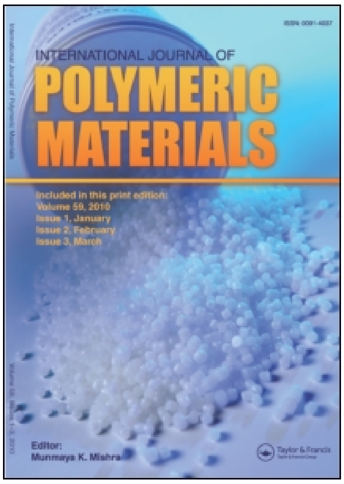

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Micromechanics Studies of Rubber-reinforced Glassy Polymers

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Micromechanics Studies of Rubber-reinforced Glassy Polymers

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A method is discussed for calculating internal stresses in rubber-modified polymers and for predicting elastic constants as well as a critical stress for onset of crazing. A simple model is used to simulate the structure and behavior of the composite, and the necessary assumptions are listed. It is possible to account for interactions between particles which to date has been neglected in other analyses.

INTRODUCTION

Many investigations have been performed to study the toughness and mechanisms of toughness enhancement in rubber modified glassy polymers such as ABS or rubber-modified acrylic polymers.[1–9] These polymers represent an unusual class of composites since most composites consist of a rigid inclusion surrounded by a more ductile or less hard matrix. In this case, a rubbery particle is filling a harder or more rigid matrix. Since the modulus of elasticity of the rubber is much less than that of the glassy polymer matrix and Poisson's ratio is greater than that of the matrix, the modified polymer will have a decreasing modulus and increasing Poisson's ratio as rubber filler content is increased. Of course the most significant benefit is that the toughness of the relatively brittle matrix polymer (e.g. styrene–acrylonitrile) can be greatly increased. The tensile strength of the matrix is reduced but the ultimate elongation is increased as the rubber content is increased. The end result is a compromise and a moderately hard material is produced with good impact strength as a result of the rubber reinforcement.

The mechanism of the toughness enhancement and energy absorption capability of this material is believed related to internal crazing of the matrix throughout the volume caused by stress concentrations around the finely dispersed rubber particles.[2,4,5,7] This crazing also manifests itself in the familiar stress whitening of rubber modified polymers. Since it is believed that stress intensifications around the particles are responsible for the crazing or cold drawing of the matrix adjacent to the rubber particles, it would be desirable to analyze for the internal stresses around the rubber particles. A finite element stress analysis method is presented in this paper for calculation of these internal stresses. Matonis[8,9] has calculated the stresses surrounding a single inclusion in an infinite medium and has reported on the stresses at the interface and in the matrix. He was particularly interested in the effect of the interface or more properly the interphase between spherical filler and matrix and the effect of interphase properties on stresses around the inclusion.

The finite element technique used in this study is not limited to the analysis of a single inclusion in an infinite matrix but can be utilized to analyze multi-inclusion problems and results are presented here for rubber (filler) contents as high as 50 percent. In addition to determining internal stresses for various filler volume fractions and filler properties, the composite modulus of elasticity, Poisson's ratio and critical stress for stress whitening or yield point can be determined.

FINITE ELEMENT METHOD

The finite element method discussed in detail elsewhere[11,12] has been employed here as a numerical stress analysis technique to analyze for the internal stresses in a rubber sphere filled composite material. A computer program for axisymmetric solids (solids of revolution) was used and a Univac 1108 computer generated the data.

The finite element method reduces the continuous structure or medium to a system of discrete elements. In the finite element approximation of axisymmetric solids, the continuous structure or medium is replaced by a system of axisymmetric elements, which are interconnected at nodal circles. It has been assumed that the rubber reinforced polymer (assumed to possess symmetry) could be approximated by a unit cell as shown in Figure 1 which when rotated 360° around axis AD produces a hemisphere embedded within a cylinder. The interparticle spacing is equal to $2\,(r_1 - r_2)$ where r_1 and r_2 are shown in Figure 1. The volume percent of filler particles (radius $= r_2$) can be altered by changing the ratio r_2/r_1 (note $AB = BC = CD = AD$ in Figure 1) and the volume percent filler can be calculated from r_2 and r_1. It should be noted that this axisymmetric representation of the rubber-filled polymer only approximates the real packing and structure of the composite.

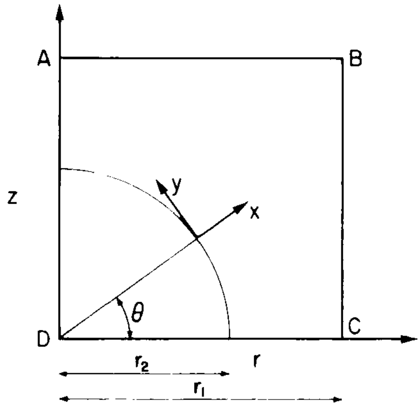

FIGURE 1 Typical cell to represent rubber modified polymer ($AB = BC = CD = AD$).

These axisymmetric cells (Figure 1) do not constitute an actual repetitive unit but are related in their dimensions to the interparticle spacing. A three-dimensional computer program without restrictions (e.g. using tetrahedral elements) would have to be used to truly model a particulate composite.

The finite elements used for the case $r_2/r_1 = 0.36$ ($V_f = 3.03\,\%$) are shown in Figure 2. The radial and tangential stresses as well as the principal stresses and their directions are determined for each element. The analysis leading to

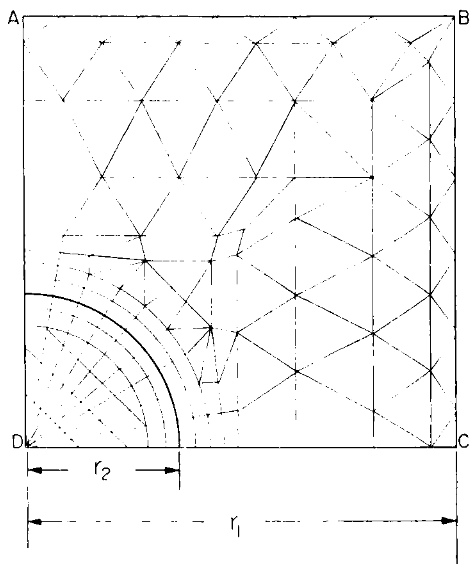

FIGURE 2 Finite element grid for $r_2/r_1 = 0.36$ ($v_f = 3.03\,\%$).

the determination of these stresses begins with the assumption for the displacement field within each element:

$$u_r(r,z) = b_1 + b_2 r + b_3 z \tag{1}$$

$$u_z(r,z) = b_4 + b_5 r + b_6 z \tag{2}$$

This linear displacement field assures continuity between elements, since "lines which are initially straight, remain straight in their displaced position". Based on this assumption and using equilibrium equations for the elements, and the relations of continuity between elements, it is possible to determine u_r, u_z for each nodal circle and the stresses in each element. A computer program written by Wilson permitted the application of this method to our problem.[13]

In order to make the above calculations the following assumptions were made concerning the material:

1) Rubber particles are spherical and of uniform size; packing of particles can be represented by axisymmetric element (Figure 1).

2) Both filler and matrix materials obey elastic stress-strain relationships.

3) Perfect bonding exists between filler and matrix (continuity of displacements at the interface).

APPLICATION OF THE FINITE ELEMENT METHOD

The finite element method permits the calculations of the stress and displacement distributions in the typical region *ABCD* (Figure 2) for certain loading and boundary conditions. It will be assumed here that the composite is stretched by a force in the *z* direction and that there are no applied tractions in the *r* direction. By symmetry, on the boundary *ABCD*

$$\tau_{rz} = \tau_{zr} = 0$$

thus the sides *AB* and *BC* remain parallel to their original positions after a displacement due to the force in the *z* direction while *AD* and *DC* remain fixed. Thus, *AB* and *BC* will undergo normal displacements and the tractions in the *r* direction must be zero so that

$$\int_{BC} \sigma_r \mathrm{d}z = 0$$

where the integral is replaced by a summation in the finite element method.

In order to satisfy the above boundary conditions the following procedure is used[14,15]:

1) Find the stress and displacement distribution (1) such that

$(u_{z1})_{AB} = 1$ (arbitrarily specified unit displacement)
$(u_{z1})_{DC} = 0$ (symmetry)
$(u_{r1})_{BC} = 0$ (specified displacement condition)
$(u_{r1})_{AD} = 0$ (symmetry)
$\tau_{rz} = \tau_{zr} = 0$ (on $ABCD$)

From these boundary conditions, σ_{r1} and σ_{z1} are determined in all elements and displacements u_{r1}, u_{z1} in all nodal circles are determined.

2) Find the stress and displacement distribution (2) such that
$(u_{z2})_{AB} = 0$ (specified displacement condition)
$(u_{z2})_{DC} = 0$ (symmetry)
$(u_{r2})_{AD} = 0$ (symmetry)
$(u_{r2})_{BC} = 1$ (arbitrarily specified unit displacement)
$\tau_{rz} = \tau_{zr} = 0$ (on $ABCD$)

3) The two above stress and displacement distributions are superimposed to obtain

$$\sigma = \sigma_1 + k\sigma_2$$
$$u = u_1 + ku_2$$

where k is determined such that the net force in the r direction along BC is zero. Thus

$$(F_r)_{BC} = \int_{BC} (\sigma_{r1} + k\sigma_{r2})\, dz = |BC|\, (\bar{\sigma}_{r1} + k\bar{\sigma}_{r2})_{BC} = 0$$

So

$$k = -\left(\frac{\bar{\sigma}_{r1}}{\bar{\sigma}_{r2}}\right)_{BC}$$

The stress on AB is thus

$$(\bar{\sigma}_z)_{AB} = (\sigma_{z1})_{AB} - \left(\frac{\bar{\sigma}_{r1}}{\sigma_{r2}}\right)_{BC} (\bar{\sigma}_{z2})_{AB}$$

and the displacement is

$$(u_z)_{AB} = (u_{z1})_{AB} - \left(\frac{\bar{\sigma}_{r1}}{\bar{\sigma}_{r2}}\right)_{BC} (u_{z2})_{AB} = (u_{z1})_{AB}$$

since $(u_{z2})_{AB} = 0$.

CALCULATION OF POLYMER COMPOSITE MODULUS OF ELASTICITY AND POISSON'S

To calculate the stiffness or modulus of elasticity of the rubber-modified plastic composite, the average stress on the boundary AB is calculated, or

$$\bar{\sigma}_z = \frac{\int_A \sigma_z \mathrm{d}A}{A} = (\bar{\sigma}_z)_{AB}$$

here A is the area of the top of the cylinder in the finite element analysis and the integral is replaced as a summation as follows:

$$\int_A \sigma_z \, \mathrm{d}A = 2\pi \int_0^{r_1} \sigma_z \, r \, \mathrm{d}r = 2\pi \sum_{i=i}^{n} \tfrac{1}{2} \, (r_i^2 - r_{i-1}^2) \, \sigma_z$$

Where r_i and r_{i-1} are the radii to the nodal circles that define the elements on the top of the cylinder, n is the number of such circles, and σ_z is the corresponding normal stress in each element.

The modulus is defined as

$$E = \frac{\bar{\sigma}_z}{\bar{\epsilon}_z}$$

where the strain used is calculated from the specified boundary displacement

$$\bar{\epsilon}_z = \frac{(U_z)_{AB}}{|BC|}$$

Poisson's ratio was calculated from the displacements

$$u = u_1 + ku_2$$

From Figure 1, the displacement of boundary AB is

$$(u_z)_{AB} = (u_{z1})_{AB} + k(u_{z2})_{AB}$$

however $(u_{z2})_{AB} = 0$, thus

$$(u_z)_{AB} = (u_{z1})_{AB}$$

Also, the displacement of boundary BC is

$$(u_r)_{BC} = (u_{r1})_{BC} + k(u_{r2})_{BC}$$

but

$$(u_{r1})_{BC} = 0, \text{ thus}$$

$$(u_r)_{BC} = k \, (u_{r2})_{BC}$$

Poisson's ratio can be written as

$$\nu = \frac{|(u_r)_{BC}|/\overline{AB}}{|(u_z)_{AB}|/\overline{BC}} = \frac{|k|(u_{r2})_{BC}\overline{BC}}{(u_{z1})_{AB}\overline{AB}}$$

and since $(u_{r2})_{BC} = (u_{z1})_{AB} = 1$

$$\nu = |k| \frac{\overline{BC}}{\overline{AB}} = |k| \quad (\overline{BC} = \overline{AB})$$

CALCULATION OF COMPOSITE CRITICAL STRESS

A composite critical stress can be calculated which might be considered the fracture strength for a brittle composite, the yield point for a ductile composite or in the case here the stress required to initiate internal crazing or cold drawing which manifests itself as stress whitening of the rubber-modified composite.

In order to calculate this composite critical stress, it was assumed that the composite would reach this stress as soon as an element of the matrix reached a large enough value of stress to cause crazing of the matrix. The spherical inclusion causes large stress concentrations and it is reasonable to expect that the critical condition will be achieved at the filler-matrix interface where the stresses are large. Since the matrix is subjected to combined stresses (triaxial) a suitable failure or crazing criterion has to be used in order to predict matrix failure or crazing under combined stresses. The Von Mises failure criterion or distortion energy theory was selected which is represented as follows

$$\tfrac{1}{2}\left[(\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^3 + (\sigma_3 - \sigma_1)^2\right] = (\sigma^*)^2$$

where σ_1 σ_2 and σ_3 are principal stresses at the point in question and σ^* is the critical stress in simple uniaxial tension.

This criterion is then applied by determining which element has the maximum value of distortion energy for the calculated applied stress $\bar{\sigma}_z$ found on boundary AB. This value of distortion energy may not exceed the value needed to fail or craze the matrix materials $(\sigma^*)^2$ and thus the composite critical stress is calculated from

$$S_c = \bar{\sigma}_z \frac{\sigma^*}{(U_{max})^{1/2}}$$

where U_{max} is the maximum value of distortion energy determined for the arbitrary specified displacement which produces the average stress $\bar{\sigma}_z$, and S_c is the composite critical stress.

INTERNAL STRESSES

The internal triaxial stresses have been calculated throughout the volume (in each element shown in Figure 2) of rubber-modified glassy polymers. The stresses have been calculated for rubber volume contents up to 44 percent. This corresponds to a minimum in interparticle spacing of $0.22r_2$ (where r_2 = radius of rubber particle). In addition, the stresses have been investigated assuming various properties for the rubber particle to determine the effect of Poisson's ratio and elastic modulus on these stresses.

For the calculations presented in this paper, the following component properties have been assumed:

Polymer matrix: E (modulus of elasticity) $= 400{,}000$ psi
ν (Poisson's ratio) $= 0.35$

rubber filler:

1) $E = 3000$ psi
   $\nu = 0.48$
2) $E = 3000$ psi
   $\nu = 0.35$
3) $E = 3000$ psi
   $\nu = 0.50$
4) $E = 1000$ psi
   $\nu = 0.48$

The volume percent filler can be determined from the ratio r_2/r_1 (Figure 1) by calculating the volume of the hemisphere contained within the cylinder when the cell in Figure 3 is rotated 360° around axis AD. The following r_2/r_1 ratios and corresponding filler contents were used in this analysis:

r_2/r_1	$v_f(\%)$
0.357	3.03
0.502	8.45
0.615	15.51
0.714	24.2
0.833	38.4
0.870	43.8

The stresses around the interface between the rubber particle and glassy matrix are shown in Figures 3, 4, and 5. The results shown in these figures are for the rubber filler with $E = 3000$ psi and $\nu = 0.48$ except when indicated in the figure. The stresses are presented as a ratio, $\sigma/\bar{\sigma}_z$, where $\bar{\sigma}_z$ can be considered the average stress applied to the polymer composite. Thus, the ratio represents the stress concentrations around the rubber particles. The stress system is defined in Figure 3. From Figure 2 it can be seen that there are nine finite elements around the interface and the calculated stresses are assumed to act at the center of each element. The effect of changing the rubber properties has a very small effect on the internal stresses as shown in Figure 3 for a change in the Poisson's ratio of the rubber. Figure 4 and 5 present the interfacial stresses for two additional volume percents of rubber. In all of the cases shown, the radial and tangential stresses at the interface are almost equivalent to the principal stresses and thus the shear stresses (e.g. τ_{xy}) are nearly zero. In Figure 4, the hydrostatic stress as well as the

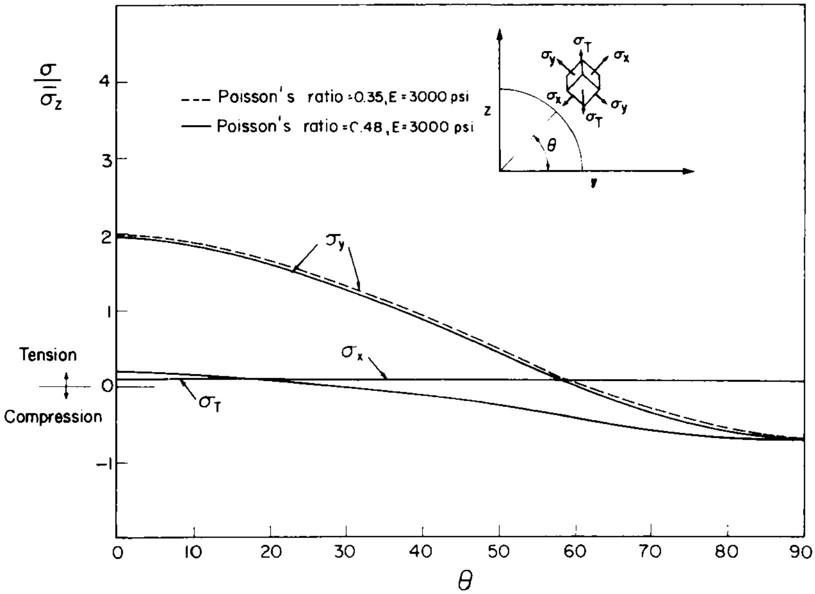

FIGURE 3 Interfacial stresses in a rubber-modified polymer (v_f = 3.03%).

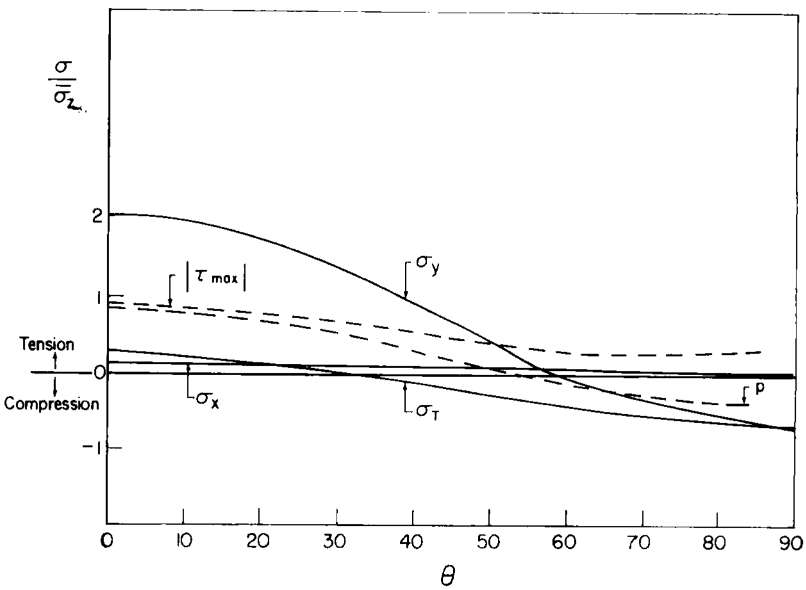

FIGURE 4 Interfacial stresses in a rubber-modified polymer (v_f = 8.45%).

absolute value of maximum shear stress has been plotted along the interface. The hydrostatic stress is given by

$$p = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3} \quad (\sigma_1 > \sigma_2 > \sigma_3 \text{ are principal stresses})$$

and the absolute value of maximum shear stress is

$$\tau_{max} = \left|\frac{\sigma_1 - \sigma_3}{2}\right|$$

The hydrostatic stress produces only volume changes without distortion and as can be seen in Figure 4, volume expansions occur for $\theta < 50°$ and volume contractions occur for values of $\theta > 50°$. The variation of the stresses at the pole ($\theta = 90°$) and equator ($\theta = 0°$) of a spherical rubber particle are shown in Figure 6 as a function of rubber filler content. If the curve for one of the tangential stresses at the equator (σ_y) is extrapolated to $V_f = 0$ percent almost perfect agreement is obtained with the theoretical solution of Goodier[16] for a single inclusion in an infinite matrix.

The decay of stresses away from the interface are shown in Figure 7. The stresses have been plotted beginning from the interface and continuing along the boundaries *AD* and *CD* as shown in Figure 7. Only the stress normal to the boundary has been plotted. It can be seen that for a low volume percent filler (3%) the normal stress along *CD* reduces to the average stress, $\bar{\sigma}_z$, at the midpoint between two inclusions while the normal stress along *AD* approaches zero as it should. However, if the results for higher

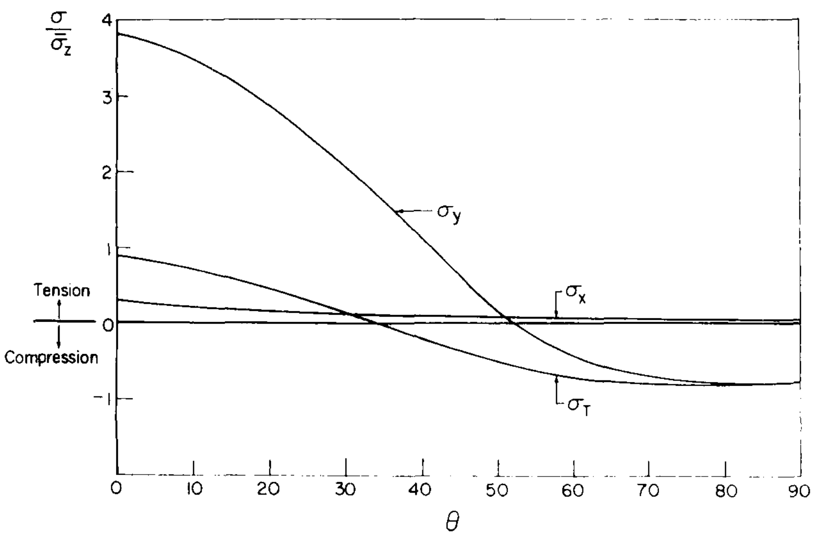

FIGURE 5 Interfacial stresses in a rubber-modified polymer (v_f = 43.8%).

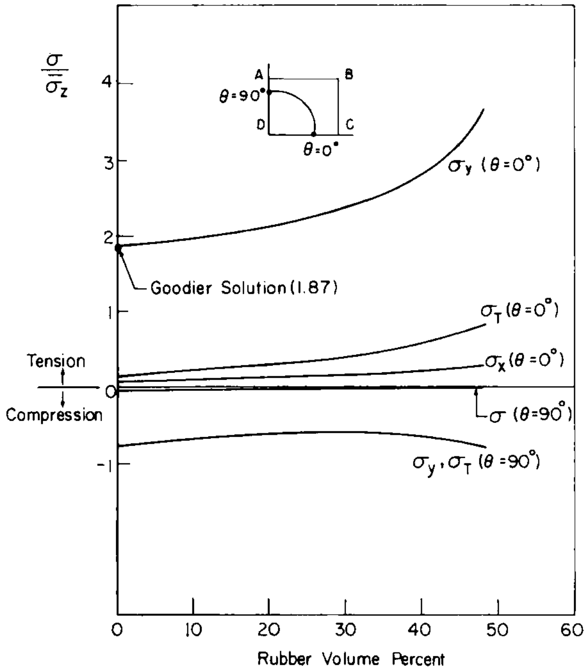

FIGURE 6 Interfacial stresses at the pole and equator of a spherical rubber particle as a function of rubber volume percent.

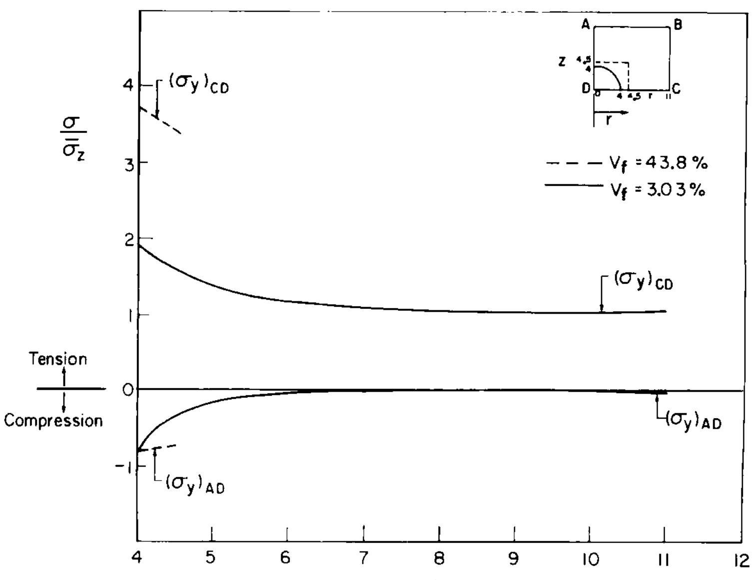

FIGURE 7 Matrix stresses in rubber-modified polymer.

volume percents are plotted as shown in Figure 7 the stress concentrations persist even at the midpoint between two inclusions because of the close particle spacing.

ELASTIC CONSTANTS

The predicted results for the modulus of elasticity and Poisson's ratio are shown in Figure 8 and Table I. Both the modulus and poisson's ratio are

TABLE I

Volume fraction rubber (%)	Summary of composite predicted properties[a]				
	Assumed filler properties		Predicted composite properties		
	E (psi)	ν	E (psi)	ν	σ^* (psi)
3.03	3000	0.48	0.380×10^6	0.346	4610
8.45	3000	0.48	0.347×10^6	0.337	4557
15.50	3000	0.48	0.307×10^6	0.326	4308
24.20	3000	0.48	0.264×10^6	0.311	3928
38.4	3000	0.48	0.200×10^6	0.285	2937
43.8	3000	0.48	0.177×10^6	0.279	2509
15.50	1000	0.48	0.304×10^6	0.319	4191
15.50	3000	0.35	0.304×10^6	0.318	4162
15.50	3000	0.50	0.305×10^6	0.316	4162

[a] Assumed matrix properties: E = 400,00 psi
ν = 0.35

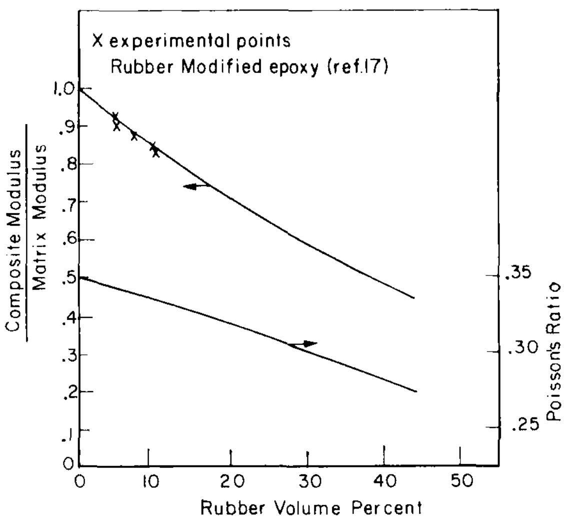

FIGURE 8 Modulus and Poisson's ratio for rubber-modified polymers as a function of rubber volume percent.

reduced by the addition of rubber particles. Because of the great difference in modulus of the matrix and filler, the filler acts almost as a void and thus both composite properties are reduced. Experimental data for the modulus of rubber particle modified epoxy resin has been compared to the predicted curve in Figure 8 for rubber contents up to 10 volume percent. Excellent agreement is obtained. It is difficult to find additional data in the literature although Fletcher *et al.*[4] and Schmitt and Keskkula[2] have presented limited modulus data on rubber-modified polystyrene. The problem in trying to compare this data to the predicted values of modulus is that the theory used here assumed elastic behavior of the components whereas the actual behavior is viscoelastic. Furthermore, the amount or rate of stress relaxation is dependent upon the rubber content[2] and if the modulus of a series of rubber-modified polymers with various rubber contents is determined at the same strain rate the results will not agree with the values predicted by this analysis. This analysis will give an upper bound since it assumes elastic behavior and would probably be accurate for tests performed at high rates of strain where relaxation would be minimized. It can be seen in Table I that for large changes in the rubber properties only slight changes in the polymer composite properties are produced.

COMPOSITE CRITICAL STRESS

The composite critical stress to initiate crazing or stress whitening is shown in Figure 9 as a function of volume percent rubber and also summarized in Table I. It has been assumed that this critical stress for the unmodified matrix is 8000 psi. As shown in Figure 9 the composite critical stress is reduced with the first addition of rubber. Although crazing may initiate at the low stresses indicated it may not be visible as stress whitening until higher stresses are reached particularly for the low rubber contents as only a small volume of material is affected. It should be noted that the failure model used here assumes perfect bonding and also assumes that crazing is initiated as soon as the first element reaches a critical stress condition. The first element to reach this condition is on the equator of the spherical particle at the interface.

CONCLUSIONS

A method has been discussed for calculating internal stesses in rubber-modified polymers and for predicting elastic constants as well as a critical stress for onset of crazing. A simple model is used to simulate the structure

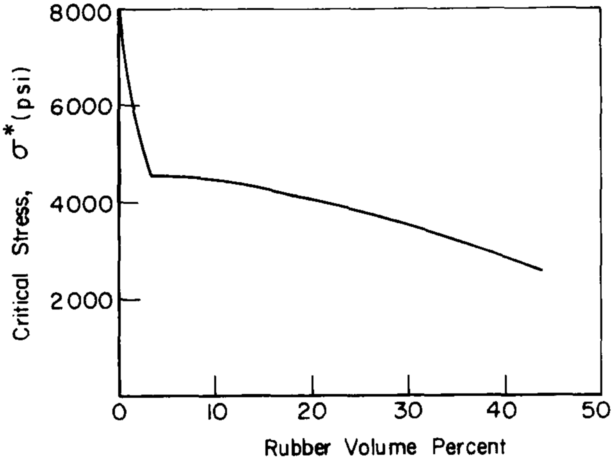

FIGURE 9 Critical crazing stress for rubber-modified polymers as a function of rubber volume percent.

and behavior of the composite as indicated by the necessary assumptions listed in the paper. However, it is possible to account for interactions between particles which to date has been neglected in other analyses. Further study is being given to the problem to develop a more realistic model by changing from an elastic to an elastic-plastic or visco-elastic matrix. Also modifications in the failure model will be studied.

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