

The Dynamic Mechanical Properties of EPDM/Al(OH)₃ Composites

Naikui Gao, Jianying Li, Shengtao Li, Zongren Peng

State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, China

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ABSTRACT: The effects of volume fraction, particle size, and surface state of Al(OH)₃ fillers on the dynamic mechanical properties of EPDM/Al(OH)₃ composites were investigated by dynamic mechanical analysis (DMA). The interfacial structure parameters of EPDM/Al(OH)₃ composites were also investigated. The results show that dynamic mechanical property and the glass-transition process of composites are distinctly influenced by the volume fraction, particle size, and surface state of Al(OH)₃ fillers. With the increase of volume fraction and decrease of particle size of Al(OH)₃ fillers, the temperature corresponding to the maximum damping factor of composites shifts to a higher temperature with lower peak value and broader half-peak width. The treatment of fillers with coupling agent can

greatly enhance two-phase interaction and thus improve the dynamic mechanical properties of composites. Consequently, a lower damping factor, broader half-peak width, and larger apparent activation energy of glass transition can be achieved. In addition, a novel method of calculating the apparent activation energy of composites is put forward based on the DMA method, which has been verified by calculating the apparent activation energy of glass transition of Al(OH)₃-filled EPDM composites. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2454–2460, 2005

Key words: composites; interfaces; fillers; dynamic mechanical property; interfacial structure parameter

INTRODUCTION

Polymer-based composites filled with inorganic fillers are widely used in electrical insulation systems and many other engineering fields.^{1–5} Typical composites are insulating materials for EPDM insulators, cable terminations, and bushings. The fillers are filled with EPDM to impart improved mechanical properties, flame retardancy, and tracking resistance. However, as composites have a great many microscopic interfaces, the surface state of the fillers has a great effect on the microscopic interfaces and consequently it brings about a lot of effects under the action of electric field, temperature, and stress,^{6–8} thus, the dynamic mechanical property of composites was greatly changed. Dynamic mechanical property is one of the most important properties for composite insulation materials, since periodic or stochastic stress and temperature will be imposed on the composites in their working state, which thus change the storage module, damping factor, dynamic viscosity, and life. Although dynamic mechanical properties of composites were investigated by some researchers,^{9–15} the results are not so satisfactory and the mechanism is not clarified because the property is influenced by many factors.

Dynamic mechanical analysis is a powerful tool to study the molecular motion and property of polymers.^{16,17} Several researchers^{18–20} have used the method to investigate polymeric blends and polymer-based composites with inorganic fillers successfully to analyze the effect of interface on molecular motion and property of polymers. Both inorganic fillers and the resultant organic/inorganic interface show great effect on the dynamic mechanical property of composites, which have not been studied and understood in detail so far. In this paper, the effects of volume fraction, particle size, and surface state of Al(OH)₃ fillers on the dynamic mechanical properties of EPDM/Al(OH)₃ composites were investigated by DMA. Also, the interfacial layer thickness was calculated by a newly proposed method.

EXPERIMENTS

The ethylene-propylene-diene monomer rubber (EPDM, Nordel 2522; Dupont Co. Ltd., Wilmington, NC) was used as the matrix material. Two types of Al(OH)₃ fillers (provided by GuiZhou Aluminum Factory, China) with average particle size 1.25 and 24.2 μm and specific surface area of 2.43 and 0.146 m²/g, respectively, were dispersed in EPDM. Other materials like crosslinking agent (DCP), antioxidant, silicone coupling agent, and stearic acid are commercial products. Table I shows the basic formulation of the composites.

Correspondence to: J. Li (Lijy@mail.xjtu.edu.cn).

TABLE I
Basic Formulation of EPDM/Al(OH)₃ Composites

Material (phr)	Content
EPDM	100
DCP	2
Antioxidant	1
Stearic acid	1
Silicone coupling agent	2
Al(OH) ₃	Varied

EPDM, Al(OH)₃, and DCP were put into a two-roll mixer of 120 ± 3 °C in sequence and blended for 10 min. Then the mixture was put into a flat vulcanizing machine at 170 ± 3 °C and vulcanized for 20 min under proper pressure. Finally, samples with a dimension of $50 \times 12.5 \times 1.4$ mm were obtained. To investigate the role of particle size and surface state of Al(OH)₃ fillers on dynamic mechanical properties of composites, polymer-based composite samples containing Al(OH)₃ fillers with different particle size and surface state were prepared.

A dynamic mechanical analyzer (DMA, Model DMA 983, TA Instruments, New Castle, DE) was used to measure the dynamic mechanical properties and differential scanning calorimetry (DSC, Model DSC 2920, TA Instruments) was used to measure the glass transition temperature of the composites. Table II shows the operating parameters.

RESULTS AND DISCUSSION

Dynamic mechanical properties as a function of temperature

Figure 1 shows the effect of temperature on the storage modulus (E') and damping factor ($\tan\delta$) of EPDM/Al(OH)₃ composite. The particle size of Al(OH)₃ fillers is $1.25 \mu\text{m}$ and the volume fraction is 0.1. E' decreases sharply with temperature in the range of -70 – 40 °C, while a transition peak of $\tan\delta$ appears at -46.3 °C. To clarify the transition process, samples of composites and pure EPDM were analyzed by DSC. As shown in Figure 2 samples of composites and pure EPDM exhibit endothermic transition at -47.7 and -57 °C, respectively, which is in accordance with the glass transition temperature (T_g) of EPDM reported elsewhere.²¹ Thus, it is suggested that variation of E' and

TABLE II
Operating Parameters of DMA and DSC

Parameter	DMA	DSC
Heating rate	$5 \text{ }^\circ\text{C min}^{-1}$	$5 \text{ }^\circ\text{C min}^{-1}$
Temperature range	-80 to 10 °C	-80 to -30 °C
Mode	Resonance mode	
Amplitude	0.3 mm	

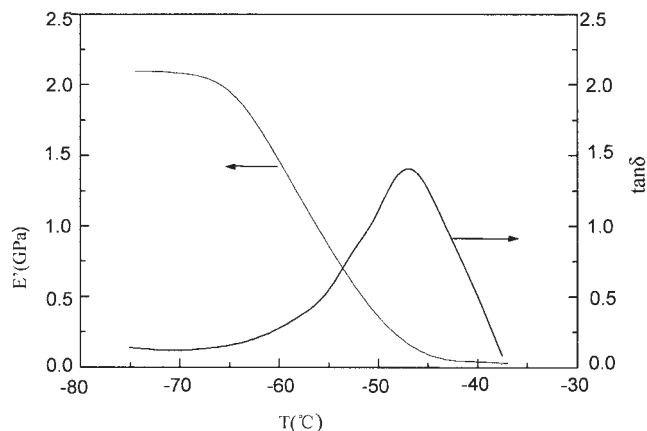


Figure 1 Temperature dependence of E' and $\tan\delta$.

$\tan\delta$ in the range of measuring temperature of Figure 1 results from the glass transition process. In addition, it can be seen from Figure 2 results that T_g of pure EPDM is lower than that of composites, which suggests that the movement of the EPDM molecule was blocked by Al(OH)₃ fillers through Al(OH)₃/EPDM interfaces.

Dynamic mechanical property of composites at glassy state

Figure 3a and b shows the dynamic mechanical results of EPDM/Al(OH)₃ composites in the glassy state with different particle size and surface state and fixed volume fraction of 0.10. From Figure 3(a), it is clear that E' of composites is larger than that of pure EPDM, and E' of EPDM/Al(OH)₃ composites with smaller Al(OH)₃ particles ($1.25 \mu\text{m}$) is larger than that of larger Al(OH)₃ particles ($24.2 \mu\text{m}$). Larger E' can be induced by coupling-treated Al(OH)₃ fillers compared with non-coupling-treated samples. This result reveals that the EPDM matrix can be reinforced by Al(OH)₃ fillers.

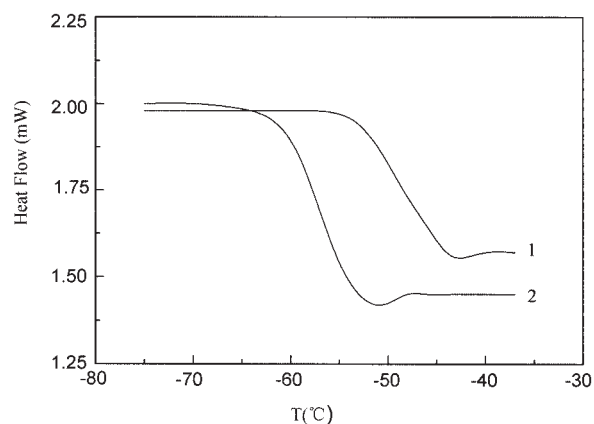


Figure 2 DSC thermograms of different samples: (1) composite; (2) pure EPDM.

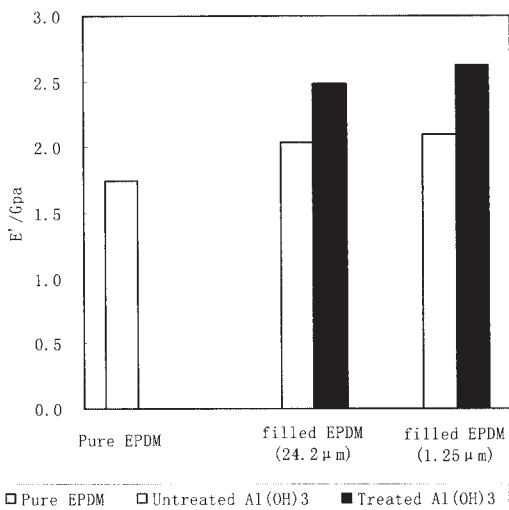
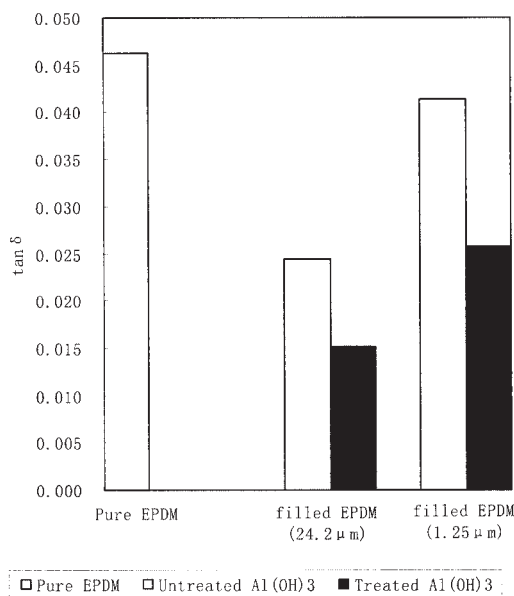
(a) E' of composites(b) $\tan \delta$ of composites

Figure 3 The dynamic mechanical results of EPDM/ $\text{Al}(\text{OH})_3$ composites at glassy state: (a) E' of composites; (b) $\tan \delta$ of composites.

Since smaller $\text{Al}(\text{OH})_3$ particles have larger specific surface area and consequently larger interface area, the E' of EPDM composites with smaller $\text{Al}(\text{OH})_3$ fillers (1.25 μm) is larger. Coupling-treated $\text{Al}(\text{OH})_3$ fillers leads to more uniform distribution of fillers in EPDM matrix as well as a stronger chemical bond between the $\text{Al}(\text{OH})_3$ phase and the EPDM phase, which can reinforce the interaction between two phases and reduce the interface defects; thus, E' of composites is largely increased. It can also be seen from Figure 3(b) that $\tan \delta$ of composites is smaller

than that of pure EPDM. This is because $\text{Al}(\text{OH})_3$ fillers reduce the effective volume of EPDM, which is the so-called "volume effect." It was reported that the volume effect gets stronger as the volume fraction of $\text{Al}(\text{OH})_3$ fillers increases.²² In addition, the mechanical loss of rigid $\text{Al}(\text{OH})_3$ fillers is much smaller than that of EPDM, which also contributes to the decrease of $\tan \delta$. To investigate the effect of surface state of $\text{Al}(\text{OH})_3$ fillers on dynamic mechanical property of EPDM/ $\text{Al}(\text{OH})_3$ composites, the interactional parameter (B) between two phases was calculated by applying eq. (1) proposed by Ziegel and colleagues^{23,24} to calculate the E' of a binary composite system composed of a continuous polymeric phase and distributed inorganic fillers phase,

$$B = \frac{E' - E'_0}{(E' + 1.5E'_0)V_f'} \quad (1)$$

where E' and E'_0 are storage modules of composites and polymeric matrix, respectively, V_f is the volume fraction of inorganic fillers; and B is the interactional parameter between two phases. B can be achieved when E' , E'_0 , and V_f are obtained. The calculated B of EPDM/ $\text{Al}(\text{OH})_3$ composites when the volume fraction of $\text{Al}(\text{OH})_3$ fillers is 0.1 is shown in Figure 4. The value of B gets larger when $\text{Al}(\text{OH})_3$ fillers are treated with coupling agent, which suggests that the interaction between the two phases is enhanced due to the chemical bond formed and changed interfacial structure.

Table III shows the T_g , peak value of $\tan \delta$ ($\tan \delta_{\max}$), the half-peak width (ΔW), and the apparent activation energy (ΔE) of composites with the volume fraction of 0.1 and different surface state of $\text{Al}(\text{OH})_3$ fillers. Compared with samples with untreated fillers, composites with coupling-treated fillers exhibit lower $\tan \delta_{\max}$, broader ΔW , and larger ΔE . This result further reveals that the surface state of fillers and inter-

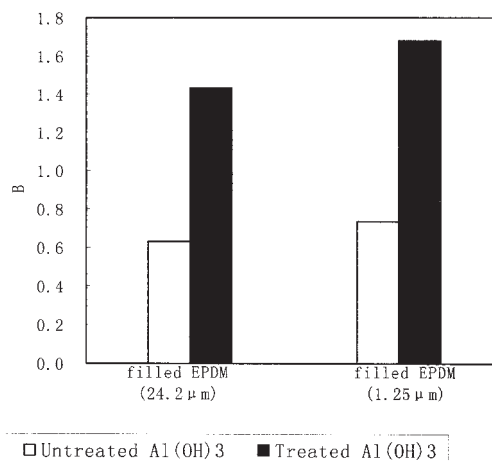


Figure 4 B of EPDM/ $\text{Al}(\text{OH})_3$ composites.

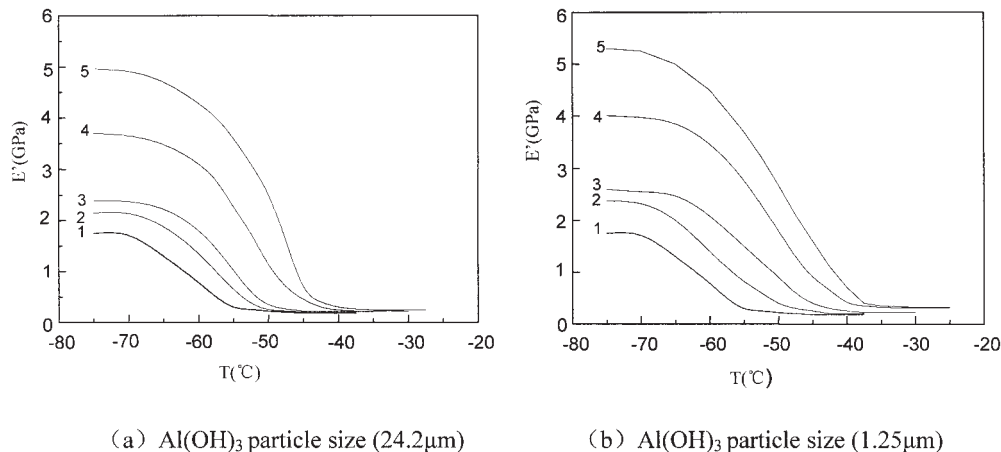
TABLE III
Comparison of Dynamic Mechanical Properties of EPDM/Al(OH)₃ Composites

Surface state of Al(OH) ₃ fillers	T_g (°C)	$\tan\delta_{\max}$	ΔW (°C)	ΔE (kJ · mol ⁻¹)
Pure EPDM	-49.5	1.46	8.8	64.8
Untreated Al(OH) ₃ fillers (24.2 μm)	-46.8	1.40	10.0	68.2
Treated Al(OH) ₃ fillers (24.2 μm)	-46.2	0.87	11.4	74.8
Untreated Al(OH) ₃ fillers (1.25 μm)	-45.7	1.38	11.2	71.5
Treated Al(OH) ₃ fillers (1.25 μm)	-45.3	0.81	14.6	76.7

facial structure can be improved; thus, the interface defects can be reduced and the local motion of EPDM molecule chains can be limited, as shown by the variation of $\tan\delta_{\max}$, ΔW , and ΔE .

Effect of the volume fraction and particle size of Al(OH)₃ fillers on E' and $\tan\delta$ of composites

Figure 5 (a, b) shows the effect of temperature on E' of EPDM/Al(OH)₃ composites with different volume fraction and particle size of Al(OH)₃ fillers, respectively. The results show that the initial glassy state E' of two composites increases with the volume fraction of Al(OH)₃ fillers. At the same temperature, E' of composites with 1.25 μm Al(OH)₃ fillers is larger than that of 24.2 μm Al(OH)₃ fillers. Under all conditions E' decreases with temperature in the range of -80–30 °C, which demonstrates that the addition of Al(OH)₃ fillers affects the glassy state module of composites as well as the glass transition process.

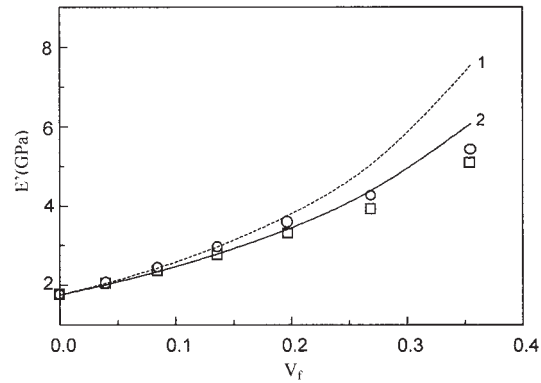


(a) Al(OH)₃ particle size (24.2 μm)

(b) Al(OH)₃ particle size (1.25 μm)

1-Pure EPDM, 2- $V_f=0.10$, 3- $V_f=0.14$, 4- $V_f=0.27$, 5- $V_f=0.36$

Figure 5 Effect of temperature and Al(OH)₃ particle size on E' of composites: (a) Al(OH)₃ particle size (24.2 μm); (b) Al(OH)₃ particle size (1.25 μm).



1- simulated curve ($B=1.6$), 2- simulated curve ($B=1.4$);

□- experimental results of Al(OH)₃ fillers(24.2 μm)

○- experimental results of Al(OH)₃ fillers(1.25 μm)

Figure 6 The simulated and experimental results of the $E'-V_f$ relation: (1) simulated curve ($B = 1.6$); (2) simulated curve ($B = 1.4$). □, Experimental results of Al(OH)₃ fillers (24.2 μm); ○, experimental results of Al(OH)₃ fillers(1.25 μm).

Based on eq. (1), the relation between E' and volume fraction (V_f) of composites at the glassy state was simulated. Figure 6 shows the simulated curve and experimental curve. The results show that when $V_f < 0.2$, two simulated curves fit with experiment and the values of B for Al(OH)₃ fillers (24.2 μm) and Al(OH)₃ particles (1.25 μm) are 1.4 and 1.6, respectively. However, when $V_f > 0.2$, the simulated curves are higher than experimental points, which shows weaker interaction and cohesion when additional inorganic fillers were added to the system.

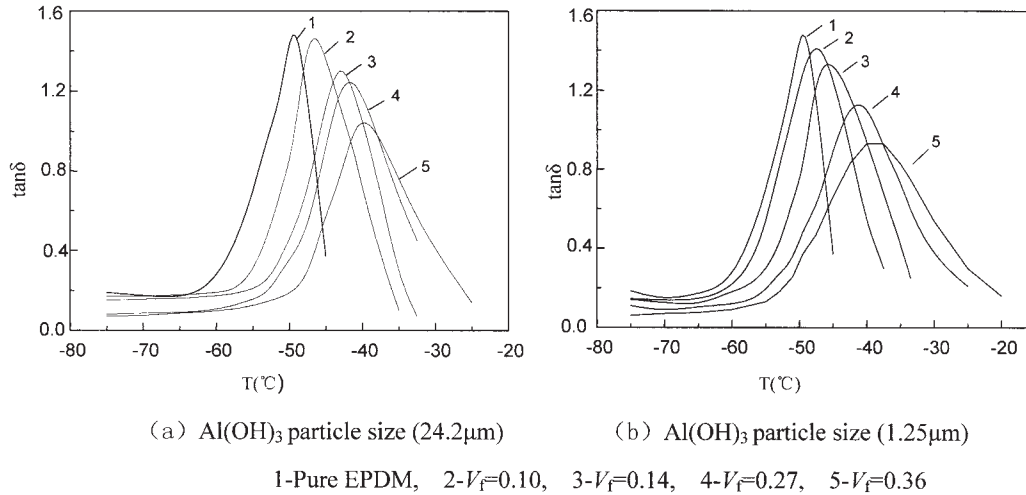


Figure 7 Effect of temperature and Al(OH)₃ particle size on tanδ of composites: (a) Al(OH)₃ particle size (24.2 μm); (b) Al(OH)₃ particle size (1.25 μm). (1) Pure EPDM; (2) $V_f = 0.10$; (3) $V_f = 0.14$; (4) $V_f = 0.27$; (5) $V_f = 0.36$.

Figure 7 (a, b) shows the effect of temperature on tanδ of EPDM/Al(OH)₃ composites with different volume fraction and particle size of Al(OH)₃ fillers, respectively. It is clear that, under both particle size conditions, with the increase of volume fraction of Al(OH)₃ fillers, the temperature corresponding to tanδ_{max} of composites shifts to higher temperature region, while tanδ_{max} is reduced and ΔW is broadened, as shown in Table IV. Such a novel phenomena of dynamic mechanical property of EPDM/Al(OH)₃ composites has not been reported before.

In the sense of molecular movement, the glass transition process of polymer is micro-Brownian movement of the noncrystalline segment in a noncrystalline or crystalline polymer, which is actually a relaxation transition and can be affected by many factors. It is suggested that Al(OH)₃ fillers block the micro-Brownian movement of EPDM molecular chains. This effect increases with the volume fraction of Al(OH)₃ fillers and leads to great variation of glass transition process, which is shown by the variation of interfacial activation energy.²⁵ It can also be seen from Figure 7 that, with the same Al(OH)₃ volume fraction, smaller Al(OH)₃ fillers lead to lower tanδ_{max}, broader ΔW, and higher tanδ_{max} temperature, which further proves that

the block of Al(OH)₃ particle to EPDM molecular movement is realized through interfaces.

New method of interfacial layer thickness calculation

It is suggested²⁶ that interfacial layer thickness closely relates to the variation of specific heat of polymeric glass transition, which can be shown as

$$\lambda = 1 - \frac{\Delta C_f}{\Delta C_0} \quad (2)$$

$$\frac{(R + \Delta R)^3}{R^3} - 1 = \frac{\lambda V_f}{1 - V_f'} \quad (3)$$

where λ is the weight constant of interface volume fraction; ΔC_f and ΔC₀ are the specific heat variation of composites with and without fillers, respectively; R is the radius of the filler particle; and ΔR is the interfacial layer thickness.

In the research of temperature dependence of damping voltage, which is proportional to tanδ, the values of two baselines besides the glass transition

TABLE IV
Comparison of Dynamic Mechanical Properties of EPDM/Al(OH)₃ Composites with Different Volume Fraction and Particle Size of Al(OH)₃ fillers

Volume fraction of Al(OH) ₃ fillers		0	0.10	0.14	0.27	0.36
Al(OH) ₃ fillers (24.2 μm)	T_g (°C)	-49.5	-46.8	-43.0	-41.8	-39.3
	tanδ _{max}	1.46	1.40	1.30	1.24	1.02
	ΔW (°C)	8.8	10.0	10.6	12.3	13.7
Al(OH) ₃ fillers (1.25 μm)	T_g (°C)	-49.5	-45.7	-45.0	-41.3	-38.2
	tanδ _{max}	1.46	1.38	1.28	1.13	0.93
	ΔW (°C)	8.8	11.2	12.1	14.5	18.8

peak are quite different. It is suggested here that the interfacial layer thickness can be calculated by the baseline difference. It is supposed that: (1) fillers are uniformly distributed in the polymer in the form of spheres; (2) fillers are separated and the interaction can be ignored.

For DMA analysis, eq. (4) can be achieved, provided eq. (2) is considered as a reference,

$$\lambda_v = 1 - \frac{\Delta U_f}{\Delta U_0}, \quad (4)$$

where λ_v is the area constant of the interfacial layer volume fraction; ΔU_f and ΔU_0 are the baseline difference of composites with and without fillers, respectively, which relate to the cross section (A) of samples, that is, $\Delta U = (U_1 - U_2)/A$; U_1 and U_2 can be obtained by the method shown in Figure 8.

The interfacial layer thickness can be calculated if λ_v achieved by eq. (4) is put into eq. (3). The calculating results of interfacial layer thickness of EPDM/Al(OH)₃ composites are shown in Table V (five specimens for each species and the measurement error of ΔU_f and ΔU_0 is $\pm 5\%$); the volume fraction and particle size of Al(OH)₃ fillers is 0.1 and 24.2 μm , respectively. The interfacial layer thickness of coupling-treated composites is larger than that of non-treated ones, which is in accordance with the rule of interfaced layer thickness of epoxy composites filled with Fe fillers or glass fibers.^{26,27} The values of interfacial layer thickness are also in the same magnitude as shown in Refs. 26,27. It is proposed that there are two types of active groups in silicone coupling agent. When Al(OH)₃ fillers were treated by the coupling agent, one active group will react with Al(OH)₃ fillers. After being put into EPDM, another active group will react with EPDM, and then a special wider interfacial layer structure can be formed in the process of crosslink. As a result, interfacial layer thickness of coupling-treated

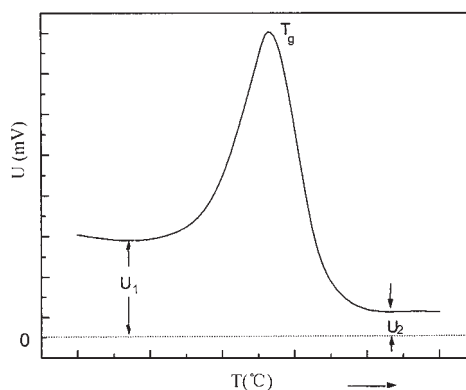


Figure 8 DMA curve applied to calculate interfacial layer thickness.

TABLE V
The Calculating Results of Interfacial Layer Thickness of Composites

Filler conditions	ΔU_f ($\text{V} \cdot \text{m}^{-2}$)	λ_v	$\Delta R(\text{nm})$
Untreated Al(OH) ₃ fillers	748	0.345	126.7
Treated Al(OH) ₃ fillers	676	0.408	149.5

composites is larger than that of coupling -untreated ones.

CONCLUSIONS

(1) With the increased volume fraction of Al(OH)₃ fillers, the temperature corresponding to $\tan\delta_{\max}$ of the composites increases, while the peak value is lowered and the width of half peak is increased. When the volume fraction of Al(OH)₃ fillers is fixed to 0.1, the particle size has a great effect on dynamic mechanical properties of composites.

(2) The interfacial structural parameters of EPDM/Al(OH)₃ composites can be greatly affected by the surface state of Al(OH)₃ fillers. Coupling-treated Al(OH)₃ fillers are helpful to improve interfaced structure, reduce interfacial defects, improve dynamic mechanical property of composites, and greatly enhance interaction between two phases. Thus, lower $\tan\delta_{\max}$ and larger ΔW and ΔE of glass transition can be achieved.

(3) The interfacial layer thickness of composites can be calculated by the DMA technique, which is regarded as an effective method.

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