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A SELF-CONSISTENT APPROACH CONSIDERING MORPHOLOGY IN A FILLED POLYMER COMPOSITE: APPLICATION FOR COMPOSITES BASED ON UNTREATED AND AMINOSILANE-TRIATED FILLERS

by

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Abstract: The differences between theory and experimental was resolved by carrying out measurements of the dynamic mechanical properties of a crosslinked polymer reinforced with spherical glass particles. The Generalized Self-Consistent Scheme (GSCS) was used to predict the effective shear modulus of the composites. For predicting dynamic mechanical behaviour of these particulate composites, the *n-layer inclusion model* developped by Hervé and Zaoui was chosen. The problem was solved for n=2 by modifying it with considering the spacial distribution of glass particles in the composite and with repeating the self-consistent model. Conditions of linear elasticity were assumed and the Poisson's coefficient was considered to vary from 0.32 in the glassy state to 0.5 in the rubbery state. The theoretical results fitted the experimental data and were compared with simulations made using other related models such as the Kerner's model.

1. INTRODUCTION

The discrepancy between theoretical predictions and experimental results for dynamic mechanical properties of particulate-reinforced polymers is one of the limitations for understanding of the effect of the role of each component, i.e. the filler, the matrix, and the interface. In fact particulate composites are generally used as model systems for studying the mechanical behaviour of composites in which the filler has a more complex geometry [1-2]. Different micro-mechanical models were proposed to predict the dynamic mechanical properties of these composite materials: Self-Consistent, i.e. Hill [3], Budiansky [4], or variational models, i.e. Hashin and Shtrikman [5]. In order to study the elastic behaviour of a two phase matrix-inclusion composites, McKensie [6], Christensen and Lo [7], and Hervé and Zaoui [8] proposed a *Generalised Self-Consistent Scheme* (*GSCS*) describing the material from a micro to a macro scale. In such an approach, the system is considered as a spherical inclusion surrounded by a matrix shell which in turn is surrounded by the effective equivalent medium (Figure 1).

In this paper, we attempt to compare theoretical and experimental dynamic mechanical properties by carring out measurements on a crosslinked polymer (epoxy) reinforced with spherical A-glass particles using a low frequency torsion pendulum operating in forced oscillations [9] .

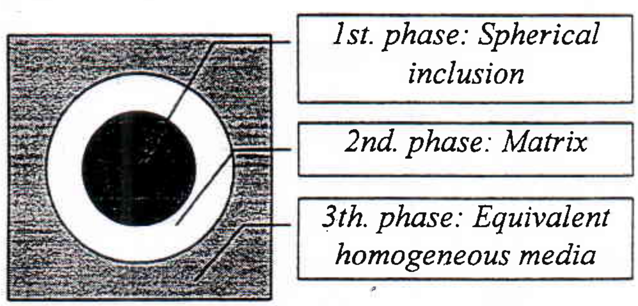


Figure 1:Three phase model

The calculated results obtained for a high volume fraction of spherical inclusions (up to 20%) and the experimental data, differ in a large range above the glass transition region, i.e. in the rubbery state. This difference can be explained by: (i) the dependence on temperature of the Poisson's coefficient [10]. Thus for glassy polymers such as epoxies, the Poisson's coefficient in the glassy state is not equal 0.5 [1-2] but close to 0.32, while above *Tg*, it increases towards 0.5 (rubbery state); (ii) the morphology of the material or the non-homogeneous dispersion of the inclusions at the mesoscopic scale (spacial distribution of the particles in the medium)[11].

2. EXPERIMENTAL

Composites based on a polyepoxy matrix filled with 10%, 20%, 30% and 50% vol. fraction of aminoSilane (γAPS)-treated and non treated A-glass beads, were prepared. The average particle sizes of the A-glass spheres were 40 μm (in number). The epoxy network was synthetized from an epoxy prepolymer (DGEBA) and a primary diamine comonomer (IPD) considering a stoichiometric ratio (amino-hydrogen to epoxy) equal to 1.

Dynamic mechanical spectrometry was carried out using an inverted torsion pendulum. This apparatus allowed the investigation of the dynamic mechanical behaviour of materials, such as the storage shear modulus, G', and the loss modulus, G'', and the internal friction $\tan\delta = G''/G'$ (loss tangent) as a function of temperature. Parallelipiedic specimens ($55*6*2$ mm^3) were machined from the casted plates. Measurements were performed from 100K to 464K at a frequency of 1Hz.

3.RESULTS AND DISCUSSION

3.1. Dynamic mechanical spectra of neat epoxy and composites

Figure 2 displays the experimental plots of G' by increasing the temperature from 100K to 500K for the neat matrix and the composites based on various volume fractions of glass beads (from 0 to 50%). Values of the DMS characteristics are repeated in Table I. These results show that with increasing the volume fraction of filler, the magnitude of the mechanical relaxation ($\tan\delta$ value at the maximum) decreases and the temperature position of the α peak is slightly shifted towards higher temperatures. The storage modulus, G', increases, where as the shear modulus in the rubbery state (G' *at* $T=464K$) is highly enhanced with increasing the filler content.

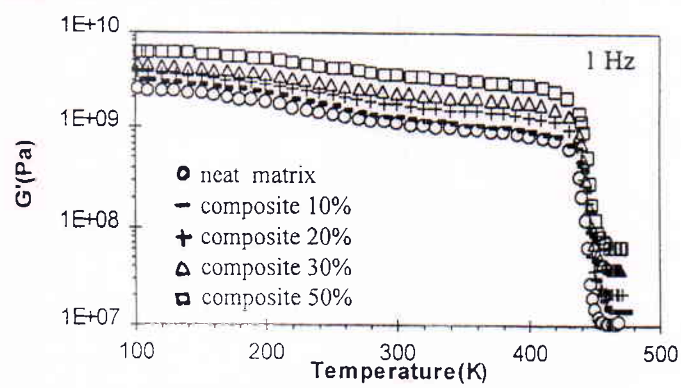


Figure 2:Experimental results

	$T\alpha$ (K)	$\tan(\delta)_{max}$	G'(MPa) (at T=100K)	G'(MPa) (at T=464K)	G''(MPa) (at T=300K)
Matrix DGEBA/IPD	446	1.08	2450	10.8	28.5
Composite 10%	447	1	3040	14.3	33.4
Composite 20%	448	0.969	3690	21.4	41.9
Composite 30%	449	0.879	4460	38.9	51.7
Composite 50%	449	0.782	6740	66.6	62.3

Table I: Dynamic mechanical properties of the neat matrix and composites materials based on various volume fractions of glass beads (Experimental data).

3.2. Modeling the DMS behaviour

Hervé and Zaoui [8] generalized the solution given by Christensen and Lo [7] and determined the effective shear and bulk modulus of the composites. As reported befor, this analysis considers a single composite sphere embedded in an infinite medium (Figure 1) of unknown effective properties. This model requires that the effective homogeneous medium has the same average conditions of stress and strain as for the spherical model described in Figure 1. After calculations performed in the case of a simple shear deformation [8], and by considering the correspondance between the elastic (G_c) and the viscoelastic (G_c^*) [12] behaviours, the final equation for dynamic shear modulus of composite (G_c^*) is given by the following second order equation:

$$X\left(\frac{G_c^*}{G_m^*}\right)^2 + Y\left(\frac{G_c^*}{G_m^*}\right) + Z = 0$$

where X, Y, and Z are constants and G_m^* is the dynamic shear moduli of the matrix.

3.3. Comparison between experimental and theoretical dynamic mechanical behaviours

Figure 3 displays the theoretical curves of G', G", and tan(δ) versus temperature for a composite material based on 30% vol. of glass for a given frequency (1 Hz). As shown in Figure 3, the experimental shear modulus in the rubbery state, is not well fitted by the model. Two parameters need to be considered: (i) the Poisson's coefficient of the matrix which is not constant from the glassy to the rubbery state; (ii) the morphology of the material, i.e. the spatial distribution of filler. Nevertheless, for the composites having a higher volume fraction of glass beads (ϕ_f>20%), the theoretical model can not be used. From the analysis of the distribution of glass beads in the epoxy matrix using microscopy techniques, the real morphology of composite can be taken into account and as a consequence, the *representative volume element (RVE)* can be considered as in Figure 4.

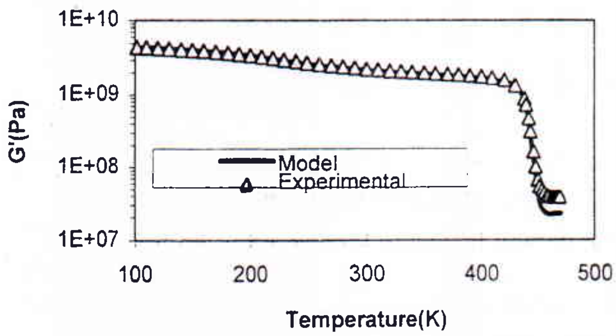


Figure 3: Storage shear modulus of a composite based on 30% vol. of glass.

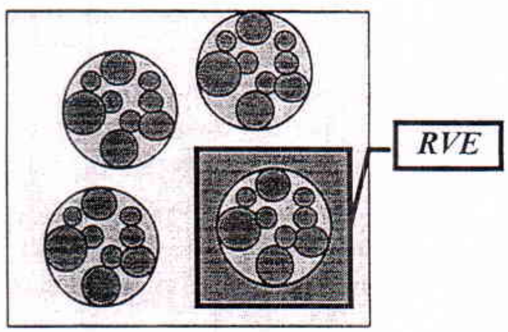
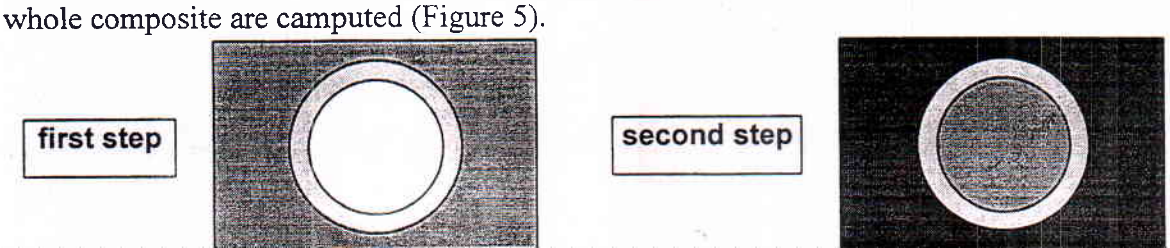


Figure 4: Scheme of the spherical composite inclusions

Thus, *highly reinforced zones(hrz)* are defined as the zone in the composite with a higher volume fraction of glass beads, ϕ_{hrz} , than the average one, ϕ_f . The problem was then solved in two steps; (i) the dynamic mechanical properties of the highly reinforced zone are calculated and, (ii) in the second step, the properties of the equivalent homogeneous media or whole composite are camputed (Figure 5).



In this two-step analysis, the Poisson's coefficient is considered as temperature dependent. The value of ϕ_{hrz} is an important parameter and it can be given by measuring the volume fraction of glass beads in these highly reinforced composite. The final calculated behaviour for a composite based on 30% vol. of glass with ϕ_{hrz} equal to 51% is given in Figure 6. These hypotheses are confirmed for the composite with a higher volume fraction of glass (50% of vol.). In the other hand, the DMS spectra were fitted using a simple model, i.e. the Kerner's one [13] (Figure 7). The difference between the calculated values given by the Kerner and Herve and Zaoui's models is very large, especially in the rubbery state.

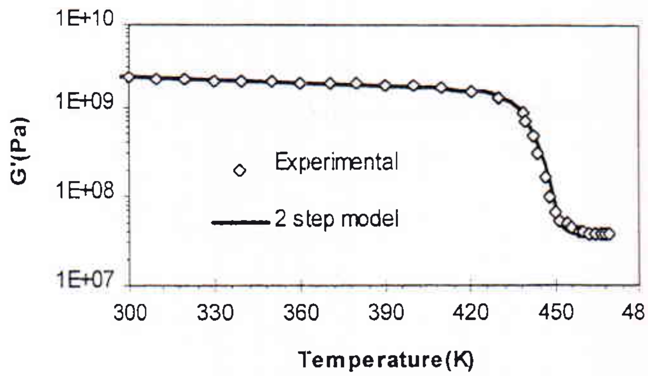


Figure 6: Calculated results(2-step; and ϕ_{hrz}=51%) given by Hervé-Zaoui's model for a composite based on 30% vol. of glass.

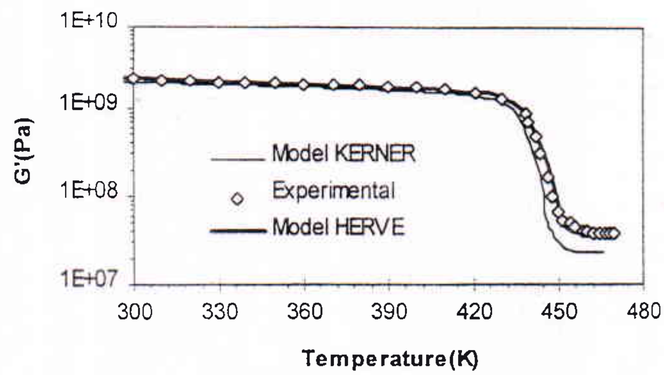


Figure 7: Comparison between the calculated results (2-step) given by Hervé-Zaoui and Kerner's models.

4. CONCLUSION

The self-consistent model developed by Hervé and Zaoui was modified by including the morphological parameters, and was used to predict the effective shear modulus of the *Spherical Composite Inclusion*. Consequently, this model, was used in two steps: in the first step, the properties of highly filled zones, were calculated with considering three components; (i) the spherical inclusion with a volume fraction higher than the mean value; (ii) a shell based on the polymer matrix; (iii) a surrounding medium of equivalent homogeneous material. In the second step, the three components considered for the calculation are; (i) the highly filled zone as a spherical inclusion, having the properties calculated in the first step; (ii) a matrix shell and, (iii) the surrounding region of equivalent homogeneous media. The calculated dynamic mechanical spectra were compared with these fitted using other related models such as the Kerner's one. This comparison shows that the Kerner's model is not usefull to describe the dynamic mechanical properties of the composites in the glass transition region, especially in the rubbery state.

Refrences

[1] T.B. LEWIS and L.E. NIELSEN, *J. Appl. Polym. Sci.*, **14**, 1449 (1970).
[2] A.E. NIELSEN and R.F. LANDEL, in "Mechanical Properties of Polymers and Composites",. *Dekker, New York (1994).*
[3] R. HILL, *J. Mech. Phys. Solids*, **13**, 213 (1965).
[4] B. BUDIANSKY, *J. Mech. Phys. Solids*, **13**, 223 (1965).
[5] Z. HASHIN and S. SHTRIKMAN, *J. Mech. Phys. Solids*, **11**, 127 (1963).
[6] J.K. McKENSIE, *Proc. Roy. Soc.*, **63**, 2 (1950).
[7] R.M. CHRISTENSEN and K.H. LO, *J.Mech. Phys. Solids*, **27**, 315(1979). Erratum **34**, 639 (1986).
[8] E. HERVE and A. ZAOUI, *Int. J. Engng Sci.*, **31**(1), 1 (1993).
[9] J.Y. CAVAILLE, M. SALVIA and P. MERZEAU, *Spectre 2000*. **16**, 37 (1988).
[10] A. AGBOSSOU, A. BERGERET, K. BENZARTI and N. ALBEROLA, *J. Mat. Sci.*, **28**, 1963 (1993).
[11] M. SHATERZADEH, J.F. GERARD, C. MAI and J. PEREZ, *J. Polym.Compos*. Submitted (1996).
[12] Z. HASHIN, *J. Solids Structures*, **6**, 539 (1970).
[13] E.H. KERNER, *Proc. Roy. Soc. Lond.*, **69B**, 808 (1956).