Relationships in a Bismaleimide Resin System. Part II: Thermomechanical Properties

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A range of bismaleimide resins of differing network structure was produced both by varying the ratios of N,N'-bismaleimido-4,4'-diphenylmethane (BMI) and methylene dianiline (MDA), and also by the use of different thermal processing cycles. Characterization of the resins by a variety of mechanical, physical, and micrographic techniques showed that properties such as modulus and yield strength varied directly with crosslink density and its associated free volume. Fracture toughness was found to increase as the crosslink density decreased, and microscopic investigation of the resin fracture surfaces identified characteristics which correlated with the resin fracture toughness.

INTRODUCTION

In a companion paper (1), we have noted that bismaleimide (BMI) resins can undergo two principal reactions during cure: one of these is a crosslinking reaction through the double bonds on the maleic moieties, and the other is a chain-extension reaction incorporating an amine hardener such as methylene dianaline (MDA). Leung, *et al.* (2), has offered evidence that the dominance of the chain extension reaction relative to crosslinking can be increased either by increasing the length of the low-temperature part of the cure cycle, or by decreasing the ratio of BMI to MDA. In Leung's work, increasing the degree of chain extension appeared to improve the fracture toughness of the resin, remarkably without lowering the modulus or glass transitions temperature.

The relative importance of chain extension versus crosslinking reactions might be expected to influence molecular rigidity, and thus the many thermal and mechanical properties related to molecular motions. This is a concept underlying much prior work in polymers. For instance, Chang, *et al.* (3-6), studied a series of diglycidylether-butanediol (DGEB)-diamino diphenyl sulfone (DDS) epoxy systems. These authors found that resin density, modulus, glass transition temperature, and yield stress all increased as the degree of cure increased. The in-crease in resin density was seen as a direct measure of the reduction in free volume as crosslinking occurred during cure. The reduction was found to correlate with a decrease in fracture toughness, as expected intuitively.

To assess the applicability of these concepts to maleimide systems, N,N'-bismaleimido-4,4'-diphenylmethane (BMI) and methylene dianiline (MDA) were obtained commercially, and used to fabricate neat resin plaques with BMI:MDA ratios of 2.5:1, 1.5:1, 1.25:1, and 1:1. Each of these formulations were prepared using two different cure cycles: one that had a 48 h low temperature hold at 145°C followed by a cure at 220°C for 6 h, and the other that had only the cure at 220°C for 6 h.

The principal reaction at the intermediate processing temperature (145°C) is a Michael addition reaction which acts to produce linear chain growth. At higher temperature (220°C), both the Michael addition reaction and a crosslinking addition reaction occur simultaneously. In general, curing at a lower temperature or increasing the amine content of the resin (lowering the BMI:MDA ratio) acts to favor the chain extension mechanism. It will be shown here that chain extension in turn favors free volume and chain mobility, with a concomitant increase in toughness. However, this toughness comes at the expense of a lowered stiffness and softening temperature.

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DISCUSSION OF EXPERIMENTAL RESULTS

Dynamic Mechanical Analysis

Dynamic mechanical properties (storage shear modulus G' and loss factor tan δ) were determined over a temperature range from $-150°C$ to $300°C$, using a Rheometrics Model 7200 mechanical spectrometer with rectangular bar specimens measuring 66.7 mm $\times$ 12.7 mm $\times$ 2.41 mm. Specimens from the full range of resin mixtures and cure cycles were examined, at a heating rate of $5°C/min$ with a strain level of 0.1%, and at frequencies of 0.16 Hz, 1.6 Hz, and 16 Hz. These data provided a convenient measure of glass transition temperature and the glassy and rubbery moduli, which in turn can be used to estimate microstructural variables related to resin flexibility. For instance, Nielson has provided an empirical expression which can be used to relate the rubbery shear modulus G to the molecular weight between crosslinks M_c:

$$\log G = 7 + \frac{293\rho}{M_c} \qquad (1)$$

where ρ is the polymer density.

The glass transition temperatures (T_g) of the various samples as obtained from the peak position of tan δ measured at 0.16 Hz are shown in *Fig. 1*. The T_g of the resin is seen to increase as the BMI content is increased, reflecting the increased crosslinking and associated reduction in molecular mobil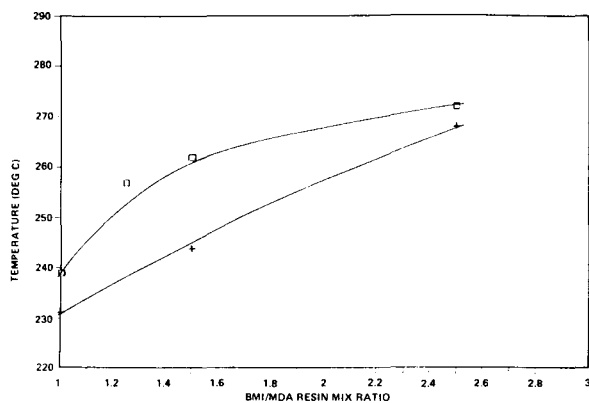ity. Conversely, the low temperature hold step favors chain extension over crosslinking for a given resin stoichiometry, leading to a reduction in the T_g. These results can be written in terms of M_c using the value of storage modulus G' at $T_g + 30°C$ in the Nielson equation; the results are shown in *Fig. 2*. Density values from dilatometry measurements described below were used in the equation. Thus the enhanced chain mobility produced by increased concentration of extended chain linear segments is reflected in an increased M_c and a decreased thermal stability.

Finally, *Table 1* lists some characteristic values from the set of dynamic mechanical spectra for the various resins: the temperatures of the three principal relaxations $T_\gamma, T_\beta, T_\alpha$ (temperatures at which tan δ reaches a local maximum); and the storage modulus G' of the resin at $20°C$. These data show an increase in G' as the crosslink density of the resin was increased. As would be expected, the glassy-state properties are relatively insensitive to changes in network characteristics, as can be seen from the small change in glassy modulus even for a tenfold change in M_c. Neither are the secondary relaxations much influenced by network characteristics, as seen in the consistent values for the secondary relaxation temperatures.

Density

The resin density provides a measure of the molecular packing within a network structure. Since most theories of yield and deformation stress the importance of intermolecular interactions, one ex-
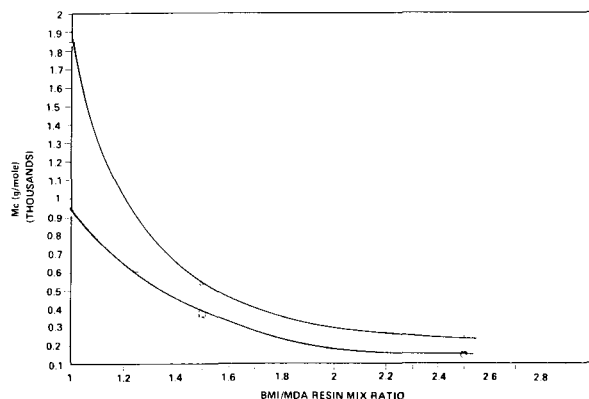

Fig. 1. *Glass transition temperatures of the resins studied as a function of the BMI/MDA ratio. The + symbol represents samples cured by the two step 145°C/220°C cure cycle and □ represents resin samples cured by the high temperature 220°C cure cycle.*

Fig. 2. *Estimates of M_c of the resins studied as a function of the BMI/MDA ratio. Symbols have the same meaning as in Fig. 1.*

Table 1. Dynamic Mechanical Properties as Measured by Rheometrics Mechanical Spectrometer.

Resin	T_α, °C	T_β, °C	T_γ, °C	G'@20°C, GPa
1:1, 48 h 145°C, 6 h 220°C	231	10	−98	1.5
1:1, 48 h 145°C	239	22	−102	1.5
1.25:1, 6 h 220°C	257	20	−104	1.7
1.5:1, 48 h 145°C, 6 h 220°C	244	13	−104	1.75
1.5:1, 6 h 220°C	262	13	−104	1.75
2.5:1, 48 h 145°C, 6 h 220°C	268	14	−103	1.75
2.5:1, 6 h 220°C	272	12	−103	1.8

pects measurements of resin density to correlate with the resin deformation behavior. Accordingly, room temperature densities of the cured resins were measured in a toluene-carbon tetrachloride density gradient column; these values are shown in *Fig. 3*.

The density was found to decrease as the BMI concentration decreased, which is expected in view of the increase in crosslink density as the BMI concentration of the polymer is increased. Further, resins which were exposed to the long hold step at 145°C had densities similar to those which were only processed at 220°C, even though these different thermal processes produced significant changes in the polymer M_c. The differences in chemical composition appear to be more important then variations in cure cycle in determining the density of the polymers produced.

Dilatometry

Thermal expansion behavior was studied with a Du Pont 943 Thermomechanical Analysis (TMA) module on the 1090 Thermal Analysis system, which monitored expansion of the specimens as they were heated from 30°C to 300°C at a rate of 1°C per min. Following the procedure performed previously on epoxy resins by Burton (7), estimates of the fractional free volume V_f were obtained from an expression of the form:

$$V_f = (\alpha_r - \alpha_g)T_g, \qquad (2)$$

where α_r and α_g represent the thermal expansion coefficients above and below T_g, respectively.

The results of the expansion experiments are shown in *Table 2*. The fractional free volume was found to increase as M_c increased. For a given resin system, the V_f was higher in the resins which were exposed to the low temperature hold step. These results are consistent with the density data and dynamic mechanical analysis presented above.

Compressive Yield Strength

Specimens for tensile testing were prepared according to ASTM D695(62), and loaded in uniaxial

compression by an Instron testing machine run at 0.051 mm/min (0.002 in/min). At least five specimens were tested at each condition. *Figure 4* shows values of yield strength obtained at 23°C.

These results are in agreement with those of the dynamic mechanical testing and the density measurements. In terms of the network structure, the yield stress increases as the restriction to molecular deformation is increased. A plot of yield stress versus M_c is given in *Fig. 5*. The yield data correlate well with the T_g values determined. *Figure 6* shows that in this case there is a direct relationship found between T_g and yield stress.

Modulus

The resin modulus was measured in flexure using a three point bend apparatus according to ASTM specification D790(63), with a deformation rate of 0.051 mm/min. The values found for Young's modulus at 23°C are shown in *Fig. 7*. These data show that, as reported by Brown (8), modulus and yield strength are affected similarly by changes in molecular mobility.

Fracture Toughness

Values of fracture toughness (K_{IC}) were obtained by measuring crack propagation in compact tension (CT) specimens measuring 12.7 mm × 12.7 mm × 4.6 mm (9), loaded at 0.051 mm/min. Hydraulic servo-operated testing machines were found to be superior to screw-type machines for this work. Specimens were precracked with a razor blade which was kept in liquid nitrogen prior to use. The speci-
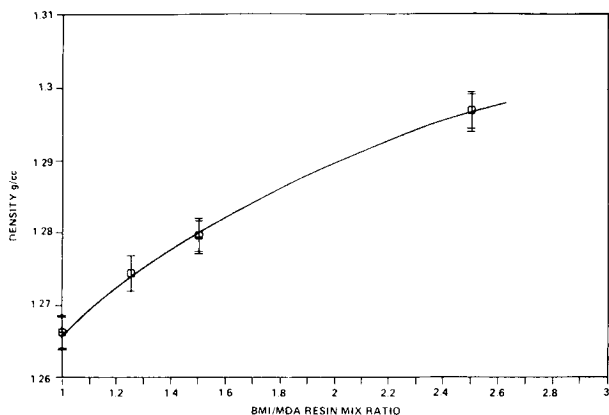
Table 2. Fractional Free Volume of Cure Resin Specimens.

Resin	V_f, %	M_c, g/mol
1:1, 48 h 145°C, 6 h 220°C	18	1800
1:1, 48 h 145°C	16	950
1.25:1, 6 h 220°C	17	620
1.5:1, 48 h 145°C, 6 h 220°C	12	570
1.5:1, 6 h 220°C	10	380
2.5:1, 48 h 145°C, 6 h 220°C	8	180
2.5:1, 6 h 220°C	7	150

Fig. 3. Density measurements for the resins studied. Symbols have the same meaning as in Fig. 1.
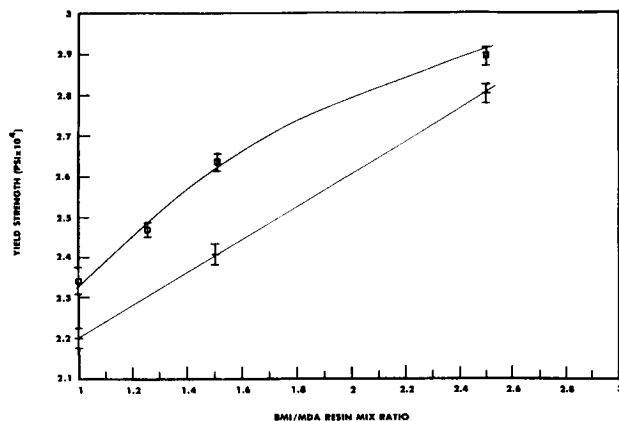

Fig. 4. Yield strength measured at 23°C. Symbols have the same meaning as in Fig. 1.
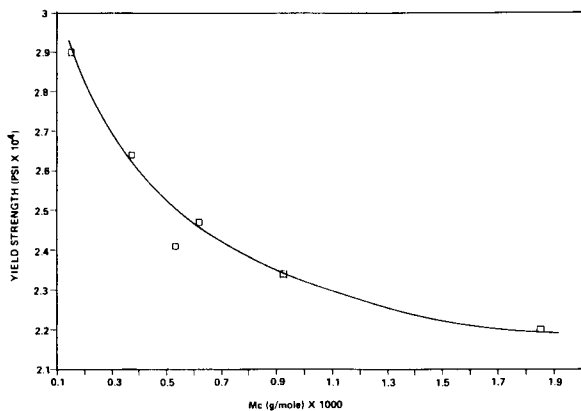
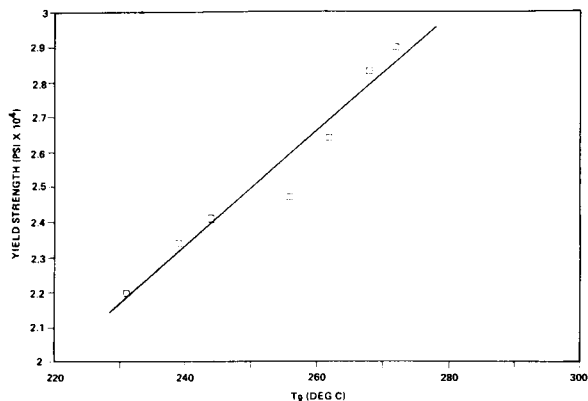Fig. 5. Yield strength as a function of M_c for the resins studied.

Fig. 6. Yield strength as a function of the polymer T_g.

systems studied. The molecular structure described by M_c directly affects the yield behavior of the polymers. The primary factor determining the fracture toughness of these BMI resins is the ability of the resin to yield. This yielding allows crack blunting, which increases the energy needed for crack growth.
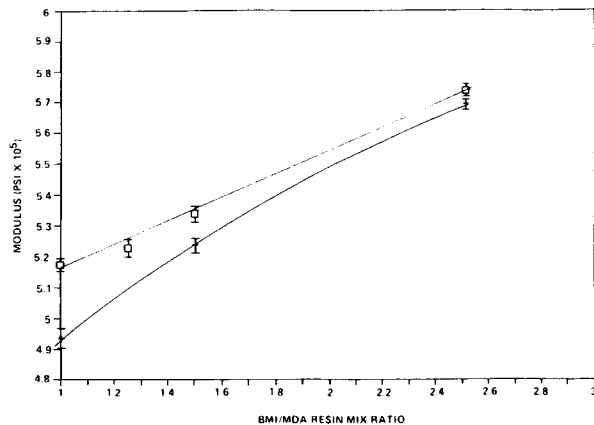

Fig. 7. Modulus data measured at 23°C. Symbols have the same meaning as in Fig. 1.
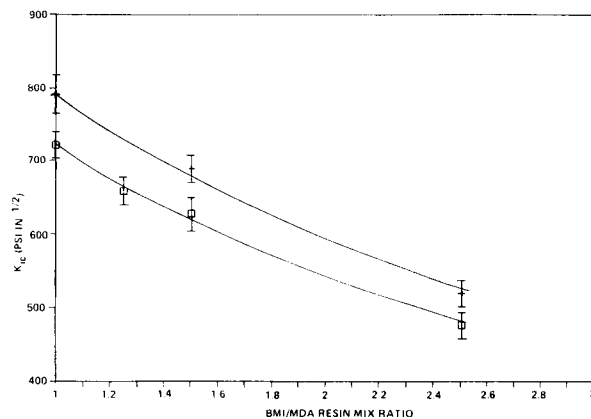

Fig. 8. K_{IC} for the polymers studied. Symbols have the same meaning as in Fig. 1.
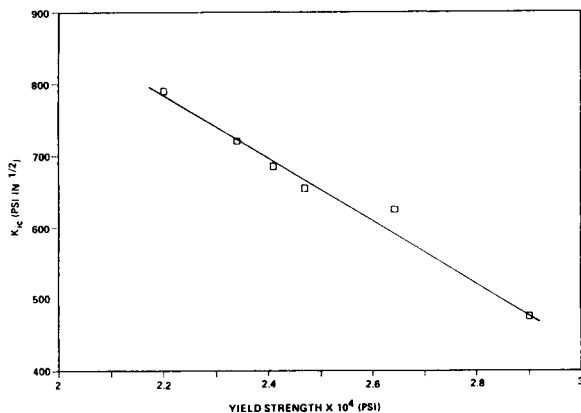
men thickness used in the testing was larger than that required for a plane strain condition. K_{IC} for this specimen geometry is given by:

$$K_{IC} = \frac{P}{b\sqrt{w}}\left[29.6\left(\frac{a}{w}\right)^{1/2} - 185.5\left(\frac{a}{w}\right)^{3/2}\right.$$
$$\left. + 655.7\left(\frac{a}{w}\right)^{5/2} - 1017\left(\frac{a}{w}\right)^{7/2} + 638.9\left(\frac{a}{w}\right)^{9/2}\right]$$
$$(3)$$

where P is the load, b is the sheet thickness, w is the width of the specimen, and a is the crack length. Testing was performed at 0.051 mm/min.

The data obtained in the fracture tests are shown in *Fig. 8*. Comparison of these data with the results shown in *Fig. 1* indicate that the toughness tends to increase as the T_g of the polymer decreases. *Figure 9* shows that the fracture toughness is directly related to the yield strength of the resins studied. *Figure 10* shows the comparison of M_c and fracture toughness. The results indicate that increasing the molecular weight between crosslinks increases the toughness of the material. All of these results considered together provide an explanation of the effect of structure on fracture characteristics of the BMI

Fig. 9. K_{IC} as a function polymer yield strength.

Microscopy of Fracture Surfaces

The features present on the resin fracture surfaces were examined with a Nikon Opti-Photmodel optical microscope and an Amray model 1000B scanning electron microscope. All samples were coated with gold prior to examination.

Optical microscopy was used on the CT specimens to measure crack lengths, and morphological features evident on fracture surfaces give an indication of deformation behavior during crack growth. An optical micrograph of a sample of 1:1 BMI to MDA resin mixture is shown in *Fig. 11*. The fracture surfaces are extremely smooth, which is consistent with the low K_{IC} values of the polymers studied. The tough resin systems exhibited more topographical features in the crack arrest region than did the brittle resins.

Electron microscopy of the fracture surfaces showed features very similar to those reported by several workers (10–12) for epoxy resins. There was

a characteristic roughness to the fracture surfaces which, as shown in *Figs. 12* through *14*, tended to increase in degree as the fracture toughness of the resin increased.

CONCLUSIONS

The results of this study provide sufficient information to allow an interpretation of the structure-property relationships in the bismaleimide resins studied here to be given. The properties of the polymers were found to vary directly with crosslink density. Trends in crosslink density and the fractional free volume could be directly correlated with trends in the yield strength and modulus. Fracture tough-
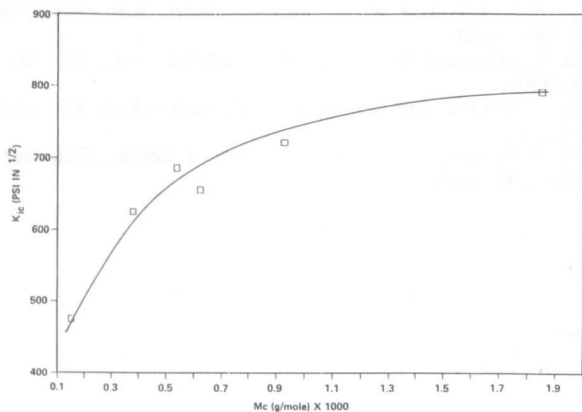

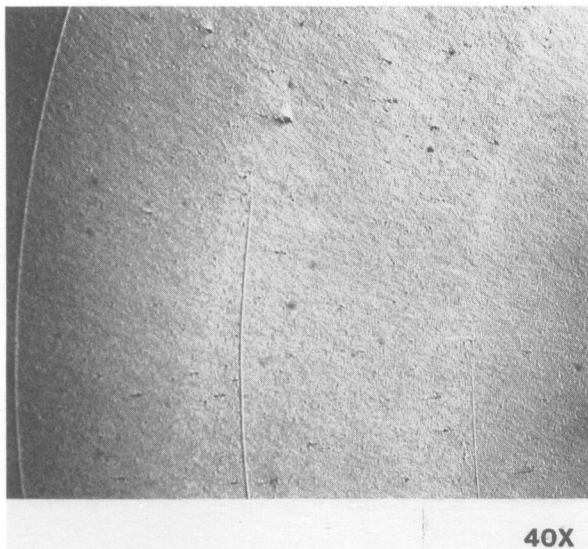Fig. 10. K_{IC} as a function of the molecular weight between crosslinks M_c.

Fig. 12. Scanning electron micrograph of fracture surface in 1:1 resin specimen.

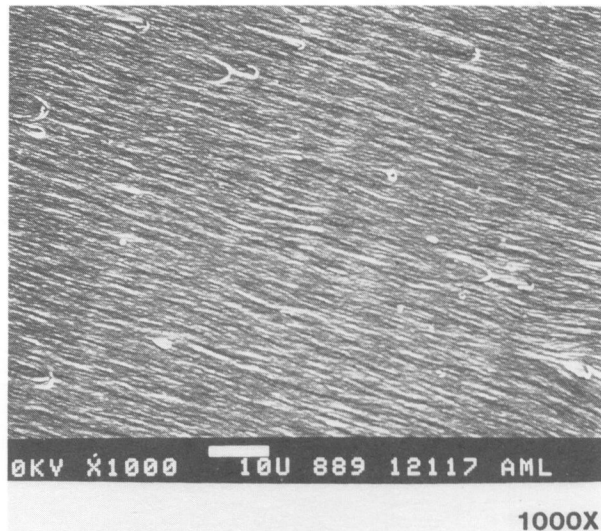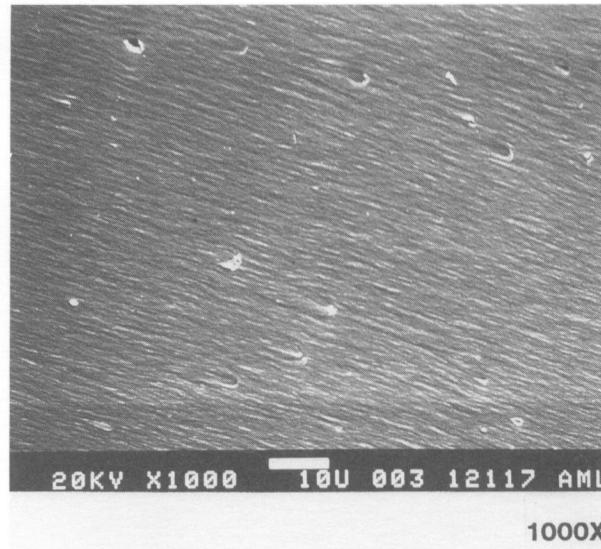Fig. 11. Optical micrograph of fracture surface in 1:1 resin specimen.

Fig. 13. Scanning electron micrograph of fracture surface in 1.5:1 resin specimen.
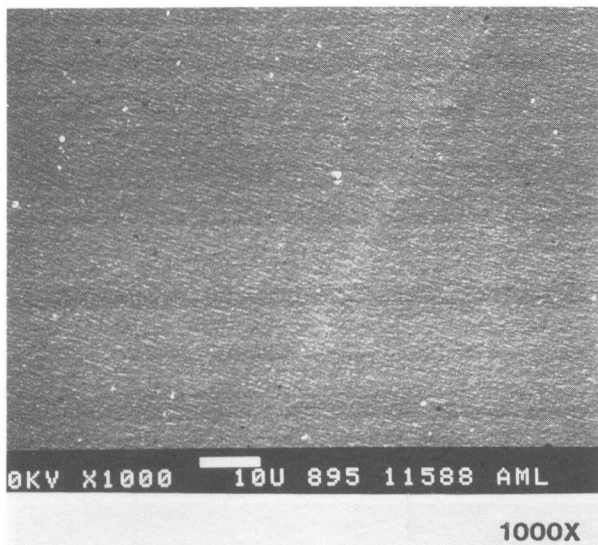
Fig. 14. Scanning electron micrograph of fracture surface in 2.5:1 resin specimen.

ness was found to increase as the crosslink density decreased and the yield strength decreased. Thus, the fracture properties of these materials were directly dependent on network structural characteristics. Microscopic investigation of the resin fracture surfaces identified characteristics which correlated with the resin fracture toughness.

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