mixer according to the experimental formula ratio and blended for 1 minute to ensure thorough mixing. The mixed material was then added to a twin-screw extruder for extrusion granulation. The screw speed of the twin-screw extruder was set at 150 rpm, and the temperature settings for each zone, starting from zone 1, were: 100, 120, 130, 140, 150, 160, 170, 180, 180, 180, 180 ℃. The granules obtained after extrusion granulation were placed back into the 60°C electric constant temperature forced-air drying oven for 4 hours of thorough drying.

According to the recipe, add compatibilizer, crosslinking agent, co-crosslinking agent, etc. to the dried pellets, and then mix them in a high-speed mixer for 1 minute to achieve uniform dispersion of the additives in the pellets. Add the mixed material to a parallel twin-screw extruder to extrude sheets, with a die thickness of 2 mm. Set the screw speed of the parallel twin-screw extruder to 120 rad/min, and the temperature settings for each zone are as follows, starting from zone 1: 100, 135, 155, 175, 195, 195, 195 ℃. Obtain EPDM/HDPE-based TPV, place the TPV on a belt conveyor for cooling and compression molding, and cool it at room temperature for more than 24 hours. Finally, use a cutter to cut the TPV into dumbbell-shaped strips for various tests.

The EPDM/HDPE-based TPV is prepared using a two-step method: first, EPDM and HDPE are blended, extruded, and granulated to obtain a masterbatch; then, vulcanizing agents, vulcanizing aids, compatibilizers, etc. are added to the masterbatch to finally prepare TPV. The preparation process is shown in Figure 1.

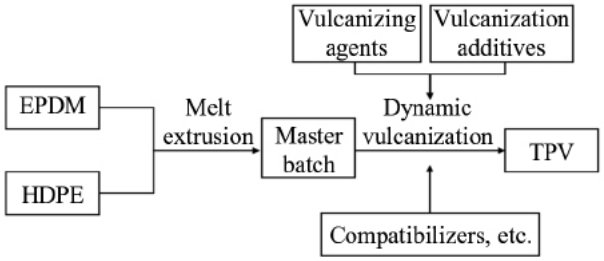

Figure 1 Preparation process diagram of EPDM/HDPE-based TPV

1.4 Analysis and testing

(1) Measurement of torque rheological torque

Weigh 40g of masterbatch, mix it evenly according to the recipe, and then add it to the torque rheometer for compaction. Maintain the processing temperature at 195℃, set the rotational speed of the torque rheometer to 120 r/min, and process for 3 minutes. After completion, obtain the torque-time curve.

(2) Tensile property test

Utilizing a universal tensile testing machine for tensile testing, the width of the tensile zone is determined to be 6 mm, the original gauge length is set to 40 mm, the thickness of the specimen is controlled at 2 mm, and the tensile rate is set to 50 mm/min. Five samples are cut from each group of samples for tensile testing, and the average value is taken to obtain the tensile strength and elongation at break.

(3) Scanning Electron Microscopy (SEM) testing

First, immerse the TPV sample in liquid nitrogen for low-temperature soaking, and after 10 minutes of continuous freezing, perform brittle fracture. Then, spray gold on the fracture surface, and finally place the gold-sprayed sample in a scanning electron microscope for microscopic morphology observation.

2 Results and discussion

2.1 Machining torque

The decomposition kinetics of the crosslinking agent BIBP has a crucial impact on the dynamic vulcanization process. Its dosage directly determines the vulcanization degree of the EPDM phase and the size distribution of the dispersed phase. The co-crosslinking agent TAIC can promote the efficiency of radical crosslinking reactions and improve the uniformity of the crosslinked network. In this experiment, a torque rheometer was used to monitor the torque evolution of the blended system in real time. The highest torque was used to characterize the development of crosslinking density and the evolution of phase structure, while the lowest torque reflected the fluidity and apparent viscosity of the melt. The torque difference was used to indicate the degree and intensity of the dynamic vulcanization reaction.

The amount of crosslinking agent BIBP significantly regulates the crosslinking kinetic behavior of EPDM, thereby affecting the processing rheological properties of the EPDM/HDPE blend system. In this study, the rubber-plastic ratio was first fixed at 60/40, and the torque changes of the EPDM/HDPE blend during the crosslinking process were investigated under five gradient BIBP dosages: 0.1 phr, 0.3 phr, 0.5 phr, 0.7 phr, and 1.0 phr, as shown in Figure 2 and Table 2.

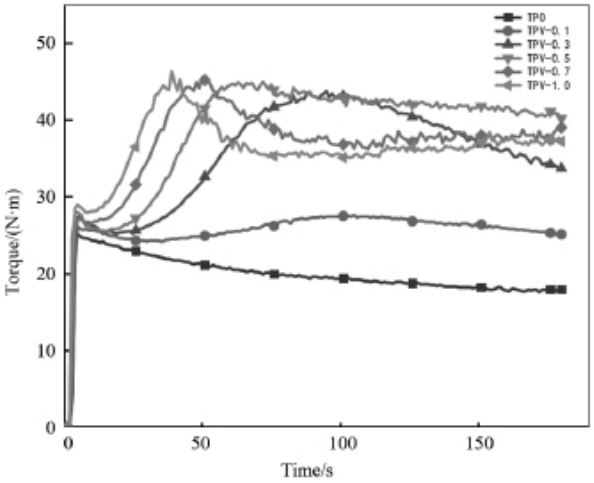

Figure 2 Effect of different bibp dosages on the torque-time curve of EPDM/HDPE blends

Table 2 Processing torque of EPDM/HDPE blends with different BIBP additions

Sample name	MH/N.m	ML /N·m
TPO	25	17
TPV-0.1	27	24
TPV-0.3	45	25
TPV-0.5	45	25
TPV-0.7	45	26
TPV-1.0	46	27

When the addition level of BIBP is 0.1 phr, there is no significant change in the torque-time curve of the EPDM/HDPE blend system, indicating that the crosslinking reaction has a limited regulatory effect on the material processing torque under these conditions. Through in-depth analysis of the dynamic vulcanization process, it was found that under the influence of trace amounts of BIBP, EPDM particles undergo crosslinking reactions and are subjected to shear forces, resulting in a decrease in their minimum torque by approximately 7 N·m compared to TPO samples. Meanwhile, the maximum torque was observed to reach 27 N·m at 80 s. When the BIBP addition level is increased to 0.3 phr, the maximum torque (MH) reaches 45 N·m at 85 s, and prior to this, the curve rises gently. This indicates that at a BIBP addition level of 0.3 phr, the crosslinking reaction and shear forces achieve a good

balance, allowing EPDM particles to achieve better dispersion and encapsulation in the HDPE matrix, thereby optimizing the processing and mechanical properties of the blend. When the BIBP addition level is increased to 0.5 phr, the time for the system's maximum torque to appear is advanced to 70 s, and its value increases to 45 N·m. This phenomenon demonstrates that the crosslinking behavior of the EPDM/HDPE blend system is dependent on the initiator concentration: as the BIBP dosage increases, the concentration of free radicals generated by its thermal decomposition rises, leading to improved crosslinking reaction kinetics, specifically manifested as an increase in the slope of the torque-time curve and an increase in system viscosity, which directly results in higher torque measurements during processing.

When the addition level of BIBP increases to 0.7 and 1.0 phr, the appearance time of MH is advanced to 50 seconds and 40 seconds respectively, and stabilizes at a level of 46 N·m. An excessively high initiator concentration leads to an excessively rapid crosslinking reaction rate, resulting in the formation of an overly large crosslinked network structure in the EPDM phase. This structure is difficult to be fully infiltrated and coated by the HDPE matrix during the melt blending process, and it breaks down under strong shear fields, ultimately forming an unevenly dispersed phase structure. This undesirable morphological evolution leads to deteriorated processing performance of the blend and also results in the final product exhibiting a powder-like morphology, which significantly deviates from the microstructural integrity and macroscopic performance requirements needed for the practical application of thermoplastic elastomers. When the BIBP content increases from 0.1 to 1.0 phr, the maximum torque of the blending system increases from 27 N·m to 46 N·m, and the time to reach MH decreases from 80 seconds to 40 seconds, indicating a nonlinear growth characteristic of the crosslinking rate. This phenomenon is directly related to the concentration of free radicals generated by the thermal decomposition of BIBP, that is, an increase in free radical concentration accelerates the formation of the EPDM crosslinked network, but excessive free radicals can lead to an uncontrolled crosslinking rate, resulting in phase reconstruction lagging behind the shear breaking process.

As observed from Figure 3, the appearance of EPDM/HDPE-based TPV products varies with different BIBP contents. When the BIBP addition is 0.3 phr, the product surface is relatively smooth and the texture is relatively uniform, indicating that the crosslinking rate and shear rate are well matched at this time. The rubber phase achieves moderate crosslinking and fine crushing during the dynamic vulcanization process, and the phase inversion proceeds smoothly, resulting in a finer microstructure of the material and a uniform and regular appearance macroscopically. When the BIBP content increases to 0.5 phr, the product surface becomes rough, and the unevenness of the structure can be observed to increase. This is due to the increased addition of BIBP, which accelerates the crosslinking rate, and the crosslinking speed of the rubber phase exceeds the shear crushing speed. Some rubber phases undergo crosslinking before they can fully disperse and blend, resulting in a rough structure and affecting the uniformity of the material's phase distribution to some extent. When the BIBP content is 0.7 phr, the roughness of the product further intensifies, possibly indicating local over-crosslinking.

An excessively high BIBP content leads to rapid crosslinking reactions in EPDM rubber, resulting in an excessive number of crosslinking points within the system. This not only makes it difficult to break down the rubber phase but may also trigger over-vulcanization of EPDM, affecting the physical and mechanical properties of the material. Additionally, the issue of BIBP residue becomes more prominent. An appropriate BIBP content plays a crucial role in the microstructure and macroscopic properties of EPDM/HDPE-based TPV. Overall, a BIBP content of 0.3 phr is more conducive to obtaining TPV materials with uniform structure and good performance.

(a) 0.3 phr (b) 0.5 phr (c) 0.7 phr

Figure 3 Macroscopic morphology of EPDM/HDPE-based TPV with different BIBP contents

2.2 Tensile properties

Figure 4 illustrates the mechanical properties of pure EPDM, pure HDPE, and TPV with different rubber-plastic ratios. It is evident that as the resin content decreases, both the tensile strength and elongation at break of TPV gradually decrease. The reason for this phenomenon is that HDPE, as the plastic phase, has higher crystallinity and intermolecular forces, providing good mechanical support to the material. On the other hand, EPDM, as the rubber phase, has better flexibility in its molecular chain but relatively lower mechanical strength. In the blend, HDPE, as the continuous phase, is the main load-bearing part of the entire TPV. As the EPDM content increases, that is, the HDPE content decreases, the continuous phase of HDPE in the system is gradually replaced by the dispersed phase of EPDM, resulting in a decrease in the overall mechanical strength of the material. The addition of EPDM may weaken the interaction between HDPE molecular chains to some extent, making the material more prone to deformation and fracture during stretching. During dynamic vulcanization, a higher plastic phase content may lead to higher melt viscosity, poorer fluidity, and excessive hardness of TPV, making it behave more like a toughened plastic rather than an elastomer. Meanwhile, compared to an EPDM/HDPE ratio of 50/50, rubber-plastic ratios of 60/40 and 70/30 are more prone to phase inversion, forming a distinct "sea-island" structure, achieving superior comprehensive performance. When the rubber-plastic ratio is 60/40, the tensile strength of EPDM/HDPE reaches 14.51 MPa, and the elongation at break is 678.42%. In terms of mechanical properties, it is slightly superior to TPV with a rubber-plastic ratio of 70/30. When the rubber-plastic ratio reaches 80/20, the rubber content in the system is too high, resulting in higher viscosity, and the decrease in plastic phase content weakens the supporting effect of the cross-linking network. At the same time, the dispersibility of the rubber phase deteriorates and the interfacial bonding force decreases, making TPV prone to fracture during stretching and reducing the elongation at break.

2.3 Analysis of brittle fracture micro-morphology

In the rubber-plastic blending system, the rubber-plastic ratio plays a crucial role in regulating the microstructural evolution of thermoplastic dynamic vulcanizate (TPV). The four sets of TPV brittle fracture morphologies shown in Figure 5 indicate that different rubber-plastic ratios significantly alter the two-phase structure and interfacial bonding state, ultimately resulting in distinct differences in the brittle fracture morphologies. The white part in the figure represents the sheared and crosslinked EPDM dispersed phase, while the black part represents the HDPE continuous phase. As the content of the resin phase in TPV increases, the size of rubber particles significantly decreases. When the rubber-plastic ratio is 80/20 and 70/30, the rubber particle size is relatively large and there are certain differences in distribution; when the rubber-plastic ratio is 50/50, the EPDM and HDPE phases exhibit a near co-continuous phase, making it difficult to form an "island-in-the-sea" structure; whereas when the rubber-plastic ratio is 60/40, compared to other rubber-plastic ratios, the rubber particle size is more uniform, and the dispersion state in the HDPE matrix is also more uniform, with no obvious agglomeration or size mutation phenomenon. The distribution of "islands" in the "sea-island" structure is more regular, indicating that the dispersion effect of the EPDM dispersed phase in the HDPE continuous phase is better at this rubber-plastic ratio.

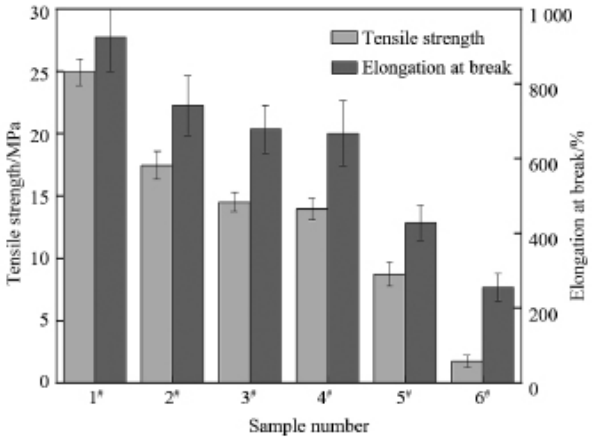

Figure 4 Tensile strength and elongation at break of TPV with different EPDM/HDPE ratios

3 Conclusion

EPDM/HDPE-based TPV was prepared using a twin-screw extruder for dynamic vulcanization. The processing torque, tensile properties, and brittle fracture microstructure of the TPV were investigated. The results show that

(1) Upon analyzing the torque variation curves and

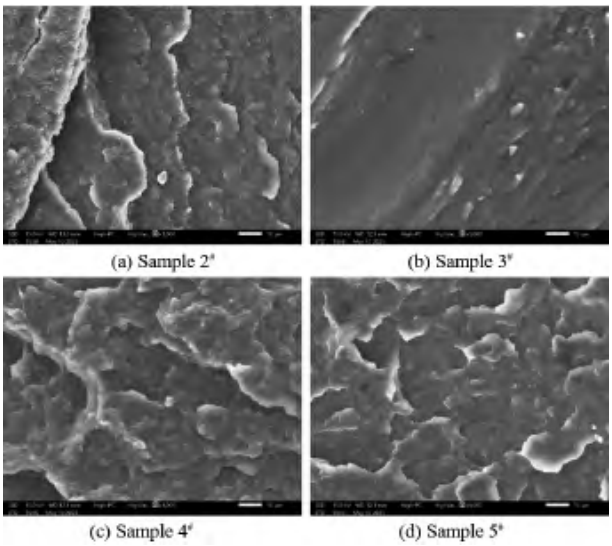

Figure 5 Microscopic morphology of brittle fracture of EPDM/HDPE-based TPV with different rubber-plastic ratios

macroscopic morphology of EPDM/HDEP blends with varying amounts of crosslinking agent BIBP, it was found that when the BIBP addition level was 0.3% (mass fraction), the torque curve of the blend rose gently, indicating a moderate crosslinking rate. The resulting TPV product exhibited good surface smoothness and uniform texture distribution.

(2) Tensile property tests on TPV with different EPDM/HDPE ratios revealed that as the resin phase content decreases, the tensile strength and elongation at break of TPV exhibit a significant decreasing trend. When the rubber-plastic ratio is 60/40, the tensile strength reaches 14.51 MPa and the elongation at break reaches 678.42%, indicating good mechanical properties.

(3) Through the analysis of the brittle fracture micro-morphology of EPDM/HDPE-based TPV with different rubber-to-plastic ratios, it was found that the four sets of rubber-to-plastic ratios exhibited different two-phase structures. When the rubber-to-plastic ratio was 60/40, a typical "sea-island" structure was formed, with smaller rubber particle sizes and more uniform dispersion, resulting in a good micro-morphology.