Improved Viscoelastic Damping Properties of Carbon Black Reinforced EPDM Composites by Blending with ENR

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Abstract: EPDM/ENR blends were prepared from saturated nonpolar ethylene propylene diene monomer (EPDM) and unsaturated epoxidized natural rubber (ENR). The dynamic mechanical properties of EPDM/ENR compounds and their vulcanizates were studied by rubber processing analyzer and dynamic mechanical thermal analyzer. The results show that the addition of ENR is helpful to improve EPDM processability. With the increase of ENR content, the tensile strength of EPDM/ENR decreases first and then increases while the elongation at break increases. The lowest tensile strength is still greater than 12.5MPa, which shows the industrial usage. The temperature range for the loss factor $\tan\delta$ being greater than 0.1 becomes wider from -40.1 °C ~ 7.7°C for pure EPDM to -40.1 °C ~ 80 °C for 80 : 20 EPDM/ENR.

Keywords: Viscoelastic damping, Rubber blend, Ethylene propylene diene monomer (EPDM), Epoxidized natural rubber (ENR), Vulcanization.

1. INTRODUCTION

Damping materials can absorb shock reducing noise and reinforcing contact sealing. EPDM is a copolymer of ethylene, propylene and a small amount of conjugated diene. Because of its excellent aging resistance, EPDM is widely used damping materials [1-3]. In fact, its glass transition temperature is relatively low being below room temperature, only *ca.* -30°C ~ -50 °C. The effective damping temperature range is relatively narrow when such effects above room temperature is especially not good [4-6]. In contrast, unsaturated epoxidized natural rubber (ENR) is strongly polar with higher glass transition temperature (Tg) exhibiting relatively strong and wide damping range in addition to good comprehensive properties. ENR with high epoxidation degree shows Tg above 0℃. Therefore, ENR was selected to blend with EPDM so as to improve the damping performance and to broaden the effective range of EPDM [7, 8].

Rubber damping materials should not only have good damping performance, but also have excellent physical and mechanical properties. Huang Ruili and others [9] added ENR with epoxidation degree of 50 (abbreviated as ENR50 hereafter) to EPDM with vinyl content of 52%, which widened the damping range to -72.3°C ~ 52.9 °C when $\tan\delta > 0.13$, but carbon black was not added to reinforce the matrix resulting in poor mechanical properties of vulcanized rubbers. Sarawut Prasertsri *et al*. [10] directly blended EPDM and ENR through internal mixer illustrating their improved compatibility is favorable of the tolerance to automobile fuel for EPDM/ENR blends. Besides, Zhao Yanfang [11] studied the effect of feeding sequence on the vulcanization characteristics and mechanical properties of EPDM/ENR. It was found that the faster vulcanization and better mechanical properties were realized by mixing the EPDM compound and the ENR compound, which were first prepared separately before subsequent master-batch, than by compounding EPDM/ENR matrix blend with other additives. This is probably due to the sufficient compounding of matrix with additives insuring the homogeneous phase distributions. This may be more important for the reinforcement component of CB and vulcanizing agent in improving the filling and cross-linking effects.

In this paper, a kind of EPDM with higher vinyl content (*ca.* 68 wt %) and a kind of ENR with epoxy degree of 50 are used for higher Tg and good damping effects of their compound blends with different ratios to improve the process-ability, the damping performance and mechanical properties of EPDM.

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2. EXPERIMENTAL

2.1. Materials

EPDM was of 3080, a product of Jilin Petrochemical Company of PetroChina. Epoxidized natural rubber (ENR50) was from Institute of agricultural products processing, Chinese academy of tropical agricultural sciences. Carbon black was of N330 from Evonik Degussa Co., Ltd. (Qingdao). Other rubber compounding agents such as zinc oxide (ZnO), stearic acid (SA), sulfur (S), accelerator M, accelerator BZ, antioxidant RD and the like are commercially available.

2.2. Sample Preparation

The basic formula of EPDM compound (parts by mass) is EPDM : N330 : ZnO : SA : M : BZ : S of 100 : 40 : 5 : 1.5 : 1 : 1 : 1.5.The basic formula of ENR compound (parts by mass) is ENR : N330 : ZnO : SA : M: RD : S of 100 : 40 : 5 : 1.5 : 1 : 1 : 1.5.

Weighed raw rubber of EPDM was put into an internal mixer to melt at 60°C for *ca.* 1min. In continuous mixing, added were sequentially the calculated amounts of SA, ZnO and carbon black before finally adding BZ, accelerator M and sulfur. The compound was discharged after the mixing torque arrived at balance. After this, EPDM compound was further punched into triangular bales by thinly passing and slicing on an open mill. The same preparation method was used in preparing ENR compound according to its own formula. Finally, EPDM compound and ENR compound were weighed in certain proportions to blend using the open mill before forming thinly baled and evenly mixed EPDM/ENR compound blend in order to slicing triangular compound.

After curing at 150°C for vulcanization time (t90) on a vulcanizing flat press, the vulcanized samples were successfully prepared before remaining for 24 hours at room temperature.

2.3. Testing and Characterization

According to the standard of ISO 37-2005 the tensile specimens were cut from vulcanized plates into dumbbell shape with thickness of 2mm. The tensile test was conducted at a speed of 500mm/min for both the upper and the lower clamps together on the tensile machine.

Tearing specimens were cut into right-angle spline according to ISO 34-1-2004 with thickness of 2mm. The test speed was also set at 500mm/min for both upper and lower clamps on the tensile machine.

The vulcanization time (t90) was obtained after being tested at 150°C using a rotorless rheometer. Dynamic rheological test for compounds were conducted on rubber processing analyzer (RPA 2000) in strain scanning with strain amplitude (γ_0) of 0.28 ~ 100%, frequency of 1Hz and temperature of 60 °C.

Dynamic mechanical thermal analyzer (DMA+450) was conducted in tensile mode with frequency of 10Hz, temperature range of -100 °C ~ 80 °C and heating rate of 2 °C /min.

3. RESULTS AND DISCUSSION

3.1. Mechanical Properties of EPDM/ENR Vulcanized Rubber

Tensile properties of EPDM/ENR vulcanizates are shown in Figure **1**. The tensile strength and the elongation at break of ENR are slightly higher than those of EPDM rubber. However, their blends in different ratios exhibit better in elongation at break than single component rubber. EPDM and ENR are incompatible although the polar ENR strengthens the interfacial layer of two rubber components. The complete compositions for each rubber contribute to its independent elastic function. Two rubber phases are mixed or even interpenetrated in domains. Such structure behaviors in series connection, which explains the remarkable ductility for the rubber blends. The effects are best when their ratio approximates one.

However, the series structure does not increase the tensile strength for their blends when compared with the EPDM or ENR rubber except such blends with predominant percentage as ENR 20:80 EPDM/ENR with the obvious interpenetrated domains. For their blends with the small component of ENR, the not good interface can not endure high load showing lower tensile strength for blends than for both rubber components. This illustrates that the modification of EPDM by ENR is better than that of ENR by EPDM due to the higher comprehensive properties of ENR than those of EPDM. Overally, the dispersed rubber blend morphology of 80:20 EPDM/ENR is in contrast with the continuous phase structure of 20:80ENR/EPDM, which corresponds to their contrast in tensile strength. It is noted the lowest strength for blends is higher than 12.5MPa, which shows their availability in industrial applications.

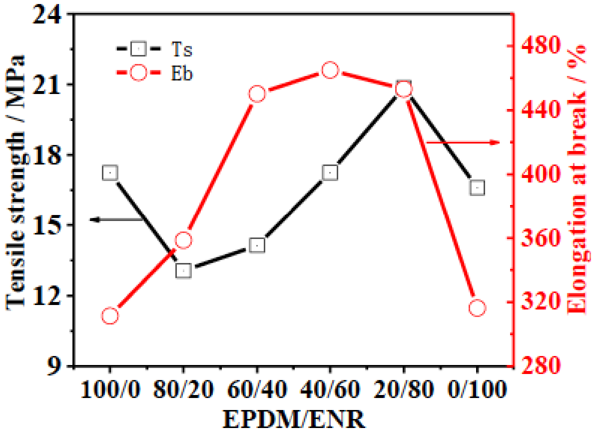

Figure 1: Tensile properties of EPDM/ENR vulcanized rubbers.

3.2. Damping Performance of EPDM/ENR in RPA Test

Under dynamic shear, the damping effects can be characterized using loss factor $\tan\delta$, the ratio of loss modulus versus storage modulus tested by RPA. $\tan\delta$ curves for EPDM rubber, ENR rubber and their rubber blends are shown in Figure **2**.

The loss factor, $\tan\delta$, rises for all compounds with increasing shear γ_0 in Figure **2a** illustrating more energy are damped in loading. The rise is slow at lower strain (*e.g.* below 10%) while this tendency become sharp after critical strain for each compound. The critical transition strains for blends are higher than both single matrix compound, *i.e.*, EPDM or ENR. At a certain strain, the loss factor of EPDM is higher than that of ENR. The loss factor for 20:80 EPDM/ENR is almost the same with that of EPDM at low strain or slightly higher than it at large strain. All of other composed blend compounds exhibit higher $\tan\delta$ than EPDM and ENR. The increment becomes stronger for the compound containing more ENR. The synergic effects imply the improved damping of EPDM by ENR, which is caused by the formed structure.

In industrial application, the compounds are vulcanized so that the crosslink network is formed to endure higher load being capable of elastic recovery after deformation. The curves of $\tan\delta$ versus γ_0 of vulcanizates are shown in Figure **2b**. After matrix being crosslinked, the vulcanized rubbers show lower damping loss than un-vulcanized compounds at 60℃. The basic variation situations in Figure **2b** are similar to those at low strain in Figure **2a**. This means that the macro/meso phase structures remain though matrix molecules chemically crosslink into network, the latter factor reinforces the composites to act as rubber. The critical strain for transition from slow to rapid increasing tendency become larger, which implies the more stable structure is formed by chemical crosslinking than by component blending or mixing. After being crosslinked, $\tan\delta$ rises from *ca.* 0.075 to ca. 0.11 when ENR is sheared at increased γ_0 from 1% to 100%. In great contrast, $\tan\delta$ rises from ca. 0.1 to 0.15 when γ_0 is increased from 1% to 10%. When $\gamma_0 > 10\%$, $\tan\delta$ goes up abruptly to 0.43 at $\gamma_0 = 100\%$. $\tan\delta$ of blend lies between that of ENR and EPDM at high γ_0. $\tan\delta$ of blend is higher when the content of EPDM versus that of ENR in the blend approximates 1, which implies the co-continuous or even interpenetrated phase structure is more favorable for damping. Besides, the major matrix component plays a greater role than the minor one. The above aspects are integrated so that the variation in $\tan\delta$ in sequence of EPDM > 60:40 EPDM/ENR > 40:60 EPDM/ENR > 80:20 EPDM/ENR > 20:80 EPDM/ENR > ENR. The great discrepancy of the situation at low strain with that at high strain is due to the following fact. The metastable meso-structure for the blends of incompatible EPDM rubber component

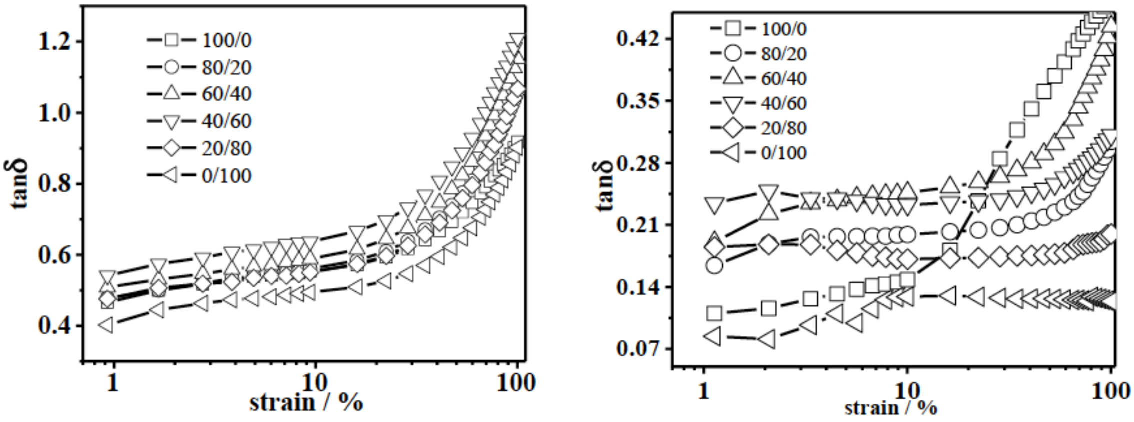

Figure 2: The curves of $\tan\delta$ (**c**) versus strain for EPDM/ENR in compound rubbers (**a**) and vulcanized rubbers (**b**).

with ENR can endue shear at low strain. Such structure tends to be destroyed in shear at high strain, where the domains of EPDM rubber component are not strongly interconnected with those of ENR one. In each component, molecular chains are more likely to produce higher relative slip and internal friction under high strain, *i.e.*, the loss factor is also higher.

3.3. DMA Characterization of Damping Performance of EPDM/ENR

The damping properties of EPDM/ENR have been studied previously at certain dynamic shear at 1Hz and at 60 °C. In fact, the damping strongly depends on the environmental temperature. Thus, dynamic tension at 10Hz was conducted using DMA in temperature scanning mode at heating rate of 2 °C /min from -100 °C to 80 °C. The results are shown in Figure **3**.

In Figure **3a**, the curve of storage modulus E' versus temperature for each vulcanized rubber include the plateau stage where E' remains constant or slightly being dropped at low temperature, the high temperature plateau where E' decreases slowly and the transition stage between them, where E' decreases suddenly with temperature. The first inflection point is often regarded as glass transition temperature, above which the composites softens such that the elastic modulus reduces quickly. Tg of EPDM is *ca*. -40°C, remarkably lower than that (*ca*. -10°C) of ENR. There are double inflection points for their blend rubbers. The one at lower temperature is of EPDM rubber component while the other at higher temperature is of ENR. It is observed that the former shifts to lower temperature when the content of EPDM decreases while the latter shifts to higher temperature when the content of ENR decreases.

When the temperature is lower than the glass transition temperature of EPDM, the rubber is in a glass state where the molecular segments are in a frozen state and entangled firmly. Therefore, the initial storage modulus is large and stable. The initial storage modulus E' increases with the increase of ENR content. When the temperature rises above the glass transition temperature, the frozen state of EPDM/ENR molecular segments is slowly released due to thermal motion. At this time,softening is more likely to occur where E' gradually decreases.

In the curves of $\tan\delta$ versus temperature in Figure **3b**, the loss peak of EPDM rubber is *ca.* -27.5 °C while that of ENR is *ca.* 3.4 °C. There are double loss peaks. The one for EPDM component shifts to lower temperature when the content of EPDM decreases in the blend while that of ENR shifts to higher temperature when the content of ENR decreases in the blend. The damping peak of EPDM is 0.397while it is lower than 0.1 in both low temperature and high temperature regions, in which the temperature region with damping greater than 0.1 is only -40.1 ~ 7.7 °C. The damping peak of ENR is 1.024 when the damping factor is greater than 0.1 in a wide temperature range (-14 °C to 80 °C). Thus, the addition of ENR into EPDM can broadens the effective temperature range of EPDM improving its damping effects. There is the polarity difference between EPDM and ENR. The rigid epoxidized NR limits the segment mobility of EPDM molecular chain. The specific peak positions of the blends and the corresponding maximum loss factors are listed in Table **1**. The peak positions of EPDM components slightly shift to low temperature after adding ENR while the Tg of ENR shifts to high temperature with the addition of EPDM. On the one

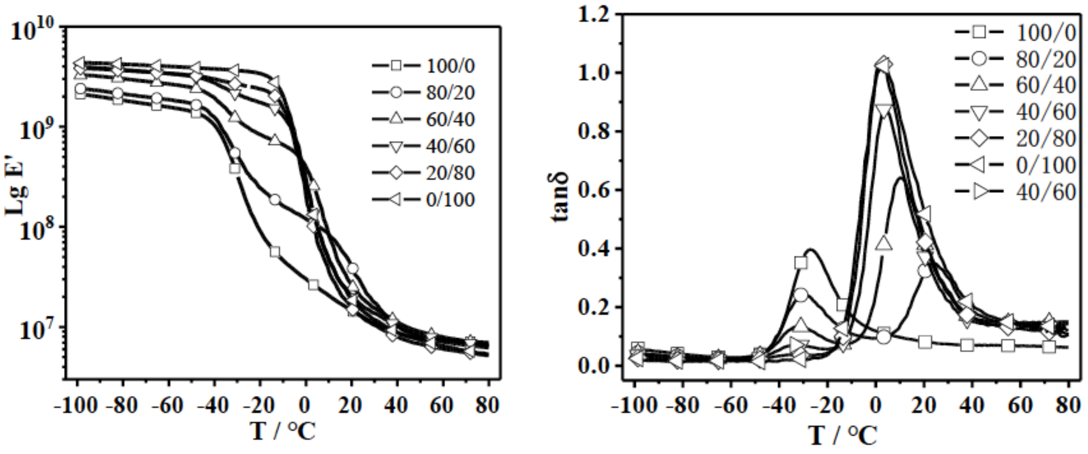

Figure 3: Storage modulus E' (**a**) and loss factor $\tan\delta$ (**b**) versus temperature T for EPDM/ENR in DMA.

Table1: Tg and $\tan\delta$ for the Components in Vulcanized EPDM/ENR Rubbers

EPDM:ENR	EPDM Component		ENR Component	
	T_{g1} /°C	$\tan\delta_{max}$	T_{g2} /°C	$\tan\delta_{max}$
100:0	-27.5	0.397	-	
80:20	-30.1	0.241	23.9	0.352
60:40	-32.6	0.134	10.3	0.642
40:60	-33.4	0.071	4.25	0.876
20:80	-33.6	0.038	2.45	1.041
0:100	-	2.18	2.18	1.024

hand, the epoxy group contained in ENR increases the rigidity of the corresponding segment, thus hindering EPDM relaxation and reducing the former. On the other hand, ENR and EPDM undergo molecular chain co-crosslinking under the action of sulfur vulcanization when the internal deformation and internal friction of the composite material are increased under the combined action of the two aspects. Thus, the addition of ENR of a certain component can obviously shift the damping temperature range to high temperature, effectively improving the damping range.

4. CONCLUSIONS

EPDM/ENR binary blend was successfully prepared by further mixing EPDM rubber and ENR rubber after their separate compounding.

The effects of different blending ratios on the processability and mechanical properties of EPDM/ENR were studied. RPA and DMA were used to characterize the damping properties of the compound.

(1) ENR rubber improved the elongation at break of vulcanized EPDM rubber. With the increasement of ENR, the tensile strength of EPDM/ENR decreases first and then increases, but the lowest tensile strength is still greater than 12.5MPa.

(2) ENR can modify the shear damping of EPDM in shear. The loss factor of EPDM/ENR is higher than that of single-component EPDM or ENR. The composite with 60: 40 EPDM/ENR has the best damping performance.

(3) ENR can modify the damping of EPDM in tension. DMA showed that ENR and EPDM show two independent damping peaks after blending. When the ratio is 80/20, the loss factor $\tan\delta > 0.1$ is widened from the original -40.1 °C ~7.7 °C to -40.1 °C ~80 °C, effectively widening the damping temperature range.

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