

# Viscoelastic Properties and Characterization of Inorganic Particulate-Filled Polymer Composites

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**ABSTRACT:** To identify effects of glass bead (GB) content on the dynamic mechanical properties of filled low-density-polyethylene (LDPE) composites, the storage modulus, loss modulus, glass transition temperature, and mechanical damping of these composites were measured using a Du Pont dynamical mechanical analysis instrument in temperature range from  $-150$  to  $100^{\circ}\text{C}$ . It was found that the storage modulus increased nonlinearly with an increase of the GB volume fraction. On the basis of Eshelby's method and Mori's work, an equation describing the relationship between the relative storage modulus ( $E'_R$ ) and filler volume fraction for polymeric composites was

proposed, and the  $E'_R$  of LDPE/GB composites were estimated by means of this equation at temperatures of  $-25$ ,  $0$ , and  $25^{\circ}\text{C}$ , and the calculations were compared with the experimental data, good agreement was showed between the predictions and the measured data. Furthermore, this equation was verified by the experimental from  $\text{Al}(\text{OH})_3$  filled EPDM composites at glassy state reported in a reference. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 3955–3960, 2009

**Key words:** polymer composite; dynamic mechanical properties; characterization

## INTRODUCTION

Dynamic mechanical properties are important parameters for characterization of processing and use properties of polymeric materials. For polymer blends or polymer composites filled with inorganic particles, the relationship between structure and properties tends toward more complexity owing to the formation of an interface between components and between the fillers and matrix. The dynamic mechanical parameters of polymer materials, such as storage modulus, loss modulus, and mechanical damping, may be measured using a dynamic mechanical analysis instrument. In addition, dynamic mechanical measurements over a range of temperatures provide valuable insight into the structure, morphology, and properties of polymeric blends and composites. A lot of dynamic mechanical analyses on polymeric blends and composites have been done.<sup>1–4</sup> Zhang et al.<sup>1</sup> measured dynamic mechanical properties of composites filled with styrene-maleic-anhydride copolymer (SMA) particles and short fibers and found that the storage modulus reaches the maximum at the SMA phase transformation temperature of approximate  $120^{\circ}\text{C}$ . Goyal et al.<sup>2</sup>

measured the dynamic mechanical properties of  $\text{Al}_2\text{O}_3$ /poly(ether ether ketone) composites and observed that the storage modulus of the composites increased nonlinearly with an addition of the volume fraction of  $\text{Al}_2\text{O}_3$ , especially at lower temperature. Goyanes et al.<sup>3</sup> made dynamic mechanical analysis of quartz particulate-filled epoxy resin. Similarly, the storage modulus increased nonlinearly with increasing the volume fraction of quartz powder. Wang and Zhao<sup>4</sup> studied the model and characterization of viscoelasticity of polyisoprene/ $\text{SiO}_2$  nanocomposite films under constant and fatigue loading. When stresses were fixed, the elastic modulus increased with an increase of the weight fraction of  $\text{SiO}_2$  particles. Since 1998, Liang et al.<sup>5–7</sup> have investigated the effects of glass bead content and size on the dynamic mechanical properties of filled polyolefin composites and got some useful findings.

Storage modulus is an important characterization of dynamic mechanical properties of polymeric materials. For particulate filled composites, a number of equations for prediction of the modulus have been derived with different methods. Among these methods, Eshelby's equivalent inclusion method is more noticeable, which is a method to analyze average stress field distribution in the case of only an inclusion an infinite body.<sup>8</sup> It is necessary to modify Eshelby's method in the case of existence of a lot of inclusions and their interaction. Mori and Tanaka<sup>9</sup> proposed a modification method in order that the

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method was available for the case of containing a number of elliptic sphere inclusions. Taya and Chou<sup>10</sup> further developed Mori-Tanaka method and presented a model including several types of inclusions. To calculate the elastic modulus, Benveniste<sup>11</sup> proposed an equation group based on the modified Mori-Tanaka method.

The objectives of this article are to propose a new quantitative characterization of storage modulus for polymer composites filled with inorganic particles, based on the previous work stated earlier, and verify it by using the measured data of the dynamic mechanical properties of glass bead-filled low-density polyethylene composites, and the relative storage modulus of EPDM/Al(OH)<sub>3</sub> composites at glassy state reported in literature.

## THEORIES

### Factors affecting storage modulus

Storage modulus is an important index for measuring the stiffness and elasticity of polymeric materials, and it has been paid extensively attention by researchers. So far, a number of quantitative descriptions on the relationship between the storage modulus and filler content and other parameters for polymeric materials have been presented.<sup>8-16</sup> For polymer composites, relative storage modulus ( $E'_R$ ) is usually used to characterize the relationship between storage modulus and other parameters, which is defined by

$$E'_R = E'_c/E'_m \quad (1)$$

where  $E'_c$  and  $E'_m$  are the storage modulus of composite and matrix resin, respectively.

For a given matrix resin, the major factors affecting  $E'_R$  of composite are filler content, geometry, size and its distribution, the distribution and dispersion status of the inclusions in the matrix resin, and the interfacial morphology between them. That is

$$E'_R = f(\phi_f, d, \xi, \dots) \quad (2)$$

where  $\phi_f$  is the filler volume fraction,  $d$  is the particle diameter, and  $\xi$  is the parameter related to the dispersion of the particles in matrix and interfacial adhesion strength.

### Quantitative description of storage modulus

For a random distribution of spherical particles in matrix, if there is no interfacial slide, then  $E'_R$  may be described with the famous Einstein equation:<sup>12</sup>

$$E'_R = 1 + 2.5\phi_f \quad (3)$$

Guth<sup>12,13</sup> generalized the Einstein equation concept by introducing a particle interaction term and proposed a following equation for spherical particles:

$$E'_R = 1 + 2.5\phi_f + 14.1\phi_f^2 \quad (4)$$

Halpin and Tsai<sup>14</sup> derived a simple and generalized equation to approximate the results of more exact micromechanics:

$$E'_R = \frac{1 + \zeta\eta\phi_f}{1 - \eta\phi_f} \quad (5)$$

and

$$\eta = \frac{m - 1}{m + \zeta} \quad (6)$$

where  $\zeta$  is a measure of reinforcement, and it depends on filler geometry, packing geometry, and loading conditions. For spherical particles,  $\zeta = 2$ .  $m = E_f/E_m$ ,  $E_m$  and  $E_f$  are the matrix resin and filler particle modulus, respectively. Nielsen<sup>15</sup> introduced a parameter of maximum particle pile density and proposed a generalized equation based on Halpin-Tsai equation.

On the basis of Eshelby's method<sup>8</sup> and Mori's work,<sup>9</sup> an equation for describing the relationship between relative storage modulus and particulate volume fraction and other parameters of filled polymer composites may be proposed as follows<sup>16</sup>:

$$E'_R = 1 + \frac{\zeta\phi_f(m - 1)}{1 + (1 - \phi_f)(m - 1)\lambda} \quad (7)$$

And

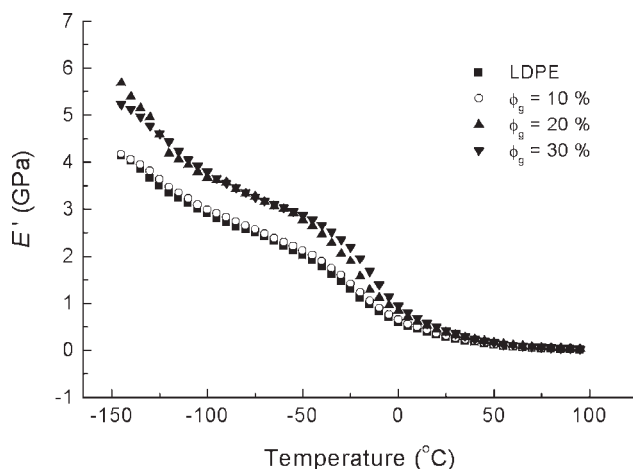
$$\lambda = \frac{7 - 5\nu_m}{15(1 - \nu_m)} \quad (8)$$

where  $m = E_f/E_m$ ,  $E_m$  and  $E_f$  are the matrix resin and filler particle modulus, respectively.  $\nu_m$  is the matrix resin Poisson ratio.

## EXPERIMENTAL

### Raw materials

A matrix resin used in this experimental was a low-density-polyethylene with trade-mark of LDPE G812 (Polyolefin, Singapore). The resin melt flow index and density were 35 g/10 min and 0.917 g/cm<sup>3</sup>, respectively. The melting temperature was 106°C.



**Figure 1** Dependence of storage modulus on temperatures of LDPE/GB composites.

A kind of solid glass bead (GB2227) with trade mark of Spheriglass<sup>®</sup> was used as filler in this test and supplied by Potters Industry Inc., USA. The GB density and mean diameter were  $2.5\text{g/cm}^3$  and  $114\ \mu\text{m}$ , respectively. The GB surface was pretreated with a silane coupling agent (CP-01) by the supplier.

### Specimen fabrication

The LDPE and glass beads were blended in a twin-screw extruder (Brabender, Plasticorder PL 2000, Germany) after simply mixing to produce the composites. The blending ratios (weight fraction) of LDPE/GB were 90/10, 80/20, and 70/30. The extrusion temperature varied from  $160$  to  $180^\circ\text{C}$ . The specimens for dynamical testing were molded with an injection machine, with width, thickness, and length of  $12.9$ ,  $3.2$ , and  $55\ \text{mm}$ , respectively. The injection temperature was from  $180$  to  $200^\circ\text{C}$ .

### Apparatus and methods

The viscoelasticity property measurements of the LDPE/GB composites were conducted using a dynamical mechanical analyzer (DMA 983, Du Pont Instruments, USA). The test temperatures varied from  $-150$  to  $100^\circ\text{C}$ , and the temperatures were increased at  $5^\circ\text{C}$  per minute. The both ends of the sample were clamped, and the center was subjected with a load. The fixed frequency was  $1\ \text{Hz}$ , and the amplitude was  $0.6\ \text{mm}$ . Three test were conducted and the average was reported for each composition.

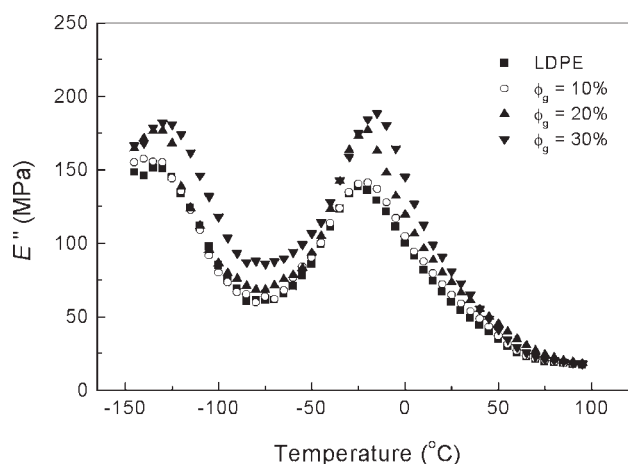
## RESULTS AND DISCUSSION

### Dependence of dynamic mechanical properties on temperatures

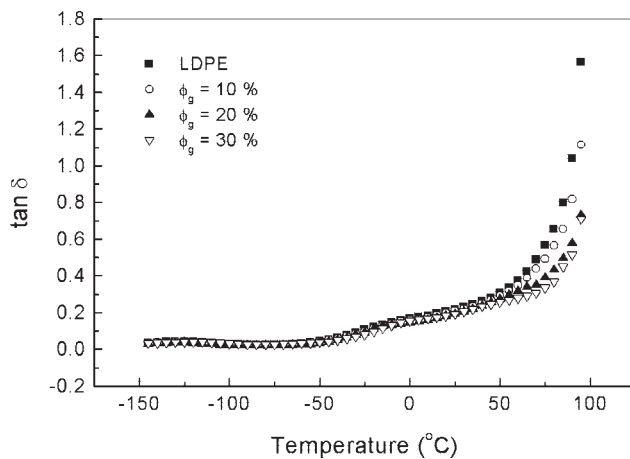
Figure 1 shows the dependence of the storage modulus ( $E'$ ) on temperatures of LDPE/GB compos-

ite systems. When temperature is within  $-50$  to  $0^\circ\text{C}$ ,  $E'$  decreases rapidly, and then it decreases gently in other temperature range with a rise of temperatures in a case of higher filler concentration. This changing point for reducing from gently to rapidly is called as turning point, the sensitivity of storage modulus of materials to temperature will be quite obvious in this case. It may be found with further observation that the turning point of storage modulus-temperature curves is about  $-25^\circ\text{C}$  for the neat LDPE resin, whereas the turning points of storage modulus-temperature curves are from  $-20^\circ\text{C}$  to  $-15^\circ\text{C}$  for the composite systems, and the location of the turning points moves toward to the right of the abscissa with an increase of the GB weight fraction. It can also be seen from Figure 1 that when temperature is fixed  $E'$  changes somewhat with variation of the glass bead content, and the difference in  $E'$  between neighbor composite systems increases with a reduction of temperatures.

Figure 2 displays the dependence of the loss modulus ( $E''$ ) on temperatures of LDPE/GB composite systems. In a range of  $-125$  to  $-75^\circ\text{C}$ , the  $E''$  decreases, whereas increases in a range from  $-75$  to  $25^\circ\text{C}$  and then decreases with a rise of temperature. There is a peak around  $-25^\circ\text{C}$  in the loss modulus-temperature curves for the neat LDPE resin or the composites. Similarly, the location of the peaks for the composites moves toward to the right of the abscissa with an increase of the GB weight fraction. In addition, the location and size of these peaks vary slightly with the glass bead content. It can also be observed from Figures 1 and 2 that the location of the turning point in storage modulus-temperature curve is roughly the same as the position of the peak in loss modulus-temperature curves for the neat LDPE resin and the LDPE/GB composites. In general, the temperature at this place is determined as glass transition temperature in this case. This



**Figure 2** Dependence of loss modulus on temperatures of LDPE/GB composites.



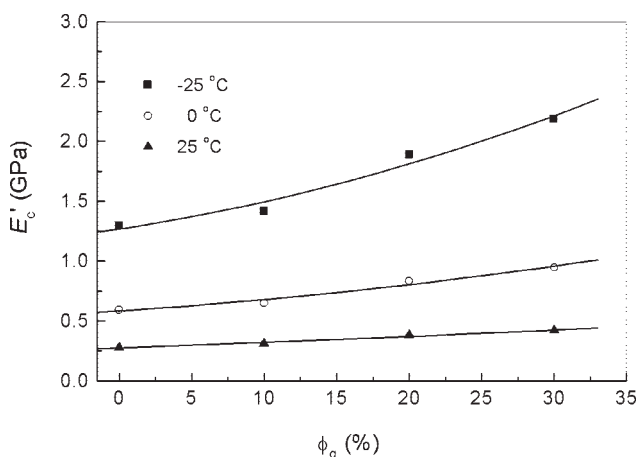
**Figure 3** Dependence mechanical damping on temperatures of LDPE/GB composites.

indicates that the glass transition temperature of these composite systems is affected somewhat by the filler content.

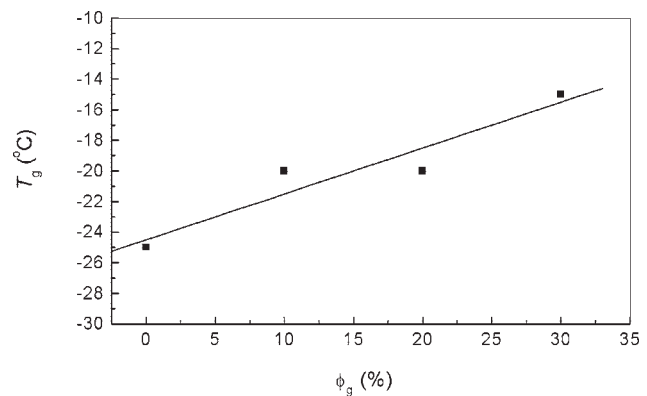
Mechanical damping ( $\tan \delta$ ) is an important parameter for characterizing the viscoelasticity of polymeric materials, which is defined by

$$\tan \delta = \frac{E''}{E'} \quad (9)$$

Figure 3 shows the dependence of mechanical damping on temperatures for LDPE/GB composites. It can be seen that the  $\tan \delta$  increases gently with a rise of temperature when temperature is lower than 75°C, and then it increases rapidly. This is because the movement of molecular chains of the matrix resin increases with a rise in temperature, leading to reduction of the storage and loss moduli correspondingly. When temperature is higher than 50°C, the  $E'$  decreases faster than the  $E''$  for these compos-



**Figure 4** Relationship between storage modulus and glass bead weight fraction of LDPE/GB composites.



**Figure 5** Relationship between glass transition temperature and glass bead weight fraction of LDPE/GB composites.

ite systems (Figures 1 and 2), resulting in rapidly increasing the  $\tan \delta$ .

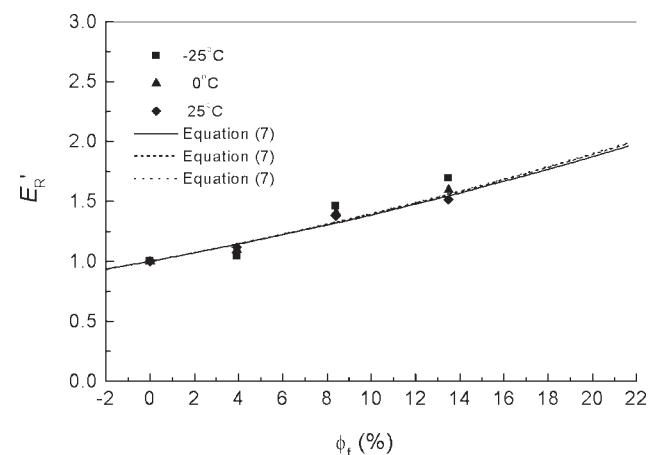
For a polymer composite filled with inorganic particles, a relationship between mechanical damping and filler volume fraction may be expressed as follows<sup>17</sup>:

$$\tan \delta_c = \frac{\tan \delta_m}{1 + 1.5B\phi_f} \quad (10)$$

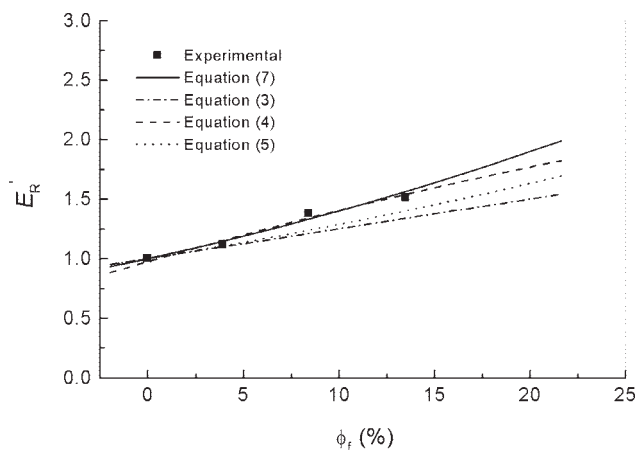
where  $B$  is the parameter between two phases,  $\tan \delta_c$  and  $\tan \delta_m$  are the mechanical damping of composite and matrix, respectively.

#### Relationship between storage modulus and GB content

It can be seen from Figures 1 and 2 that the storage modulus of the composites reduces quickly with a rise of temperature within  $-25$  to  $25$ °C, and the glass transition temperature is around  $25$ °C. Therefore, It is



**Figure 6** Comparison between predictions and measured data of relative storage modulus for LDPE/GB composites at different temperature.



**Figure 7** Comparison between estimations of relative storage modulus of LDPE/GB composites at 25°C by means of various equations.

beneficial to investigate the influence of temperature on the storage modulus by comparing the storage modulus of the composites at -25°C, 0°C and 25°C. In addition, polymeric materials are usually used in a temperature range from -25 to 25°C. Thus, it is meaningful in practice for studying the dynamical properties of polymeric materials in this temperature scope. Figure 4 illustrates the relationship between the storage modulus ( $E'_c$ ) of the LDPE/GB composites and the glass bead weight fraction ( $\phi_g$ ) as temperatures are -25, 0, and 25°C, respectively. It may be seen that the  $E'_c$  increases nonlinearly with an increase of  $\phi_g$  when the test temperature is constant.

When inorganic particles are blended into a matrix resin, they play a role of framework in polymeric composite because their stiffness is much greater than that of the matrix, and they will block the movement of the molecular chains of the matrix resin, leading to increase the stiffness of filled polymer composite materials. Therefore, if the distribution or dispersion of the inclusions in the matrix is uniform, the more the inorganic particles in the matrix, the higher the stiffness of polymeric composites is. In this case, the storage moduli of polymer composites will increase with an increase of the filler particles (Fig. 4). In the previous work, the authors<sup>18</sup> observed the tensile specimen fracture morphology of LDPE/GB composites and found that the distribution or dispersion of the inclusions in the matrix is roughly uniform.

**Relationship between glass transition temperature and GB content**

Glass transition temperature ( $T_g$ ) is defined as the critical temperature of beginning movement of molecular chains from freezing state, it is an important parameter for characterizing heat-proof property of polymeric materials. Figure 5 displays the relationship between glass transition temperature and glass bead weight fraction of the LDPE/GB composites. It can be seen that the  $T_g$  increases approximately linearly with an increase of  $\phi$ , that is

$$T_g = \alpha + \beta\phi_g \tag{11}$$

where  $\alpha$  and  $\beta$  are the parameters related to the viscoelasticity of polymeric materials. The values of  $\alpha$  and  $\beta$  may be determined by using a linear regression analysis method. According to the experimental results of the LDPE/GB composites shown in Figure 5, the  $\alpha$  and  $\beta$  are respectively -24.5 and 0.3°C, and the regression coefficient is about 0.95. It should be noted that  $T_g$  can also be determined by means of a differential scanning calorimeter (DSC).

**Comparison between predictions and measured data of  $E'_R$**

Figure 6 shows the relationship between the relative storage modulus and the glass bead volume fraction of the LDPE/GB composites as temperatures are -25, 0, and 25°C, respectively. Similarly, the  $E'_R$  increases nonlinearly with an addition of  $\phi_f$ . The values of the  $E'_R$  are estimated by using of eq. (7) under these test conditions, and the results are also showed in Figure 6. where  $v_m = 0.38$ ,  $E_f = 68.95\text{GPa}$ . The results illustrate good agreement between the predictions and the experimental measurements of  $E'_R$ . For inorganic particles, a relationship between weight fraction and volume fraction is given by<sup>19</sup>:

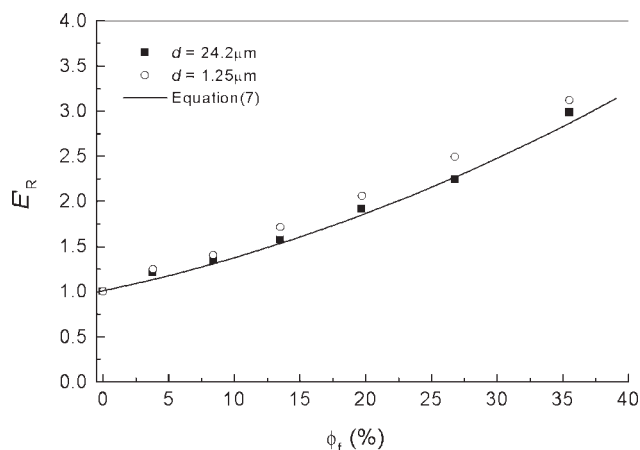
$$\phi_g = \frac{\phi_f\chi}{1 - \phi_f + \phi_f\chi} \tag{12}$$

where  $\chi = \rho_f/\rho_m$  and  $\rho_f$  and  $\rho_m$  are the density of the filler and matrix resin, respectively.

In addition, the values of the  $E'_R$  are also calculated by using Einstein equation, Guth equation, and Halpin-Tsai equation under these test conditions, and the results are as showed in Figure 7. It can be

**TABLE I**  
Measured Storage Modulus of EPDM/Al(OH)<sub>3</sub> Composites at Glassy State<sup>20</sup>

$\phi_f$ (%)	0	3.8	8.4	13.5	19.7	26.8	35.5
$E'_c$ (GPa) ( $d = 1.25 \mu\text{m}$ )	1.75	2.18	2.46	3.00	3.60	4.36	5.46
$E'_c$ (GPa) ( $d = 24.20 \mu\text{m}$ )	1.75	2.11	2.35	2.75	3.35	3.92	5.21



**Figure 8** Comparison between predictions and measured data of relative storage modulus of EPDM/Al(OH)<sub>3</sub> composites at glassy state.

seen that the predictions of  $E'_R$  by application of eq. (7) are closer to the measured data from the experiments of these composites than those by the other equations when temperature is 25°C.

Gao et al.<sup>20</sup> measured the dynamic mechanical properties of Al(OH)<sub>3</sub> filled ethylene-propylene-diene mischpolymer (EPDM) composites and found that the effects of the volume fraction and particle diameter of Al(OH)<sub>3</sub> on the dynamic mechanical properties of the composite systems were significant. Table I lists the measured data of the storage modulus of the composites at glassy state. It can be seen that  $E'_c$  increases with an increase of  $\phi_f$ , whereas decreases with an increase of the particle diameter ( $d$ ).

Similarly, the values of the  $E'_R$  of the EPDM/Al(OH)<sub>3</sub> composites at glassy state are estimated by using of eq. (7), and the predictions are compared with the measured data, the results are also showed in Figure 8, where  $v_m = 0.38$ ,  $E_f = 71.70$  GPa. The results illustrate good agreement between the predictions and the experimental measurements of  $E'_R$ , as listed in Table I.

## CONCLUSIONS

The storage modulus of LDPE/GB composites decreased with a rise of temperatures when the GB content was constant, and some turning points of storage modulus-temperature curves were about -25°C, and moved toward to the right of the abscissa with an increase of the GB weight fraction.

The glass transition temperature of these filled systems increased approximately linearly with an

increase of the GB weight fraction, and the storage modulus of the composites increased nonlinearly with an increase of the GB volume fraction under given experimental conditions.

Equation (7) describes a relationship between the relative storage modulus and particulate volume fraction and other parameters of filled polymer composites. The  $E'_R$  of LDPE/GB composites at 25°C was estimated by using eq. (7), and the estimations were compared with the calculations of Einstein equation, Guth equation, and Halpin-Tsai equation, respectively. The results showed that the predictions of the relative storage modulus by means of eq. (7) were relatively closer to the measured data from the experiments of the composites.

Furthermore, eq. (7) was verified by using the measured data of the relative storage modulus of EPDM/Al(OH)<sub>3</sub> composites at glassy state reported in literature. Good agreement was showed between the estimations and the experimental data of the  $E'_R$ .

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