

Glass-Transition Behavior of Particle Composites Modeled on the Concept of Interphase

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Synopsis

The thermomechanical behavior of particle composites was investigated in their transition region. In particular, the value of the glass-transition temperature T_g , which constitutes an upper limit for the structurally important glassy region, was examined. According to experimental evidence existing in the literature the introduction of a reinforcing filler in a polymeric matrix causes T_g of the latter to increase, unless mechanical imperfections counterbalance the reinforcing effect or even produce a T_g for the composite which is lower than that of the matrix. Based on mechanical theories, valid for the mechanical moduli of viscoelastic particle composites, a model was introduced that explains why the glass transition of composite materials may be reduced in some cases, whereas it may be increased in others. The concept of interphase between inclusions and matrix was used for the development of the model. Interphase is assumed to be a region, which is created between the matrix material and the filler particles, both considered as homogeneous and isotropic, whose thermomechanical properties and volume fraction may be determined from the overall thermomechanical behavior of the composite.

INTRODUCTION

The glassy region of polymeric composites is structurally important for the material because, in this region, the material behaves almost elastically and possesses satisfactory mechanical properties. Therefore, its upper limit in a temperature scale, defined by the *second*, or *glass*, or *β -transition temperature*, T_g , is of practical interest. Glass-transition temperature T_g is a sensitive parameter with respect to every aspect of the material microstructure, or any factor related to the external conditions, or the loading mode. For example, with epoxy polymer matrices the following characteristics influence the behavior of the composite: the molecular structure of the prepolymer,¹ the molecular structure of the curing agent,² the percentage of the curing agent in relation with the stoichiometric amount,³ or the composition of the curing agent, if it is a mixture of more than one reactants,⁴ and, finally, the heat treatment, i.e., the postcuring time and temperature. Moreover, mechanical imperfections, such as voids, flaws, or microcracks in the matrix, as well as the load history of the material are expected to influence T_g considerably. There are now many experimental data showing the changes in T_g of a polymer under the influence of the surface of a filler.⁵ These data have been obtained by applying various methods, i.e., dilatometric, dynamic measurements of the mechanical properties or specific heat, NMR, dielectric relaxation, radiothermoluminescence, etc. Since each of these methods has its own particular limitations, the results obtained are not always mutually comparable, while the general character of change in T_g with rise in filler concentration is maintained, the rate of change is nonidentical. This rate

of change presents a maximum when low-frequency methods (dilatometry or calorimetry) are used. As the frequency of the action is raised, ΔT_g decreases.

In Ref. 6 an extensive experimental study was carried out on an epoxy matrix in which various fillers, such as different types of glass microspheres and fibers, were embedded. It was found that, in all occasions, T_g was increasing with the amount of filler at least, up to a certain extent. Similar behavior was observed with the rubber-carbon black systems⁷⁻¹⁰ in which the rubber molecules are attached to the filler particles by strong forces approaching the nature of chemical bonds.¹¹

According to the results of Ref. 12, the rise of T_g with any particular filler content depends on the total surface of the filler and the conditions of formation of the contact of filler with polymer. A contradicting result, however, has appeared in Refs. 13 and 14, concerning a DGEBA resin, cured with 8 phr triethylene-tetramine and filled either with aluminum particles or three different particle sizes of iron powders. The samples of these composites were tested by means of flexural vibrations or examined in a thermomechanical analyzer. As may be seen from Figures 10-12 in Ref. 14, the glass-transition temperature T_g in all cases was found to be considerably lower for the composite than for the respective matrix. As a rule, T_g was now found to be decreasing with increasing particle size, while no similar behavior was observed with the storage moduli and the loss factors of the composite. Reduced T_g was also found by Molotkov et al.¹⁵ for resin matrices, filled with finely cut fiber glass and aluminum particles.

By introducing in the cases of composites the concept of interphase, it is possible to explain this contradicting behavior of the composite materials, as far as it concerns the glass-transition behavior. The interphase, having different thermomechanical and viscoelastic properties than the polymeric matrix, considerably affects the respective behavior of the composite. Based on some simplifying assumptions, a theoretical estimate of the variations of glass transition was attempted, which actually proved the important role of interphase on the properties of the composite material.

REPRESENTATION OF THE MODEL

The model, introduced in this paper, is based on the mechanical behavior of the particle composite materials. This behavior has already represented in a previous paper.¹⁶ However, for the better understanding of the analysis a brief discussion will be attempted here. First of all, it should be clarified that the composite material was treated as a three-phase material in which the three distinct regions are as follows. The first region is the polymeric matrix, which is considered as viscoelastic, and is characterized by its modulus of elasticity E_m . The second region is occupied by the dispersed particles, which constitute the inclusions or fillers and have a modulus of elasticity E_f .

A third phase is created around the fillers and is constituted from macromolecules of the polymer with different physical and physicochemical properties than the macromolecules of the polymeric matrix. In some cases these molecules create strong bonds with the particles of fillers and this fact is described by a large value of the adhesion coefficient, expressing the adhesion efficiency between the

polymeric matrix and the filler. In other cases, however, the bonds between filler and matrix are weak, and this corresponds to a low value of the adhesion coefficient K .

This phenomenon can be explained by an adsorption interaction between the matrix material close to the fillers and the filler particles, as well as by the mechanical imperfections such as voids, cracks, flaws, field singularities, and positions of imperfect adhesion which are concentrated in a thin layer around each inclusion. Moreover, this interphase layer contains the zones where shrinkage stresses are developed during the curing process, which are in many cases the main cause of the above-mentioned anomalies.¹⁷⁻¹⁹

The intermediate phase, or interphase, is considered as consisting of a homogeneous and isotropic material of finite thickness, with a different modulus of elasticity E_i than the two other moduli. The representative volume element of this model is constituted from three separate regions with the respective V_m, V_f, V_i volume fractions of the three phases, i.e., the matrix, the filler, and the interphase. According to the analysis of Ref. 16 a simple relationship was established connecting the moduli of elasticity of the composite material to the particular moduli of the phases, which has the form:

$$E = E_f V_f K + E_m V_m + E_i V_i \quad (1)$$

This equation constitutes a generalized form of the well-known law of mixtures for a composite material with three phases.

The simplifications which were made for establishing this relation cancel out all secondary effect terms, containing Poisson's ratios for each phase. However, the contribution of the interphase to the modulus of the composite was retained through the term $E_i V_i$, since it was assumed that this contribution always plays a significant role in the definition of the transition region of the composite. Now by applying the correspondence principle of linear viscoelasticity and starting from eq. (1) we may obtain an expression for the loss factor of the composite material $\eta(\omega)$, which depends on the frequency ω of the applied vibrational load. The loss factor is a convenient parameter for the determination of T_g , since its maximum value corresponds to the center of the transition region and expresses the amount of energy dissipated as a fraction of the energy stored in the system. At the transition frequency ω_g the loss factor assumes its maximum value, hence it is valid that:

$$\left. \frac{\partial \eta(\omega)}{\partial \omega} \right|_{\omega=\omega_g} = 0 \quad (2)$$

We denote by E_m'', E_m' the loss and the storage moduli of the matrix, E_i'', E_i' the loss and the storage moduli of the interphase, η_m, η_i the loss factors of the matrix and interphase, respectively. In applying the correspondence principle to eq. (1) use will be made of the following expressions:

$$E_m = E_m'(\omega) + iE_m''(\omega) = E_m'[1 + i\eta_m(\omega)], \quad \eta_m(\omega) = E_m''(\omega)/E_m'(\omega)$$

$$E_i = E_i'(\omega) + iE_i''(\omega) = E_i'[1 + i\eta_i(\omega)], \quad \eta_i(\omega) = E_i''(\omega)/E_i'(\omega) \quad (3)$$

Equation (3) lead to the expression for the loss factor $\eta(\omega)$ of the composite given by:

$$\eta(\omega) = \frac{E_m''(\omega)\eta_m(\omega)V_m + E_i''(\omega)\eta_i(\omega)V_i}{E_m'(\omega)V_m + E_f V_f K + E_i'(\omega)V_i} \quad (4)$$

If ω_g, ω_{gm} represent the transition frequencies of the composite material and the matrix, respectively, the relative magnitude of these quantities may define any relation between the glass-transition temperatures of the matrix T_{gm} and of the composite T_g . Indeed, if $\omega_g \cong \omega_{gm}$, then $T_g \cong T_{gm}$ and inversely, if $\omega_g > \omega_{gm}$, then $T_g < T_{gm}$. This result is based on the fact that the loss factor takes its peak value in the middle of the transition zone, where the glass transition is defined. In the same area the creep compliance master curves acquire their maximum slope.

The relative position of the transition frequencies ω_g and ω_{gm} could now be determined by finding the derivative $\partial\eta(\omega)/\partial\omega$ and defining its value at $\omega = \omega_{gm}$. Then, if this value is negative, it is valid that $\omega_g < \omega_{gm}$, because in this case the loss factor $\eta(\omega)$ has already reached its maximum value. Inversely, if $[\partial\eta(\omega)/\partial\omega]_{\omega=\omega_{gm}} > 0$, then the loss factor $\eta(\omega)$ will still be in the zone where its value is increasing and so it will take its peak value at $\omega_g > \omega_{gm}$. The two cases of relative values of the loss factor are schematically presented in Figure 1.

Now following this reasoning we define the derivative of eq. (4) and we have

$$\frac{\partial\eta(\omega)}{\partial\omega} \Big|_{\omega=\omega_{gm}} = \left[\left(-\frac{\partial E'_m}{\partial\omega} \right) \eta_m V_m E_f V_f K + \left(\frac{\partial\eta_i}{\partial\omega} \right) E' E'_i V_i + \left(\frac{\partial E'_i}{\partial\omega} \right) \eta_i E_f V_i V_f K - \Delta E \right] [(E')^2]^{-1} \quad (5)$$

where

$$E' = E'_m(\omega) V_m + E'_i(\omega) V_i + E_f V_f K \quad (6)$$

$$\Delta E = \left(\frac{\partial E'_m}{\partial\omega} E_i - \frac{\partial E'_i}{\partial\omega} E'_m \right) (\eta_i - \eta_m) V_m V_i \quad (7)$$

and

$$\frac{\partial\eta_m(\omega)}{\partial\omega} \Big|_{\omega=\omega_{gm}} = 0 \quad (8)$$

In the above expression [eq. (5)] the quantities $(\partial E'_m/\partial\omega)_{\omega=\omega_{gm}}$ and

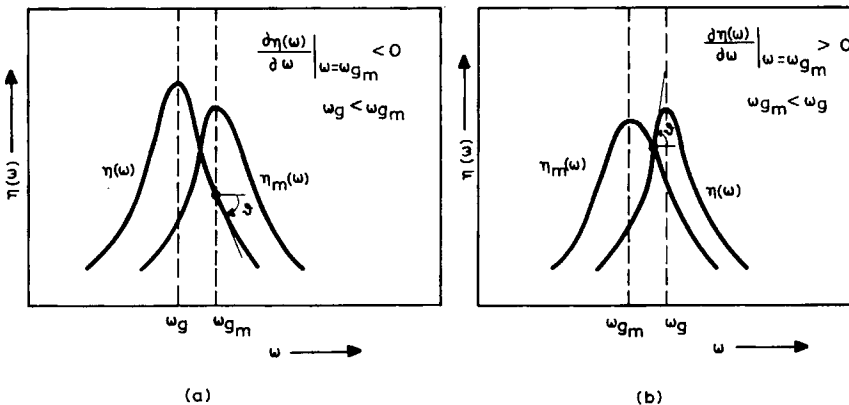


Fig. 1. Typical curves for the loss factors of the matrix and the composite in their transition region in terms of frequency ω . (a) Case $\omega_g < \omega_{gm}$; (b) case $\omega_{gm} < \omega_g$.

$(\partial E'_i/\partial\omega)|_{\omega=\omega_{gm}}$ always have positive values because the storage moduli are always increasing functions of frequency in the transition zone. The contribution of the term $(\partial E'_i/\partial\omega)$ is very small as compared to the contribution of the term $(\partial E'_m/\partial\omega)$ because it is multiplied by the volume fraction of the interphase V_i which always takes values smaller than 5% of the total volume of the composite. For better illustration of this reasoning we define the ratio:

$$\frac{(\partial E'_i/\partial\omega)\eta_i V_i}{(\partial E'_m/\partial\omega)\eta_m V_m} = \frac{(\partial E'_i/\partial\omega)(E''_i/E'_i)}{(\partial E'_m/\partial\omega)(E''_m/E'_m)} \frac{V_i}{V_m} \tag{9}$$

If we now express the loss and storage moduli of the matrix and the interphase as functions of the frequency ω , these quantities are generally expressed by the relations:

$$\begin{aligned} E'_m &= f_1(\omega)E_m, & E''_m &= f_2(\omega)E_m \\ E'_i &= f_1(\omega)E_i, & E''_i &= f_2(\omega)E_i \end{aligned}$$

where the functions $f_1(\omega)$ and $f_2(\omega)$ are model dependent and particular for each model. Thus, for the Maxwell model they take the form:

$$f_1(\omega) = \frac{\omega^2\tau^2}{1 + \omega^2\tau^2} \quad f_2(\omega) = \frac{\omega\tau}{1 + \omega^2\tau^2}$$

whereas, for the Voigt model, they are expressed by:

$$f_1(\omega) = 1, \quad f_2(\omega) = \omega\tau$$

In these expressions it was assumed that the relaxation time τ of the matrix and the interphase are approximately equal.

After introducing these functions in eq. (9) this ratio takes the form:

$$\frac{(\partial E'_i/\partial\omega)(E''_i/E'_i)}{(\partial E'_m/\partial\omega)(E''_m/E'_m)} \frac{V_i}{V_m} = \frac{E_i}{E_m} \frac{V_i}{V_m}$$

where, according to Ref. 16, $V_i/V_m < 0.05$ and $E_i/E_m \simeq 7$, so that this ratio has a value smaller than 0.35.

The positive quantity ΔE also yields a small contribution in eq. (5) because it takes the following form:

$$\begin{aligned} \Delta E &= \left(\frac{\partial E'_m}{\partial\omega} E'_i - \frac{\partial E'_i}{\partial\omega} E'_m \right) (\eta_i - \eta_m) V_m V_i \Big|_{\omega=\omega_{gm}} \\ &= \frac{\partial \log(E'_i E'_m)}{\partial\omega} \Big|_{\omega=\omega_{gm}} [E''_i(\omega_{gm}) - E''_m(\omega_{gm})] V_m V_i \end{aligned}$$

with

$$\begin{aligned} \frac{\partial \log(E'_i E'_m)}{\partial\omega} \Big|_{\omega=\omega_{gm}} &> 0 \\ [E''_i(\omega_{gm}) - E''_m(\omega_{gm})] &= f_2(\omega_{gm})(E_i - E_m) > 0 \\ 0 < V_m V_i &\ll 1 \end{aligned}$$

However, the quantity ΔE has a negative contribution in eq. (5) because it is always a positive quantity and it is subtracted from the rest of eq. (5).

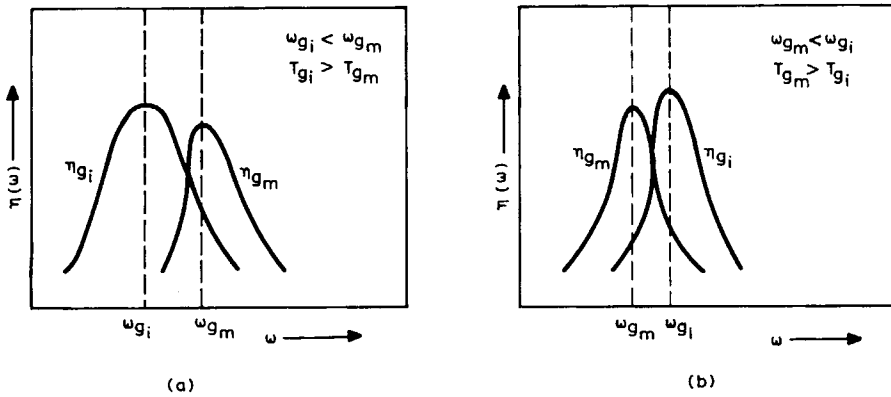


Fig. 2. Typical curves for the loss factors of the matrix and the interphase in their transition region. (a) Case $\omega_{gi} < \omega_{gm}$; (b) case $\omega_{gm} < \omega_{gi}$.

After introducing these simplifications to relation (5) we come to the conclusion that the sign of the expression $(\partial\eta/\partial\omega)|_{\omega=\omega_{gm}}$ depends mainly on the terms $(\partial E_m'/\partial\omega)|_{\omega=\omega_{gm}}$ and $(\partial\eta_i/\partial\omega)|_{\omega=\omega_{gm}}$. The first term $(\partial E_m'/\partial\omega)|_{\omega=\omega_{gm}}$ is always positive, whereas the value of the second term $(\partial\eta_i/\partial\omega)|_{\omega=\omega_{gm}}$ depends on the relative position of the glass transition of the interphase. If $T_{gi} > T_{gm}$, then $\omega_{gi} > \omega_{gm}$. This means that the loss factor of interphase has reached its peak value at a frequency smaller than ω_{gm} and it has already started decreasing with $(\partial\eta_i/\partial\omega)|_{\omega=\omega_{gm}} < 0$ [see Fig. 2(a)].

If $T_{gi} < T_{gm}$, the opposite behavior takes place and this is indicated in Figure 2(b).

So what exactly occurs in a composite material is a matter defined from the interphase region of the polymer around the fillers. Namely, in materials where there are strong bonds between the fillers and the polymeric matrix, the interlayer bounds should have glass-transition temperatures larger than the rest of the matrix and the composite presents a higher value for T_g .

On the contrary, for composite materials with weak bonds between fillers and matrix, i.e., with poor adhesion between them and with a lot of impurities around the fillers, the glass transition of the interphase should be smaller than the rest of the matrix and, consequently, the glass-transition temperature T_g of the composite is reduced.

By comparing the two previous terms we can also derive important results about the contribution of the volume content of the filler on T_g of the composite. According to the conclusions of Ref. 15, the volume fraction of interphase is nonlinearly increased as the volume content of the filler increases. This has the meaning that the contribution of the term $(\partial\eta_i/\partial\omega)|_{\omega=\omega_{gm}}$ becomes larger with increasing content of fillers, because it is multiplied by the volume fraction V_i , while the contribution of the positive term $\partial E_m'/\partial\omega$ will be decreased linearly as V_m decreases.

CONCLUSIONS

The value of the glass-transition temperature, which constitutes an upper limit for the structurally important glassy region, was examined in this paper. According to extensive experimental evidence existing in the literature, the intro-

duction of a reinforcing filler in a polymeric matrix causes T_g of the latter to increase in some cases, and to decrease in others.

Based on a model for the definition of the modulus of elasticity of the particle composites, an explanation of this anomalous behavior of T_g was given. The basic consideration of this model was the concept of interphase, i.e., a phase created from matrix material around each particle of the filler, which has different properties than the rest of the matrix material. This difference leads to two well-separated regions of the composite with two different glass transitions. The combination of these two glass transitions determines the total glass transition of the composite material.

In the case where the T_{gi} of interphase is larger than the T_{gm} of the matrix, the composite increases its glass transition, as compared to the respective T_{gm} , while in the case where $T_{gi} < T_{gm}$ the particle composite possesses a lower glass transition than T_{gm} . This phenomenon, which depends on the mechanical imperfections between matrix and filler particles, presents different degrees of strength and may counterbalance partially or totally the reinforcing effect of the dispersed particles of the composite material.

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Received June 16, 1981

Accepted January 28, 1982