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Model construction of particle size in dynamic vulcanization of PVDF/SR blends—matching degree between crosslinking and shearing rates

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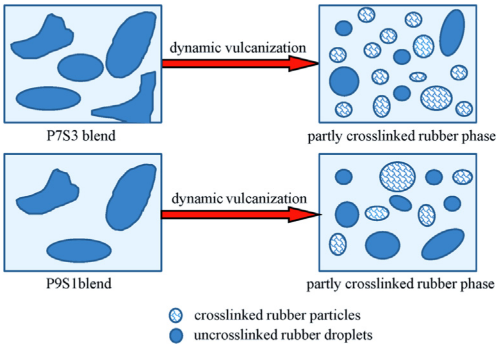
HIGHLIGHTS

- New model construction of particle size in dynamic vulcanization of PVDF/SR system.
- A good matching of shear and cross-link helped to achieve a uniform crosslink of SR.
- A minimum of particle diameter polydispersity was achieved at 90 rpm.

GRAPHICAL ABSTRACT



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ABSTRACT

Peroxide-induced dynamic vulcanization of poly (vinylidene fluoride)/silicone rubber (PVDF/SR) blends was studied in this paper. We controlled the size of rubber particles by changing the rotor speed, and discussed the influence of shearing on the particle diameter and the particle diameter polydispersity (d_p). The size of SR particle was confirmed to be decreased with increasing the rotor speed. However, a good matching degree of shearing and crosslinking rate helped the SR phase to achieve a uniform crosslinking, as well as a narrow d_p. In this particular PVDF/SR system, the suitable rotor speed was found to be 90 rpm, at which the d_p reached a minimum of 1.1981 and 1.1614 for the P9S1 and the P7S3, respectively. At last, we discussed the influences of the macroscopic breaking energy (E_{dk}) and the coalescence (P) on the number-average particle diameter (D_n) of the SR. This work is thus devoted to construct a model for predicting the particle size in dynamic vulcanization of PVDF/SR blends.

1. Introduction

Polymer blending of ready-made materials always draws great attention in material design due to that it not only conquers weakness of single material but also generates new properties from the synergy effect of components [1]. For example, blending of poly(vinylidene fluoride) (PVDF) and silicone rubber (SR) is meaningful to partly substitute the expensive synthetic fluorosilicone materials. Their blends integrate the typical fluoropolymeric characteristics and silicone characteristics, which can satisfy the potential specific applications in

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commercial, civil and military fields [2,3]. Unfortunately, differing to the well-known polypropylene (PP)/ethylene-propylene diene terpolymer (EPDM) system, the great interfacial tension in PVDF/SR system facilitates breakup and coalescence of dispersed SR droplets [4] in PVDF melt simultaneously under a rotational shearing. This inevitably results in large and wide distribution of particles size which is unfavorable to the mechanical performances of the PVDF/SR blends.

Dynamic vulcanization is a reactive blending technique, during which the rubber phase is crosslinked to be stable particles and finely dispersed throughout the thermoplastic phase under intensive shearing. We consider that dynamic vulcanization is feasible to achieve fine phase structures for the PVDF/SR system because the crosslinking stables the size of rubber particles and prevents their secondary coalescence [5,6]. Since the concept of dynamic vulcanization was first proposed in 1960s by A. M. Gessler et al. [7], researchers [8–27] have made persistent efforts in development of this specific processing technique. However, putting emphasis on the phase evolution [11,12] during dynamic vulcanization, most of studies focused on the size reduction since a decrease in rubber particle size brought a significant increase in the mechanical properties of blends [13]. There are very few discussions on several important factors that are known to also influence the final performance of blends, directly or indirectly, in particular the distribution of disperse particles diameter [14]. Additionally, most of constructed models for predicting rubber particle diameter were based on the balance between the breaking-down rate and coalescence of the disperse rubber droplets in an ideal simple blending system [15,16]. They do not work well in dynamic vulcanization since the situation of the probability of coalescence collision and the macroscopic breaking energies of the disperse rubber particles [17] are more complex during dynamic crosslinking of rubber phase.

Therefore, to fabricate useful PVDF/SR blends, the dynamic vulcanization for this system should be studied firstly. In this paper, we regulated the diameter of rubber particles by changing the rotor speed, and discussed the influences of shearing on the particle diameter and the particle diameter polydispersity. Finally, we constructed a model to predict the particle size in dynamic vulcanization of the PVDF/SR blends. We hope this study would provide a well-work model for dynamic vulcanization of PVDF/SR system and lay a foundation for design of useful PVDF/SR blends to partly replace the high-cost synthetic fluorosilicone materials in future.

2. Experimental methods

2.1. Raw materials

Poly(vinylidene fluoride) (PVDF 502) was purchased from Guangzhou Li Chang Fluoroplastics. Co. Ltd (China). Silicone rubber (SR) was a commercial rubber (KE 571-U, Shin-Etsu, Japan). Dicumyl peroxide (DCP), used as crosslinking agent, was purchased from Sinopharm Chemical Reagent Co. Ltd. (China) and was purified by anhydrous alcohol recrystallization before use. N,N-Dimethylformamide (DMF) were purchased from Shanghai Richjoint Chemical Reagents Co., Ltd. (China), purity ≥ 99.5% (A.R.). Dimethylbenzene were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China), purity ≥ 99% (A.R.).

2.2. Sample preparation

In this paper, the weight ratio of PVDF/SR was fixed at 90/10 and 70/30, w/w. The dosage of DCP was fixed at 2 wt% of the SR. The dynamic vulcanization of PVDF/SR blends were done in an internal mixer (POTOP Torque Rheometer, China) at 190 °C under various rotor speeds (50 rpm, 70 rpm, 90 rpm, 110 rpm and 130 rpm). PVDF was first added into the internal mixer and melt-mixed for about 3 min. After reaching a stable torque, the masticated SR was incorporated and mixed together with the PVDF melt until a stable torque. Then DCP was added to induce the dynamic vulcanization. The total mixing process lasted about 10 min. For brevity, we designated the resultant blends according to the PVDF/SR ratio and the rotor speed, e.g., the dynamically vulcanized PVDF/SR (70/30) was defined as P7S3. The P7S3 was prepared at a rotor speed of 50 rpm, and then it was defined as P7S3R50.

2.3. Apparent crosslink density measurement of the SR phase

The crosslink density of the rubber phase, represented by volume swell ratios, was determined by the equilibrium swelling experiment. All of the weighed specimens were immersed in dimethylbenzene at an ambient temperature for a period of 120 h to reach swelling equilibrium. Then, the swollen samples were taken out and wiped carefully with tissue paper to remove the solvent. Immediately after that, the samples were weighed again on an analytical balance, and the apparent cross-link density was calculated by the following equation [18–20].

$$V_R = \frac{1}{1 + (\frac{m_2}{m_1} - 1) \times \frac{\rho_r}{\alpha \rho_s}} \tag{1}$$

where m_1 and m_2 are the mass of the sample before and after swollen; ρ_r and ρ_s are the SR ($\rho_r = 0.98\ \mathrm{g/cm^3}$) and dimethylbenzene density ($\rho_s = 0.86\ \mathrm{g/cm^3}$), respectively; α is the mass fraction of SR in the sample.

2.4. Scanning electron microscopy (SEM)

To observe the SR particles, the blends was extracted by hot N,N-Dimethylformamide (DMF) and then dried completely. The morphology of the sample was then characterized by a S1530 microscopy (Japan). In order to prevent electrostatic charge build-up during observation, the samples were coated with a thin gold layer before morphological observation.

3. Results and discussion

3.1. Dynamic vulcanization

The dynamic vulcanization of PVDF/SR blends was conducted in a torque rheometer. The shape of rotors and the inside of the mixing chamber are shown in Fig. 1 to give a visual cognition of the place where the dynamic vulcanization occurred. As seen from Fig. 1a, two rotors rotate in opposite directions in the mixing chamber, which provides powerful shearing. Under shearing, the melt flow in such a mixer is very complicated, especially during the crosslinking of rubber phase. Matching degree between the crosslinking rate of rubber phase and the

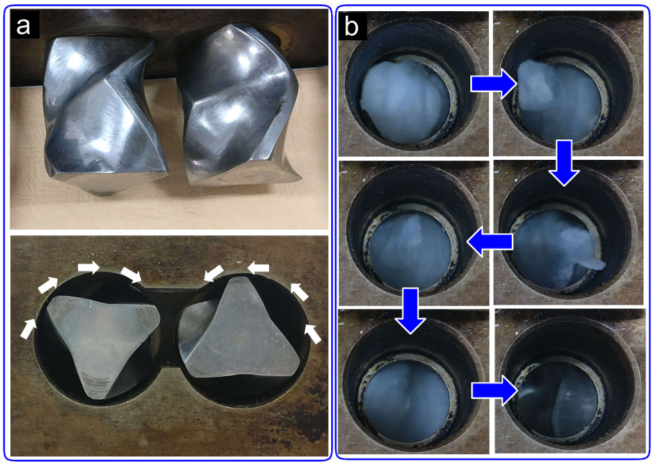

Fig. 1. Photogram of (a) the mixing chamber and rotors of Haake Rheometer and (b) the material feeding process.