

Improved dispersion in a dynamically vulcanized ternary polymer blend by employing the core-shell concept



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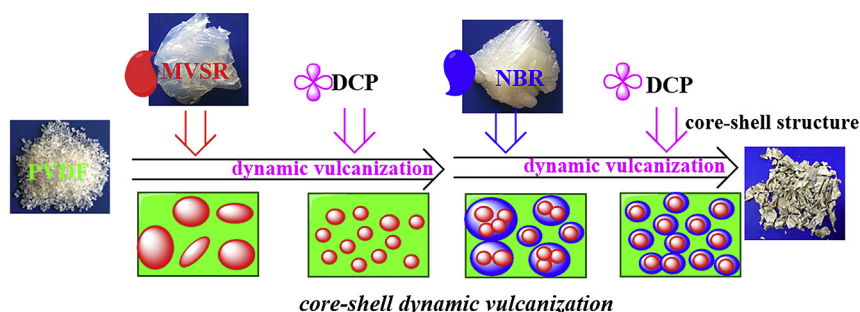
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HIGHLIGHTS

- Designed core-shell dynamic vulcanization, forming a SR/NBR core-shell structure.
- Super toughness: notched impact strength 47.4 kJ/m² without completely fracture.
- Calculated impact strengths of 118.5 kJ/m² for completely fractured blends.
- Core-shell conception in dynamic vulcanization to solve poor interface in blends.

GRAPHICAL ABSTRACT



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ABSTRACT

It is meaningful and practicable to design poly(vinylidene fluoride) (PVDF)/silicone rubber (SR) blends to partly substitute the expensive synthetic fluorosilicone materials. Unfortunately, there is a significant difference between the surface energies of PVDF and SR phases, which results in an unstable interface and deteriorates the mechanical properties of their blends. In this paper, we introduced nitrile butadiene rubber (NBR) into PVDF/SR blend to serve as an interlayer which reduced the direct contact between PVDF and SR phases. Formation of the stronger NBR/PVDF interface was beneficial to the impact energy transfer, which significantly improved the toughness of the blends. It was found that the two-step method was better than the one-step method. We hope our study could open up an avenue to design a super-toughened fluorosilicone blend, and, also contribute to solve the problem of poor interfaces in multicomponent polymer blends.

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1. Introduction

Polymer blending is considered as one of the most versatile and economical method to fabricate new materials [1–4]. Core-shell structures can be obtained in multicomponent polymer blends

[5–10] due to that the different polymer pairs require to minimize the surface free energy. However, this is a spontaneous process which was limited in a few multicomponent polymer blends. We find that the dynamic vulcanization [1,11], a kind of reactive blending to achieve specific phase morphology that the crosslinked rubber particles are dispersed in a continuous plastic phase, may provide a potential platform to realize the formation of core-shell structure. Once a rubber component is crosslinked to be stable particles, they will possibly serve as the “core”. When a second

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suitable rubber component is able to encapsulate the “core”, then a crosslinked core-shell rubber particle can be formed after a second-stage dynamic vulcanization. This opens up an avenue for solving poor interfaces in polymer blending systems, for example the fluorosilicone blends.

Fluorosilicone material has received great attentions due to its advanced application. However, the difficulty in fabrication and the high cost limit their further commercial applications [12,13]. Therefore, to fabricate a fluorosilicone blend is meaningful and practicable. Poly(vinylidene fluoride) (PVDF) may be a good choice to blend with silicone rubber (SR) due to its mild processing temperature ($m.p \approx 170 \text{ }^\circ\text{C}$). The former has typical fluoropolymeric characteristics of excellent resistances to high temperatures, UV irradiation, and aggressive chemicals [14–16], and the latter has excellent silicone characteristics such as the resistances to low temperature, oxidation and climate [17]. Unfortunately, the large interfacial tension between PVDF and SR is unfavorable to the mechanical properties of their blends [18,19]. Particularly at high loading level of SR, severe phase separation could fail the preparation of PVDF/SR blends [19]. Therefore, how to reduce the negative PVDF/SR interface should be firstly solved in this blending system.

Dynamic vulcanization provides a potential platform to solve this problem [20–28]. We noted that nitrile butadiene rubber (NBR) had good compatibility with PVDF due to the strong interaction between CF_2 group of PVDF and polar nitrile group of NBR [29]. If the NBR component could serve as an interlayer to reduce the poor PVDF/SR interface, the final blend should exhibit considerable mechanical properties. In this paper, we designed a two-step dynamic vulcanization, by which we prepared PVDF/NBR/methyl vinyl silicone rubber (MVSR) ternary blends. To the best knowledge of us, there was no report about dynamically vulcanized PVDF/NBR/MVSR ternary blends and, as expected, the final blends showed super-toughness which laid an applied foundation for design of high-performance fluorosilicone blends to satisfy the potential applications in commercial, civil and military uses. This study also opens up an avenue to solve poor interface in polymer blends.

2. Experiments and methods

2.1. Materials

PVDF (density: 1.77 g/cm^3 , melting point: $168 \text{ }^\circ\text{C}$, MFI = 22 g/10 min ($230 \text{ }^\circ\text{C}$, 5 kg)) was purchased from Changshu Hong Jia Fluorine Technology Co. Ltd (Jiangsu, China). MVSR (vinyl content of 0.24%, molecule weight of $7.6 \times 10^5 \text{ g/mol}$) was purchased from Shenzhen Mu Wei Technology Co. Ltd (Guangdong, China). Nitrile butadiene rubber (NBR-N41, 29% acrylonitrile content, $ML(1 + 4, 100 \text{ }^\circ\text{C}) = 77.5$) was purchased from Lanzhou Petrochemical Company (China). Dicumyl peroxide (DCP) was purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). Other chemicals were used as received.

2.2. Dynamic vulcanization of PVDF/NBR/MVSR blends

Dynamic vulcanization was performed in a Haake Rheocord 90. It was designed by steps as followed: 1) PVDF was firstly shear-melted at about $175 \text{ }^\circ\text{C}$. Then MVSR was added and mixed to achieve an equilibrium torque. In order to form the SR-core structure, DCP was added here to crosslink the MVSR droplets. The crosslinking was lasted for about 2 min 2) After that, NBR was added to encapsulate the crosslinked MVSR particles. At last, DCP was added again to crosslink the NBR. The mixing was continued to reach the final stable torque. The torque curves were self-recorded by the Haake Rheocord 90.

Then the dynamically vulcanized PVDF/NBR/MVSR ternary blends were chopped into small granules and molded by an injection molding machine TTI-160F (Welltec Machinery & Equipment Co. Ltd., China). In this paper, the weight ratio of plastic/rubber was fixed at 60/40 and the weight ratios of NBR/MVSR were 10/30, 20/20 and 30/10. The dosage of DCP was 2 wt% of the whole rubber phase. The final blends are coded according to the PVDF/MVSR/NBR ratio, e.g. P6S3+N1 represents a sample in which the PVDF: MVSR: NBR = 60:30/10(wt%/wt%/wt%).

2.3. Characterization

Morphology of the blend was observed by using a SEM (ZEISS Merlin, Germany) equipped with energy-dispersive spectrometer (EDS) (X-Max^N20, Oxford, England). The FT-IR absorption spectra were obtained by a Tensor 27 Spectrometer (Bruker, Germany) with a resolution of 4 cm^{-1} and 32 scans. Colloid and Interfacial Rheometer (MCR302, Anton Paar) was utilized to study the rheological behavior of the blends. The experiments were performed at $210 \text{ }^\circ\text{C}$. The frequency sweep was logarithmically increased from 0.01 to 100 rad/s at constant strain amplitude of 5%. TEM was done on a JEM-100CX II transmission electron microscope (JEOL, Japan). Ultra-thin sections were sliced using an ultramicrotome (Leica EMUC6, Germany). Dynamic mechanical properties were measured by DMA 242C (NETZSCH, Germany) in a tensile mode: frequency of 1 Hz and -150 to $100 \text{ }^\circ\text{C}$ at a heating rate of $3 \text{ }^\circ\text{C/min}$. Tensile behavior was conducted on a universal testing instrument (Shimadzu AG-1, 10 kN, Japan) with a crosshead speed of 50 mm/min. The notched Izod impact strength was measured with an impact test machine (ZWICK5331, German, Zwick/Roell) at room temperature. All of the above tests were repeated at least four times.

3. Results and discussion

3.1. Preparation of PVDF/NBR/MVSR ternary blends

The idea for preparation of fluorosilicone blends with considerable mechanical properties is try to reduce the direct contact between the PVDF and the MVSR phases. Our strategy is to introduce NBR to act as a barrier to isolate PVDF and MVSR. It was based on a designed core-shell dynamic vulcanization in two steps, as illustrated in Fig. 1a. At the first step, MVSR was crosslinked to be stable particles [30]. Because of the soft nature of the uncrosslinked

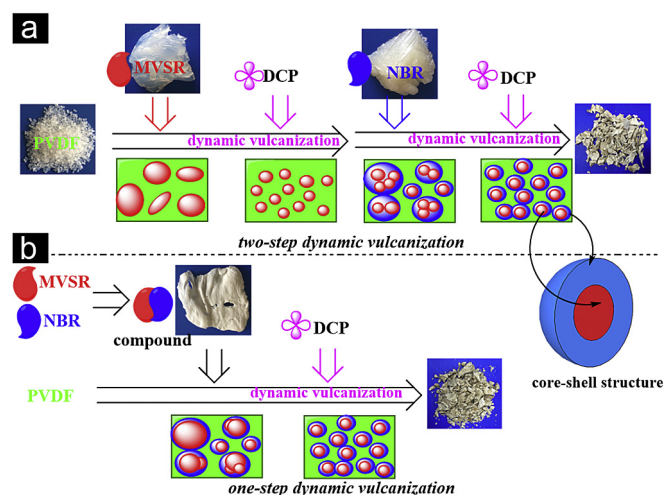


Fig. 1. Schematic of dynamic vulcanization for PVDF/NBR/MVSR ternary blends: (a) two-step method; (b) one-step method.

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