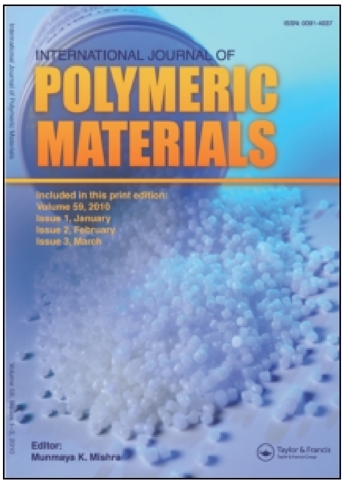

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Influence of Internal Stresses on the Glass Transition Temperature of Filled Polymers

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Influence of Internal Stresses on the Glass Transition Temperature of Filled Polymers

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It is assumed that, in a system of filler in polymer, an internal stress distribution is associated with a shift in the glass transition temperature of the polymer. Experimental results supporting this theory are presented.

INTRODUCTION

It is known from literature data[1,2] that blending of incompatible polymeric materials or incorporation of a filler in a polymer system can produce a shift of the apparent location of the corresponding glass transition temperatures. It has also been proposed[1] that in some cases this shift is not due primarily to the adsorption of polymer on the filler at the interface, but rather to volumetric strains present in the system. In this short communication a theory taking account of the observed effect is presented and the shift is interpreted in terms of an internal stress distribution. Experimental results supporting the basic ideas are also referred to.

THEORY

Consider a polymeric material thoroughly mixed with a filler, assumed to have a higher softening point than the polymer. The composite is assumed to be carefully annealed so that no internal strains are present. If the system now is heated, the matrix and filler certainly will exhibit different thermal expansion. Due to this difference an internal stress (or strain) field will be developed within the material. The molten polymer can also be rapidly cooled to the solid state, this also giving an internal stress around the filler particles. Assuming that the filler particles have a spherical shape the radial stress outside a sphere can be written as Eq. 1.

$$\sigma_r = -\frac{2E_p\,\epsilon_{\mathrm{misfit}}}{\frac{2E_p}{E_f}(1-2\nu_f)+(1+\nu_p)}\cdot\frac{a^3}{r^3}\ (r \geq a) \tag{1}$$

where σ_r is the radial stress, E the elastic modulus, ν Poisson's ratio, a the radius of the spheres and $\epsilon_{\mathrm{misfit}}$ denoted the difference in thermal expansion of the matrix and filler. The indices p and f relate to the polymer and filler, respectively.

A simple and approximately correct expression for $\epsilon_{\mathrm{misfit}}$ would be

$$\epsilon_{\mathrm{misfit}} = (\alpha_p - \alpha_f)\Delta T \tag{2}$$

α denotes the linear thermal expansion coefficient and ΔT is the difference between the softening point of the polymer and the temperature from which the system is heated. Above the softening point only very weak thermal stresses appear.[4] The influence of the developed stress field on the glass transition temperature is to a first approximation given as

$$\Delta T_g = p\left(\frac{\partial T_g}{\partial p}\right) \tag{3}$$

where p usually is the applied hydrostatic pressure. Taking $p = -\sigma_r$ and combining Eqs. (1), (2) and (3) finally gives the sought dependence of ΔT_g on the thermal strain distribution.

$$\Delta T_g = \frac{2E_p(\alpha_p - \alpha_f)\Delta T}{2E_f(1-\nu_f)+(1+\nu_p)}\cdot\left(\frac{\partial T_g}{\partial \sigma_r}\right)\frac{a^3}{r^3} \tag{4}$$

DISCUSSION AND COMPARISON WITH EXPERIMENTAL RESULTS

It must be realized that Eq. (4) only refers to the T_g-value of the polymer matrix. An analogous analysis for the filler could be performed but is omitted here. It is obvious that the stress fields from the different spheres overlap each other to some extent. Assuming a good dispersion of filler particles the mean stress $\bar{\sigma}_r$ for the material between two particles is approximately given by

$$\gamma = \frac{\bar{\sigma}_r}{\sigma_{\max}} = 2\frac{1}{\beta - 1}\int_1^\beta \frac{1}{x^3}\,dx \quad (x = r/a) \tag{5}$$

where β is given in Figure 1. In Figure 1 the overlapping stress field from two neighbouring particles is shown. It may be noted that the predicted T_g-shift is independent of the particle size, only the filler content affects the glass transition.

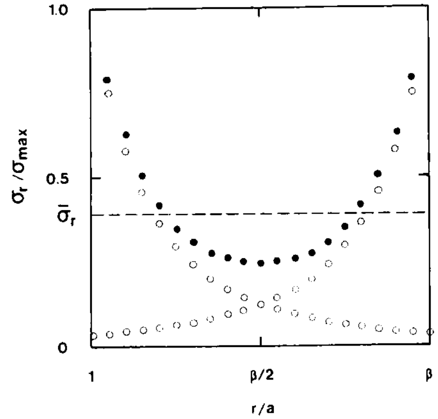

FIGURE 1 The individual stress fields surrounding two particles whose surfaces are located at 1 and β, respectively (unfilled rings). The filled rings correspond to the overlapping stress fields from the particles and $\bar{\sigma}_r$ is the mean stress given by Eq. (5).

Inserting tabulated values for the quantities in Eq. (4) for polystyrene and cellulose particles and using the very simple double overlapping approximation one obtains

$$\Delta T_g \approx 5\gamma \tag{6}$$

In Figure 2 ΔT_g is given as a function of the cellulose content. Above 50% cellulose ΔT_g levels out and becomes independent of the filler content. In Figure 2 also experimental results on the ΔT_g dependence reported by Alftan and de Ruvo[5] are shown. Considering the simplicity of the model used the agreement is very satisfying. The shape of the ΔT_g (% cellulose)-curve is similar and furthermore the experiments also indicate a negligible influence of the filler particle size.[5] In Ref. (5) also results on polyvinylacetate-cellulose-composites are included. Also for this system the T_g-shift can be accounted for using Eq. (4). Finally, it may be noted that the importance of internal stresses due to different expansional behaviour of the components when considering the properties of composites are not restricted to the polymeric substances. Recently, this effect has been studied in detail by Donald and McMillan for glass-ceramic composites.[6]

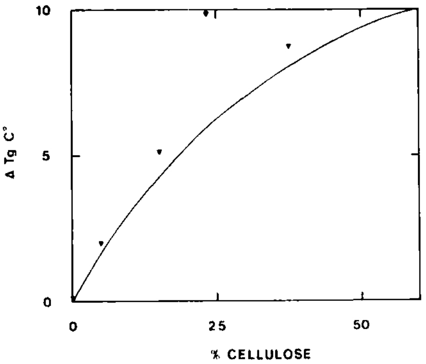

FIGURE 2 Shift of T_g versus cellulose volume content. The solid line corresponds to Eq. (6) and the triangles to experimental results presented in Ref. (5).

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