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# Simultaneous enhancement and percolation behaviors of damping and mechanical properties of ethylene–propylene–diene rubber by introducing phase-change organic acid

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ABSTRACT

Ethylene–propylene–diene rubber (EPDM)/stearic acid (SA) composites with improved strength and high damping performance were prepared by blending. With increasing SA content, the damping and mechanical properties of EPDM both quickly increased and there existed a percolation threshold of SA loadings, respectively. By analyzing the viscoelastic properties and cross-linking process of EPDM composites, it could be thought that the two percolations were attributed to two different cross-linked networks caused by phase-change organic acid, respectively. The percolation of damping performance coincides with that of liquidlike–solidlike transition of EPDM molecular chains, which was due to the decreasing cross-linking density, caused by restricting the decomposition of vulcanizing agent by SA, and enhanced the mobility of EPDM chains. The mechanical percolation was mainly dependent on the formation of a physical rubber–filler network by increasing crystal SA, which behaved as a filler before phase-change happened.

## 1. Introduction

The unwanted vibrations result in the fatigue and failure of structures, which inevitably cost industries in maintenance, repair, and replacement. Therefore, vibration damping has become a priority research area in a number of industries including car manufacturing, aerospace, and sports equipment manufacturing, both from a fundamental research point of view and practical requirement in the area of suppressing vibration and noise [1]. In general, elastomers and other amorphous thermoplastics with a glass transition temperature below room temperature are attractive for damping due to their viscoelasticity [2]. However, they also have some disadvantages. First of all, the damping range of homopolymers is generally 20 °C–30 °C because of their narrow glass-transition region, which is not broad enough for practical applications [3]. Moreover, a marked change in the storage modulus inevitably accompanies the glass-rubber transition, which often limits the availability of the materials in industrial use [4]. Hence, much research has been done on damping modification of polymeric materials in an attempt to obtain high-performance damping materials with high damping peak, high modulus to meet different practical requirements, such as the addition of inorganic fillers or polymer blends [5,6]. Unfortunately, the introduction of inorganic particles can provide high strength and modulus, whereas the damping peak height is decreased sharply while the damping peak position is slightly shifted [5]. On the other hand, most polymers are not miscible from a thermodynamic point of view because the entropy contribution to the Gibbs energy of mixing is negligible. Mixing of two homopolymers thus often leads to a coarse heterogeneous phase structure with low adhesion between the components [7]. And the optimized temperature regions are not largely broadened. These facts show that the improvement of damping peak height and modulus cannot be accomplished simultaneously by conventional means [8].

As we know, cross-linking causes substantial changes in the relaxation processes and is a widely used method for the modification of polymer properties [9]. The increasing of cross-linking density can provide high strength and modulus, whereas the damping performance above glass transition temperature decreases. SA is usually used as a processing acid during the sulfur cross-linking of rubber [10]; however, it can decrease the cross-linking density of rubber by suppressing the decomposition of vulcanizing agent, when we replace the sulfur with dicumyl peroxide (DCP). Hence, SA could be used to control the cross-linking density and modify the mobility of EPDM chains and damping performance of elastomers. At the same time, despite its restricting the cross-linking at high temperature, SA as a phase-change material crystallizes at low temperature and acts as a filler by increasing the modulus [11]. Thus, utilizing the different properties of SA at different temperature, we could regulate the cross-linked network and the

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mobility of EPDM chains by introducing the phase-change organic acid SA and simultaneously enhance the damping and mechanical properties of elastomers.

In this work, ethylene–propylene–diene (EPDM) terpolymer was chosen as sample, and the effects of SA on the structure and property of EPDM were investigated. On one hand, we get EPDM/SA composites with simultaneous improved strength and damping performance. On the other hand, it is also interesting to found there exists a liquidlike–solidlike transition, which coincides with an abrupt increase in the damping performance in EPDM/SA composites. The liquidlike–solidlike transition relevant to cross-linked network is extremely sensitive to SA, which causes substantial changes in the damping property [8]. The mechanical strength shared some similarities with the percolation phenomenon occurring in filler strengthened rubber [12]. The percolation mechanisms of damping performance and mechanical strength in EPDM/SA composites will be discussed.

## 2. Experimental

Ethylene–propylene–diene monomer rubber (EPDM Vistalon™ 7001) containing 73 wt% of ethylene and 5 wt% of ethylidene norbornene (ENB) was supplied by ExxonMobil Co., USA. Dicumyl peroxide (DCP) powder, 40% on whiting carrier, was bought from AKZO NOBEL Cross-linking Peroxides (Ningbo, China) Co., LTD. Stearic acid (SA) was kindly supplied by Sinopharm Chemical Reagent CO., LTD. The EPDM pellets were placed into an oven with a preset temperature at 60 °C for 3 h and mixed on an XSS-300 rheometer (Shanghai KeChuang Rubber Plastics Machinery Set LTD., China) at 90 °C for 40 s, then the SA was added and continued at 60 r/min for 200 s. Finally, DCP was added. Then they were cured on platen press under 11 MPa pressure at 160 °C for the optimum curing time ($t_{c90}$), obtained from the Moving Die Rheometer (GOTECH Co., China). The maximum torque (MH) and the minimum torque (ML) were also obtained from the rheometer at the same time.

In order to characterize the degree of cross-linking of the EPDM, the equilibrium swelling experiments were carried out at 30 °C using xylene as swelling solvent [13]. Samples with an initial mass $M_i$ were introduced into the xylene over a 36-h period to permit them to achieve swelling equilibrium. Then the samples with swelled mass $M_s$ were dried under vacuum at 85 °C for 36 h and weighted in order to obtain their dry mass $M_d$. The soluble fraction $F_s$ and the swelling ratio $Q$ are calculated from the following relations [13]:

$$F_s = \frac{M_i(1\text{-}\varepsilon)\text{-}M_d}{(1\text{-}\varepsilon)M_i} \tag{1}$$

$$Q = 1 + \frac{\rho_{\text{polymer}}}{\rho_{\text{xylene}}}\frac{M_s - M_d}{(1\text{-}\varepsilon)M_d} \tag{2}$$

in which $\varepsilon$ is the weight ratio of SA, and $\rho_{\text{polymer}}$ and $\rho_{\text{xylene}}$ are density of the EPDM and the xylene, respectively.

Dynamic mechanical analysis (DMA) tests were conducted on a PerkinElmer Diamond apparatus (USA), in tension mode, under nitrogen atmosphere, from −100 °C to 185 °C. The films had the dimensions of 45 × 6 × 2 mm$^3$. Multifrequency scans (0.1, 0.5, 1, 5, and 10 Hz) were made in the same temperature range, at the heating rates of 2 °C/min. The drops in $E'$ curves and the peaks of $E''$ and tan $\delta$ plots report on the relaxations in polymers. The frequency sweep tests were carried out isothermally in the same dynamic mechanical analyzer in tension mode geometry. Measurements were made at 13 different frequencies in the 0.01- to 100-Hz range at different temperatures between 40 °C and 150 °C. After a frequency sweep was completed, the temperature was increased by 10 °C. The sample dimensions were 45 × 6 × 2 mm$^3$. The mechanical property study was performed on an instron universal tester (CMT 4204, SANS Co., China) according to the GB/T 528-1998 standard, with a crosshead speed of 500 mm/min. Differential scanning calorimetry was performed on a Pyris Diamond DSC (Perkin-Elmer, USA), and all measurements were made at a scan rate of 20 °C/min under continuous nitrogen gas flow.

## 3. Results

Dynamic mechanical analysis (DMA) is an efficient tool to measure the viscoelastic properties of polymers. Fig. 1a shows that the mechanical relaxation spectrum at 5 Hz for the cross-linked elastomers of different SA amount. The transition, which occurs near the temperature of −33 °C, is considered as the glass transition ($T_g$), and $T_g$ is hardly influenced by the presence of SA,as listed in Table 1. With the increase of temperature, there appears high tan $\delta$ level in a wide temperature range for EPDM samples, especially for those with high SA contents (3–15 phr). We define the shadowed area as a damping performance TA [14]. The TA values of EPDM composites were listed in Table 1. The hybrid material with larger TA value have a more excellent damping property with the increase of SA content, which shows that the damping property can be controlled by introducing the SA. Especially importantly, the temperature range of high damping level is broadened beyond the glass-transition zone of elastomer. It can also be seen that the TA value quickly increases and shows a percolation behavior when the content of SA is higher than 1 phr. The abrupt change is at 1 phr, which is sometimes related to the so-called percolation threshold concentration [15]. This can be explained by a classical liquid–solid transition and may be related to the obviously change of a chemical cross-linked network [16].

In order to study the transition of the mobility and relaxation of macromolecular chains, we investigated the influence of SA on the cross-linking density of EPDM. Fig. 2a shows the difference between the maximum and the minimum torque (MH-ML) decreased with increasing SA content, which indicates EPDM becomes less cross-linked. Fig. 2b shows the swelling ratio $Q$ and the soluble fraction $F_s$ increased with increasing SA content, which indicated EPDM become less cross-linked. Particularly, it can be seen from the fore semi-parts of Fig. 2a and b that the $Q$, the $F_s$, and the (MH-ML) decrease fast and there is an inflexion (about at 1 phr) in the curves.

The cross-linking process begins by formation and expansion of linear chains that soon start to branch, and subsequently to cross-link, originating three-dimensional networks. Gelation is the significant phenomena that determines the characteristics of the final polymer network [17]. The transformation from a viscous liquid to an elastic gel is named the "gel point." After considering the relationship between

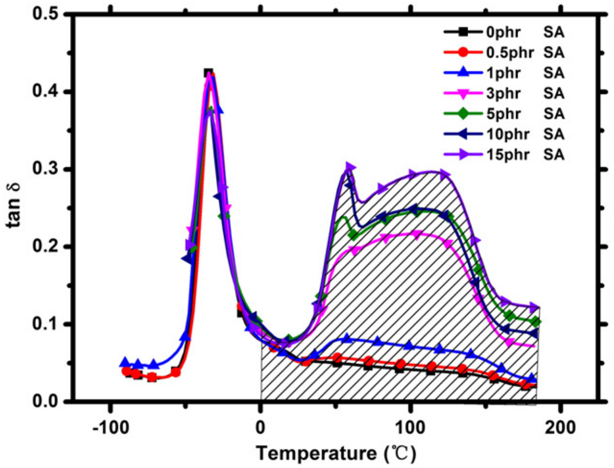

**Fig. 1.** (Color online) Variation of tan δ with temperature, at 5 Hz, resulted in DMA experiments performed with various SA amount. Example of schematic diagram method for calculating damping performance tan δ area, TA.(The content of all compounded ingredients are given as usual, based on a total of 100 parts of rubber by weight) (The lines are guides to the eyes).