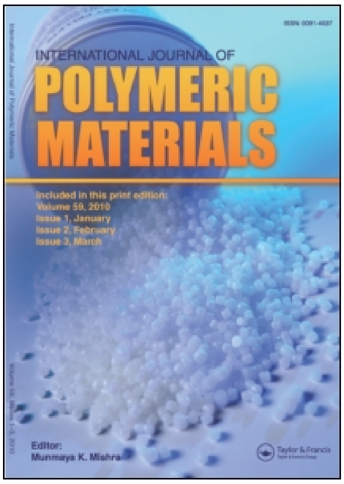

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Prediction of the Slope Discontinuity in Stress-Strain Behaviour of Polymeric Composites with Spherical Inclusions

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The estimation of the point of discontinuity in the slope of stress-strain curves (commonly referred to as "knee") generally observed with composite polymeric materials could be an important problem for the specific application of the composite items. In this work, we have used the results from classical elasticity theory to calculate the residual thermal stresses and proposed simplifying assumptions to calculate a "lower bound" on the applied stress value at which the "knee" can occur. The theoretical predictions have been then compared with the experimental data on various polymeric composites containing glass beads and the agreement is found to be very sound. The proposed equation can be reliably used in engineering design.

INTRODUCTION

The increasing use of polymeric composite materials in practice has given rise to a considerable research effort directed towards a better understanding of their mechanical behaviour. We are mainly concerned here with thermoplastic materials which have been reinforced with a variety of particulate media, e.g. beads, short fibres, $CaCo_3$, etc. Although the effort in the past has mainly concentrated on reinforcement by long continuous fibres, the importance of particulate composites is increasing due to the considerable ease in processing and also in producing items with complex shapes. The short fibres of course have a disadvantage in terms of the reduced modulus and strength in compari-

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son to the long continuous fibres. However, the relatively inexpensive processing for short fibre composites makes them fairly attractive.

In order to be able to design with these materials, we have to know their mechanical behaviour which in turn is very intimately linked with the processing conditions. Depending upon the circumstances we may either have a poor adhesion or a good adhesion between the matrix-filler interface. However, in general, it does turn out (especially for spherical fillers) that the adhesion is somewhat poor. The consequences of this can be observed in the stress-strain curves obtained in uniaxial tensile tests,[1-5] which show a clearly visible discontinuity in the slope. The presence of such a discontinuity has very important practical consequences. For example, Refs. 3 and 6 show how the polymers become permeable to water after such a discontinuity is detected. It is understandable also that the modulus reduces significantly after the appearance of such a discontinuity. It is hence important to be able to have an (at least conservative) estimate of the stress value on the stress-strain curve at which such a discontinuity (often referred to as a "knee" in the literature) appears.

In this paper, we focus our attention on describing the physical mechanisms responsible for such a behaviour, as well as to provide a quantitative criterion for the evaluation of the stress value at the point of the "knee". The proposed criterion will then be validated with the experimental support.

DISCUSSION

Normally rigid fillers are used in composite manufacture and these fillers have a lower thermal expansion coefficient than the polymer matrix itself. During the forming process, the thermoplastic material is cooled from the melting point to the room temperature. This in turn produces thermal stresses in the matrix which are compressive in nature. During a uniaxial tensile testing, the applied stress value multiplied by the stress concentration factor reaches the value of the compressive thermal stress. Under these conditions de-wetting around the inclusion starts to occur. As soon as de-wetting occurs, the point of maximum stress concentration moves from the pole to the equator and the crazing phenomenon sets in. The physical phenomenon of the formation of voids together with the occurrence of crazing manifests itself in the stress-strain curve as a discontinuity in the slope and in some polymers as characteristic stress whitening.[3] It is thus clear that in order to be able to define the point of slope discontinuity, we have to have an *a priori* estimation of the thermal stresses. We shall now describe how a conservative estimate of these thermal stresses could be made.

If the process of cooling during the forming process of the composite material is carried out slowly enough (or if annealing is done) then the thermal stresses present around the rigid inclusions correspond *at least* to those built up during the cooling from the glass transition temperature of the polymer to the room temperature. In some sense this gives us a completely conservative estimate of the thermal stresses. As remarked earlier the applied stress reaches a value given by actual residual thermal stress divided by the stress concentration factor, de-wetting starts to occur and "knee" appears. Since we are essentially going to be concerned with the no adhesion case (and the partial adhesion will only increase the "knee" stress value) and also the cooling corresponding from glass transition to room temperature (and normal rapid cooling will produce larger thermal stresses and then result in a larger "knee" stress value), the estimate obtained on the basis indicated is the most conservative one.

The actual calculation of such thermal stresses is of course very complex particularly in multiparticle systems. But we shall propose a simple approach which gives rational predictions. To aid our analysis we imagine the filled polymer as a collection of spherical composites of various sizes such that each spherical composite contains a filler particle and a concentric shell of polymer material. We will further assume that the thermal stresses and strains induced in the composite are well within the bounds where the theory of classical thermoelasticity may be applied.

The thermal stresses thus generated can be found from the theoretical work of Laszlo[7] who obtained an analytical solution for the thermal stresses built up in a compound sphere by applying the theory of elasticity. The compressive stress p is given by

$$p = \frac{2\, E_p\, E_f\, (\alpha_p - \alpha_f)\, \Delta t}{(1 - \nu_p)\, E_f\, \dfrac{(1 + 2\phi)}{1 - \phi} + 2E_f\, \nu_p + 2(1 - 2\nu_f)\, E_p} \tag{1}$$

Here the subscripts $_p$ and $_f$, stand for the polymer matrix and the filler, respectively. ν, E, α and Δt are the Poisson ratio, the tensile modulus, the linear thermal expansion coefficient and the temperature difference during cooling. ϕ is the filler concentration in volume percent. It is understandable that the thermal stresses are also dependent upon the shape of the filler particle. For a cylindrically shaped particle, similar considerations may be hence applied. Both the tangential and radial stresses in the core of the compound cylinder are invariably equal to p, the radial stress at the junction of two components. The stresses in the compound cylinder are found to be

$$p = \frac{\beta_2 + \beta_3}{\beta_1\, \beta_3 - 2\beta_2^{\,2}}\, (\alpha_p - \alpha_f)\, \Delta t \tag{2}$$

where

$$\beta_1 = \frac{1 - \nu_f}{E_f} + \frac{\nu_p}{E_p} + \frac{1 + \phi}{(1 - \phi)E_p} \tag{3}$$

$$\beta_2 = \frac{\nu_f}{E_f} + \frac{\phi\,\nu_p}{(1-\phi)E_p} \tag{4}$$

and

$$\beta_3 = \frac{1}{E_f} + \frac{\phi}{(1-\phi)E_p} \tag{5}$$

Consider the behaviour of a composite specimen under an applied uniaxial tensile stress. Under these conditions, the stresses around the particle are not uniform, the non uniformity being governed by the stress concentration factor which varies locally. This problem has been considered by Goodier[8] for spherical and cylindrical inclusions. A uniaxial tension T applied at a distance from the spherical cavity can be shown to produce a tensile hoop stress on the equator of the cavity of magnitude $\frac{(27 - 15\nu_p)}{14 - 10\nu_p} T$, and this falls away rapidly as we approach the pole. In the case of a perfectly rigid spherical inclusion, a different type of stress concentration is produced. In simple tension, it can be readily shown that for commonly encountered values of ν_p, the stress concentration factor is approximately 1.9 at the poles. Similar considerations for a cylindrical hole give a value of 3. Typical consideration for a cylindrical rod in cement, for instance, shows that a radial stress of about $1.5T$ is produced when subjected to simple transverse tension, and about $1.7T$, when subjected to two such tensions at right angles. For rubber inclusion, the maximum stress concentration value is 2 at the equator.

The discussion so far has been focused on the stress concentration factor for a single filler particle embedded in an infinite matrix. Let us now consider the effect of finite filler concentration. The work of Matsuo *et al.*[9] indicates that with increasing filler concentration there is likely to be an increase in the stress concentration factor for the case of rubber filled Polystyrene. Similar considerations would of course be applicable to voids. Specifically, Matsuo *et al.*[9] considered the interaction of the stress fields between two spherical particles by assuming that these were simply additive. Their experimental data were in good agreement with their theoretical calculations. More complex analysis will have to be employed when multiparticle systems are involved, since the interaction is more complicated. Hamada *et al.*[10] considered a numerical method for calculating stress concentration factor for an infinite plate with many holes subjected to uniaxial tension. They considered equispaced cylindrical holes at an angle to the direction of the applied tensile stress and showed this to be an important factor in defining the stress concentration. They also show that decreasing the distance between the adjoining cylindrical holes reduced the stress concentration factor when the cylindrical holes were in line or almost linked with the direction of applied stress. Further, Wang *et al.*[11] show that in the case of thermally induced residual stresses, the maximum stress concentration factor occurs at an angle of 38° measured from the top pole for a steel ball embedded in a polystyrene matrix. It is interesting to note that Koufopoulos and Theocaris[12] show that the stress concentration factor at this point reduces with increasing filler concentration. In conclusion, at this stage it could be said that the above theoretical models, although simplified, and the limited experimental evidence do support the view that the stress concentration factor tends to reduce as compared to its value for a single rigid particle embedded in an infinite matrix. (It should be noted that the reduction of stress concentration is only in the direction of the applied stress.) The maximum value of stress concentration factor may thus be employed for a *conservative estimate* of the stress at the "knee" point.

The foregoing discussion thus provides us with a basis for developing a working equation for the calculation of the stress. The possible simplifications which we wish to propose in the light of the discussion so far can be summarized by stating that for a conservative estimate of the stress, (a) we assume that the process of cooling is carried out slow enough, so that the difference between the glass transition temperature and the room temperature is the appropriate one to use, (b) we assume that since the increasing volume concentration has opposite influence on the induced thermal stresses and the stress concentration factor, the limiting value of $\phi \to 0$ and stress concentration factor $= 1.9$, both valid for a single particle in an infinite matrix may be used. We thus propose the following equation

$$\sigma_k = \frac{(1.05)\, E_p\, E_f\, (a_p - a_f)\, (T_g - T_r)}{(1 + \nu_p)\, E_f + 2(1 - 2\nu_f)\, E_p} \tag{6}$$

where T_g and T_r are the glass transition temperature and the room temperature, respectively. The lower bound on the stress value σ_k at the "knee" point is thus completely defined in terms of the thermal and mechanical properties of the polymer and the processing temperature difference. We now assume that when such a stress value given by Eq. (6) is reached, the external applied stress just balances the thermal compressive stress and the conditions for the occurrence of a knee are initiated. This critical point thus gives an estimation of the "knee" point.

RESULTS

The validity of this model giving essentially the lower bound on "knee" point will now be tested by examining the experimental data. It is important to note here that a well-defined "knee" is essentially observed in the no-adhesion case, which is valid for clean beads only. Partial or intermediate adhesion and good-adhesion is unlikely to show the "knee" point. The experimental data were

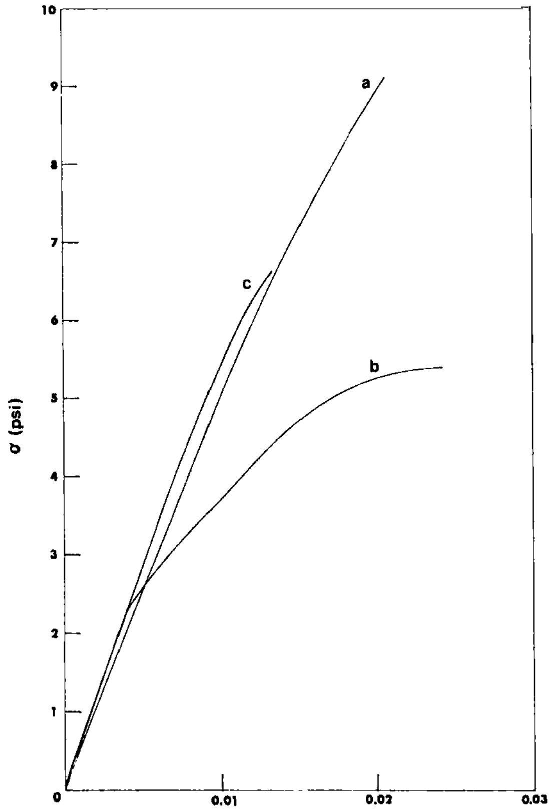

FIGURE 1 Stress-strain curve for (a) unfilled SAN; (b) SAN filled with clean beads; (c) SAN filled with treated beads. $\phi = 0.21$, $\epsilon = 0.13\ \text{min}^{-1}$, $T = 20°C$.

obtained to demonstrate this point. Figure 1 shows a stress-strain curve for Styrene-Acrylonitrile—glass bead composite. Curve (a) shows the behaviour of the unfilled polymer, Curve (b), the one of composite with clean beads and Curve (c), the one of composite with Silane (A 1100) treated beads. Note that the filler volume content is 21 %.

Experimental data on "knee" from this work and the literature work will be reported and tested now. Table I shows the experimental values of the stress at "knee" for Polystyrene (PS, Monsanto, Lustrex H-77) Styrene Acrylonitrile (SAN, Monsanto, LNA 21-1000), Polyvinylchloride (PVC, Electrochemical Industries, Frutaron, Israel), Polyphenylene Oxide (PPO, General Electric 631-111), and Epoxy (Shell Chemical Co., Epon 828). The data on expansion coefficients and Poisson ratios are taken from Ref. 13. The values of moduli are taken from the experimental data reported in Refs. 1–5. Eq. (6) was used for the

TABLE I

Comparison of the predicted stress value at "knee" from this work and the corresponding experimental values

Polymer	$\alpha_p \times 10^4$ (°C)$^{-1}$	T_g (°C)	ν_p	$E_p \times 10^5$ (psi)	p (psi)	$\sigma_{k,e}$ (psi)	$\sigma_{k,t}$ (psi)
PS	0.6	100	0.33	3.7	2380	1500	1250
SAN	0.7	100	0.33	4.8	3620	2300	1900
ABS	0.95	100	0.37	2.4	2520	1750	1330
PVC	0.9	85	0.35	4.5	3550	1880	1870
PPO	0.8	210	0.33	3.0	6270	3300	3300
Epoxy	volumetric mold shrinkage 0.06		0.4	3.9	8300	4500	4370

Filler properties (Glass) $\alpha_f = 5 \times 10^{-6}$ (°C)$^{-1}$; $\nu_f = 0.2$; $E_f = 1.1 \times 10^7$ psi.

calculation of the stresses. The theoretical values of stresses ($\sigma_{k,t}$) resulting from Eq. (6) have been reported in Table I along with the observed experimental values, $\sigma_{k,e}$.

It is gratifying to see the close agreement between the theoretically predicted and the experimentally observed values. It is seen that the predicted values are within 0 to 24% of the experimental values. It is remarkable to see that Wang *et al.*[11] performed experiments with a single $\frac{1}{8}''$ diameter ball embedded in a Polystyrene sample and they noticed surface crazes at a value of 1200 psi whilst the value predicted by us on a theoretical basis is 1250 psi. A critical look at Table I also shows that $\sigma_{k,t}$ values are never greater than the experimental $\sigma_{k,e}$ values, In view of the assumptions made earlier, our calculations really provide a lower bound on the stress value for the occurrence of "knee" and hence these observations are completely consistent.

In passing it should be noted that we cannot predict quantitatively the "knee" point for the intermediate adhesion case. However, the data reported by Narkis[5] and Lavengood *et al.*[2] show that for the intermediate adhesion case, the stress at the "knee" is always larger in comparison to the "no adhesion" case. This is of course in qualitative agreement with the predictive method developed here and could not certainly be explained if the "knee" was a manifestation of only crazing phenomena.[5]

It does appear that Eq. (6) can be reliably used in design practice for predicting the stress value at which "knee" is likely to occur. The estimation will be a conservative one due to the "lower bound" character of the implicit assumptions and hence safe to use.

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