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Thermal stresses in rubber-modified glassy polymers

Thermal stresses that develop in particulate composites during cooling from the fabrication or moulding temperature due to differential thermal contraction of the two phases, can significantly affect strength and toughness of these materials [1–7]. In rubber-modified glassy polymers the thermal expansion coefficient of the rubbery particles is markedly higher than the one of the glassy matrix; when sufficient interphase adhesion is secured, the differential thermal contraction imposes a triaxial tension on the particles and tensile radial and compressive tangential stresses on the surrounding matrix.

According to a mechanism proposed by Schmitt [4], a state of triaxial tension in rubber particles is essential for their toughening action. According to Beck *et al.* [5], the presence of compressive tangential stresses in the matrix surrounding a rubber particle, reducing the maximum local stress produced by an external traction load, contributes to the ductile behaviour of these polyblends. Assuming perfect adhesion between the two phases and neglecting any possible viscoelastic stress relaxation, Beck *et al.* determined the thermal stress distribution for the simple model of a single spherical particle surrounded by an indefinite matrix. On the basis of typical values for the material constants of glassy polymers and rubbers, they also showed the significant order of magnitude of the thermal stresses that can be set up in these composites by ordinary temperature variations. Bohn [7] pointed out that Poisson's ratio of rubbers lies closer to 0.5 than the value taken by Beck *et al.*, and this further raises the level of these thermal stresses.

While the model assumed by Beck *et al.* applies to the case of simple, homogeneous rubber particles included in the glassy matrix, actual rubber-modified glassy polymers, such as toughened polystyrene, ABS, rubber-modified acrylic resins, etc., present a more complex morphology, namely the rubber particles occlude varying amounts of matrix material. The dispersed rubbery phase is thus in itself a particulate composite. In the case of toughened polystyrene the particles may consist prevailingly of polystyrene occlusions surrounded by rubber membranes [8]. To analyse the behaviour of these materials more realistically, the heterogeneous nature of the dispersed phase cannot be disregarded. The aim of this work is a quantitative assessment of the effect of such particle sub-inclusions on thermal stress distribution and magnitude.

In order to take into account the presence of particle subinclusions, one of two methods can be followed: (a) to assume Beck's results for stress distribution but introduce a composite value for the elastic moduli as well as for the thermal expansion coefficient of the composite particle; or (b) to re-model the composite particle. We chose the second way, but followed Beck *et al.* in considering a single particle embedded in an indefinite matrix, assuming perfect adhesion at the interfaces, and neglecting any time-dependence of viscoelastic nature. The elasticity problem can still be easily solved to yield an exact solution in closed-form if the spherical symmetry is maintained in the idealized geometrical structure of the composite particle. We then modelled the composite particle as two concentric spheres, i.e. all the particle subinclusions will be thought of as concentrated in a single spherical region, surrounded by a spherical rubbery shell.

In spherical co-ordinates, from the condition of symmetry there are no shearing stresses: the only non-zero components are the normal stresses (principal stresses) in the radial and in a (any) tangential direction, σ_R and σ_t, respectively. By applying the classical theory of linear elasticity [9], the following expressions for these thermal stresses are obtained:

Subinclusion $(0 < R < b)$

$$\sigma_R = \sigma_t = p \cdot \Phi(\phi)\, \sigma^0_{R(a)} \tag{1}$$

Shell $(b < R < a)$

$$\sigma_R = \left[1 - (1-p)\left(\frac{a^3}{R^3} - 1\right)\phi\right] \cdot \Phi(\phi)\, \sigma^0_{R(a)} \tag{2}$$

$$\sigma_t = \left[1 + (1-p)\left(\frac{a^3}{2R^3} + 1\right)\phi\right] \cdot \Phi(\phi)\, \sigma^0_{R(a)} \tag{3}$$

Matrix $(R > a)$

$$\sigma_R = \frac{a^3}{R^3} \cdot \Phi(\phi)\, \sigma^0_{R(a)} \tag{4}$$

$$\sigma_t = -\frac{a^3}{2R^3} \cdot \Phi(\phi)\, \sigma^0_{R(a)} \tag{5}$$

having set

$$\sigma^0_{R(a)} = \frac{\frac{4}{3}(\alpha_r - \alpha_g)(T_0 - T)}{\left(\frac{1}{G_g} + \frac{4}{3}\frac{1}{K_r}\right)} \tag{6}$$

$$\Phi(\phi) = \frac{\sigma_{R(a)}}{\sigma^0_{R(a)}} = [1 + (1 + pq)\phi]^{-1} \tag{7}$$

where $$p = \left(\frac{1}{G_r} - \frac{1}{G_g}\right) \bigg/ \left(\frac{1}{G_r} + \frac{4}{3} \cdot \frac{1}{K_g}\right)$$

$$q = \frac{4}{3}\left(\frac{1}{K_g} - \frac{1}{K_r}\right) \bigg/ \left(\frac{1}{G_g} + \frac{4}{3} \cdot \frac{1}{K_r}\right),$$

and R is the radial distance from the centre of the particle; a and b are the radii of the particle and of the subinclusion, respectively; $\phi = b^3/(a^3 - b^3)$, is the volume ratio of subinclusion to shell; $(T_0 - T)$ is the temperature change giving rise to the stresses, T_0 being the temperature where the material sets, and T the temperature at which the stresses are evaluated; α is the volume coefficient of thermal expansion (assumed constant over the temperature range $\overline{T_0 T}$); K and G are the bulk and shear moduli, respectively, at temperature T; and subscripts r and g stand for rubber and glass, respectively.

Further, $\sigma_{R(a)}$ denotes the radial stress at the outer surface of the particle, $\sigma^0_{R(a)}$ the same stress for a corresponding simple rubber particle (compare Equation 6 above with Equation 1 in [5]), and $\Phi(\phi)$ their ratio. For $b = 0$ and hence $\phi = 0$, Φ becomes unity and the above expressions reduce to those obtained by Beck *et al.* [5]. Since $q > -1$, and $0 < p < 1$ for $G_r < G_g$, Φ results to be a monotonous function of ϕ, decreasing from $\Phi = 1$ as $\phi = 0$ to $\Phi = 0$ as ϕ tends to infinity. Thus $\Phi(\phi)$ represents a reducing factor for the stresses in the matrix due to the presence of the subinclusion in the particle.

For typical rubber-modified glassy polymers of practical interest, G_g and K_g are of the order of $10^{10}\,\mathrm{dyn\,cm^{-2}}$, while G_r of $10^7\,\mathrm{dyn\,cm^{-2}}$. With this approximation $p = 1$, and the above expressions for thermal stresses simplify as follows:

Particle (subinclusion and shell, $0 < R < a$*)*

$$\sigma'_R = \sigma'_t = \Phi'(\phi)\, \sigma^0_{R(a)} \tag{1'–3'}$$

Matrix $(R > a)$

$$\sigma'_R = \frac{a^3}{R^3} \cdot \Phi'(\phi)\, \sigma^0_{R(a)} \tag{4'}$$

$$\sigma'_t = -\frac{a^3}{2R^3} \cdot \Phi'(\phi)\, \sigma^0_{R(a)} \tag{5'}$$

with

$$\Phi'(\phi) = [1 + (1 + q)\phi]^{-1}. \tag{7'}$$

We can then observe that the distribution of thermal stresses within and around the composite particle is formally the same as the one found by Beck *et al.* [5] for the simple rubbery particle, i.e. the particle undergoes a uniform state of triaxial, hydrostatic tension in spite of its composite structure, while in the matrix only deviatoric stress components are present. The magnitude of the thermal stresses, however, is reduced by the presence of glassy subinclusion in the particle by a factor Φ', inversely related to the volume fraction of subinclusion. Thus, for a given rubber content in the polyblend the level of thermal stresses decreases as more glassy polymer is transferred from the matrix into the dispersed phase.

Although our analysis is based on a very simplified model of the composite particle, we believe that the main effects of the sub-inclusions on thermal stress distribution and magnitude have emerged.

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Comments on "Magnetic parameters of ferrite inclusions observed in magnesium oxide substrates used in nickel ferrite film growth"

In a recent paper [1], Tooke reports ferrimagnetic resonance measurements on ferrite precipitates produced by oxidation of thin films of $NiFe_2$ on MgO single crystal substrates at temperatures of the order of 1200° C and subsequent cooling to room temperature. The precipitates are shown to be coherent, with the [001] axis perpendicular to the plane of the substrate. The parameters g and K_1/M are determined by measuring the angular variation of the resonance field. The experimental values are $g = 2.000 \pm 0.004, K_1/M = -144 \pm 3$ G.

When discussing his results, the author states that the values above "are not consistent with nickel ferrite". This is expected, since the precipitates are formed after diffusion into the substrate [2] and should contain at least some magnesium ions. There remain two distinct possibilities: the inclusions might be either magnesium nickel ferrite ($Ni_{1-x}Mg_xFe_2O_4$), as suggested by Engin and Fitzgerald [2], or pure magnesioferrite ($MgFe_2O_4$). In this context, the experimental value of the g-factor ($g = 2.000$) provides an important clue. It is well known [3, 4] that the Ni^{2+} ion, having a non-zero orbital angular momentum, produces a significant increase in the g-factor relative to its free-electron value (2.0023). In ferrites with composition $Ni_{1-x}Zn_xFe_2O_4$, for example, the g-factor is 2.020 for $x = 0.8$ and increases rapidly with increasing nickel content [5]. On the other hand, the g-factor of magnesioferrite is close to 2.00, since Mg^{2+} is a non-magnetic ion [3, 4]. This seems to show that the inclusions have a very low nickel content. This is substantiated by the fact that the experimental value of the anisotropy parameter ($K_1/M = -144$ G) is consistent with pure magnesium ferrite with an inversion parameter corresponding to the temperature of the heat treatment. For $MgFe_2O_4$ specimens quenched in water from 1200° C, the experimental value is $K_1/M = -138$ G [6], certainly compatible with Tooke's results when the uncertainty in the temperature of the heat-treatment of his samples is