Polymer Bulletin 7, 369-376 (1982)

Polymer Bulletin

Model Glassy Inhomogeneous Polymer Networks

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Summary

A new procedure for the preparation of model polymer networks having an inhomogeneous distribution of crosslinks has been developed. Emulsion polymerized polystyrene/divinylbenzene microspheres, of uniform particle size, are swollen with styrene monomer, which is later polymerized in situ. The resulting network consists of discrete sites of crosslinked material dispersed in an interpenetrating matrix, and is suggested as a model for the nodular morphology which has been observed in some epoxy networks. The results of initial studies showing the effects of nodule size and concentration on the fracture toughness of the glassy networks are presented.

Introduction

In endlinking reactions commonly used to form thermosetting polymers, it is unclear whether or not inhomogeneous network formation takes place. Electron microscopy studies of free, etched, and fracture surfaces of crosslinked epoxy resins have revealed the presence of a nodular morphology on the scale of 10-1000 nm. Nodules are suggested to be sites of higher crosslink density resulting from intramolecular crosslinking and cyclization reactions (LABANA et al. 1971). This conclusion is supported by the observation that upon etching the internodular material is preferentially attacked by the etchant (RACICH and KOUTSKY 1976). On the other hand, observations of nodular morphology in linear thermoplastic polymers question the claim that nodules are crosslinking inhomogeneities (DUSEK et al. 1978). Experimental evidence from sources other than electron microscopy does not reveal the causes of the observed morphology. Small angle x-ray scattering indicates that cured epoxy resins contain inhomogeneities (UHLMANN 1979). However, this technique does not prove that epoxies are inhomogeneous with respect to

0170-0839/82/0007/0369/$ 01.60

crosslink density distribution. Kinetic studies and statistical modelling of the curing reaction between a bisphenol A diglycidyl ether and an amine curing agent indicate that up to, and somewhat beyond the gel point, such a system would cure without the formation of inhomogeneities (LUNAK and DUSEK 1975).

There have been attempts to relate the observed nodular morphology with the physical properties of cured epoxy resins. Relationships between nodule size and fracture energy were reported by MIJOVIC and KOUTSKY (1979). Later, YAMINI and YOUNG (1980) found no relationship between nodule size and fracture energy. A relationship between the characteristic flaw size and the nodular morphology observed on the 10-100 μm scale was reported by KIM et al. (1978). In these three studies, variations in nodular morphology were observed as a consequence of variations in either the reactant stoichiometry or curing cycle, therefore nodular morphology cannot be considered as a truly independent variable.

Difficulty in characterizing the structure of epoxy networks has proven to be a major obstacle to understanding both the source of the nodules observed by electron microscopy, and relationships between nodules and physical properties. A model system was suggested by KELLEY et al. (1982) in which the characteristics of the nodular network can be varied and controlled. Such an inhomogeneous network may shed light on the controversy surrounding the relationship between nodular morphology and physical properties of thermoset polymers, but is also a system of interest in its own right, since the properties of such a network have not been studied in a systematic way.

Experimental

Crosslinked polystyrene microspheres, which would later serve as the nodular phase of the inhomogeneous network, were produced by emulsion polymerization, using the recipe of PIIRMA and JAMES (1976). Latex particles ranging from 60 to 180 nm in diameter were obtained by varying the concentrations of the two emulsifiers, Emulphogene BC-840, and sodium dodecyl sulfate (SDS). The divinylbenzene content in the monomer feed was held constant at 5% by weight. The crosslinked polystyrene latices were characterized by transmission electron microscopy, using a JEOL JEM 120U transmission electron microscope. A Zeiss particle analyzer was used to measure individual particle sizes from the electron micrographs. The number-average diameter, D_N, the weight average diameter, D_W, and the uniformity ratio, $U = D_W/D_N$, were calculated from the measured diameters of at least 100 particles per sample. Values of U ranged from 1.02 to 1.09.

After characterization, the crosslinked polymer latices were coagulated in methanol and were washed and dried. Blending of the microgel spheres with styrene monomer containing 0.1% benzoyl peroxide was carried out in a dry box under nitrogen. Alternatively, the crosslinked polystyrene latex was mixed with high molecular weight linear polystyrene latex. This latex mixture was coprecipitated into methanol, then washed and dried. The combination of linear polystyrene and polystyrene microgel was then mixed with styrene containing 0.1% benzoyl peroxide. Although not yet studied extensively, this blending method is expected to provide controlled differences in the degree of interpenetration of the linear matrix and dispersed gel.

Polymerization and molding of the model polymers were carried out in one step in an aluminum compression mold. The mold, having cavity dimensions 2.5 x 12.0 cm, produced samples suitable for fracture testing. The sample thickness was controlled by the amount of material placed in the mold and was usually 0.1-0.3 cm. The molding cycle consisted of 2000 pounds pressure for 8 hours at 115°C. Fracture toughness of the model polymers was determined by the double torsion test, first reported by KIES and CLARK (1969) and described in detail by WILLIAMS and EVANS (1973). The double torsion test piece is shown in Figure 1. The sample is supported at each side by rollers, and is loaded from above, over a crack inserted at one end. A groove in the center guides the crack along the sample. The stress intensity factor, K, for the double torsion geometry is given by the following equation for the plane strain case:

$$K = PW_m \left[\frac{3}{(1-\nu)Wd_n d^3}\right]^{\frac{1}{2}}$$

where P is the applied load, W_m and W are the widths of the moment arm and sample, respectively, d_n is the sample thickness at the groove, d is the sample thickness, and ν is Poisson's ratio. The fracture toughness, K_{IC}, is given by the critical value of the stress intensity factor. The tests were conducted on an Instron Universal tester equipped with a compression cell. The crosshead speed was 0.02 inches per minute and all tests were conducted at room temperature, 21-23°C. Fracture surfaces were examined by transmission electron microscopy of single stage carbon-platinum replicas.

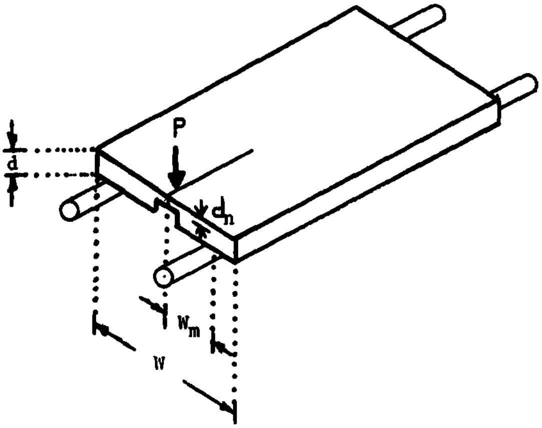

Figure 1. Double torsion test piece

In preparation for thermal analysis studies, polymer samples were stored at 150°C under vacuum for 48 hours and were then cooled slowly to room temperature. Glass transitions were measured by differential scanning calorimetry at heating rates of 20, 10, and 5°C per minute and extrapolated to zero heating rate. A Dupont 990 Thermal Analyzer was used.

Results and Discussion

Fracture Studies

The first objective of these studies was to vary nodule content and observe its effect on fracture toughness. Samples with various amounts of 95 nm diameter polystyrene microgel containing 5% divinylbenzene were prepared, with the proportions of microgel, styrene, and linear polystyrene shown in the following table. The dependence of fracture toughness on nodule content is shown in Figure 2. The fracture toughness decreases sharply with increasing nodule content.

Unstable crack propagation was obtained for the samples containing 0, 10, 25, and 33% nodules. The difference between the initiation fracture toughness, K_{ICi}, and the arrest fracture toughness, K_{ICa}, was approximately 0.1 $MNm^{-3/2}$. The error bars associated with the K_{ICa} values have been omitted from Figure 2 for clarity, but are approximately the same as

Model Inhomogeneous Glassy Polymers

Sample Designation	Microgel g	Styrene g	Linear Polystyrene g	% Microgel
A	0	6.0	6.0	0
B	1.0	6.5	2.5	10
C	3.0	6.0	3.0	25
C_1	3.0	9.0	0	25
D	4.0	5.0	3.0	33
E	6.0	6.0	0	50
F	9.0	3.0	0	75
G	12.0	0	0	100

observed for K_{ICi}. The samples containing 50% nodules exhibited only stable crack propagation. At this level, a significant portion of the styrene monomer was diffused into the microgel before being polymerized; therefore, the internodular material probably consists of very short polystyrene chains which would be expected to have a low fracture energy.

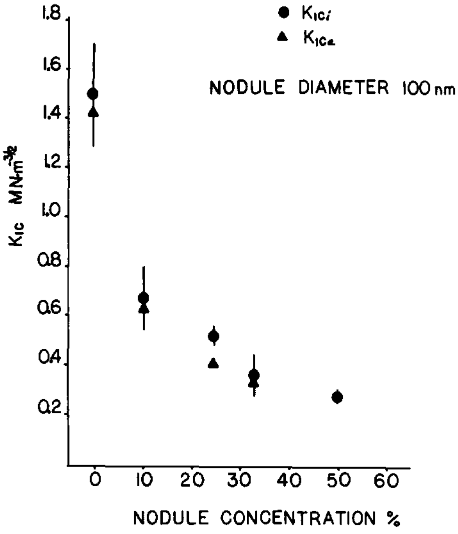

Figure 2. Room temperature fracture toughness of polystyrene model polymers as a function of nodule concentration.

In the light of the work done by MIJOVIC and KOUTSKY (1979), the role of nodule diameter in determining fracture toughness was of interest. Samples containing either 25% or 50% nodules of various sizes were prepared and polymerized as previously described. The dependence of fracture toughness on nodule size is shown in Figure 3. Nodule diameter does not influence fracture toughness in this case, at least in the range of nodule diameters studied.

Transmission electron microscopy revealed differences in fracture surface morphology among the samples tested, as shown in Figure 4. While the fracture surfaces of the samples containing no microgel exhibited few morphological features at magnifications of 30,000, those samples containing microgel particles exhibited the expected nodular morphology.

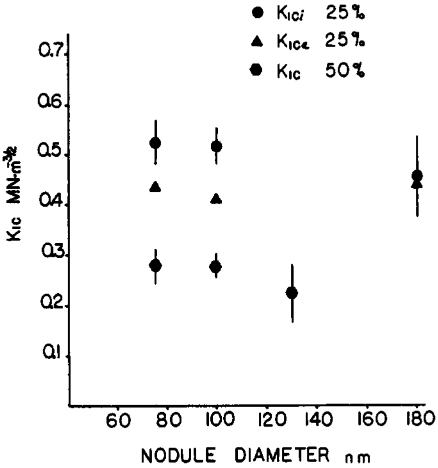

Figure 3. Room temperature fracture toughness of polystyrene model polymers as a function of initial nodule diameter.

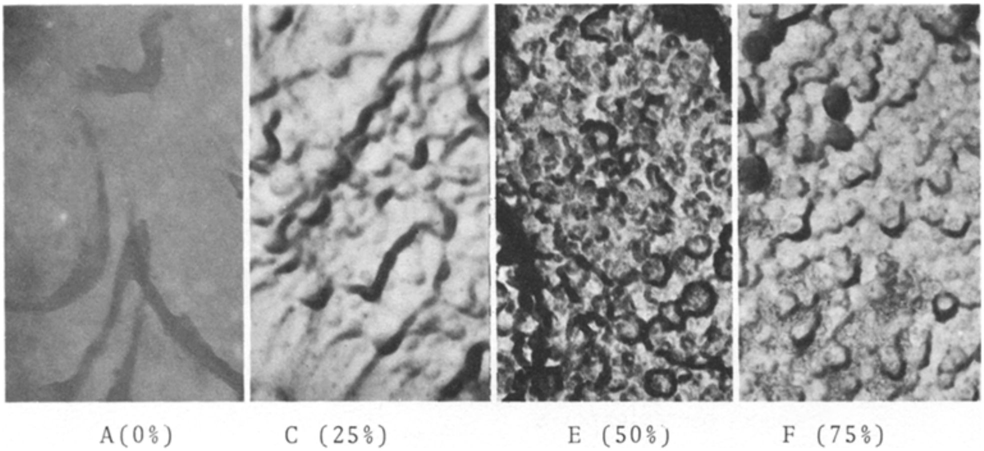
A(0%) C (25%) E (50%) F (75%)

Figure 4. C-Pt fracture surface replicas of polystyrene model polymers having various concentrations of 100 nm diameter microspheres.

DSC Studies

The question of whether an inhomogeneous network will exhibit multiple glass transitions corresponding to regions of higher and lower crosslink density was addressed by KREIBICH and SCHMID (1975), who found splitting of the glass transition of epoxy thermosets upon annealing below the network T_g. The observance of a lower glass transition in addition to the original was attributed to annealing-induced phase separation of higher and lower crosslink density regions. They also noticed that annealing at or below T_g results in an endothermic peak in the DSC scan, which is superimposed on the glass transition. This effect has also been documented in cured epoxy resins by OPHIR et al. (1978), who attribute it to enthalpic relaxation of the network. Similar effects have been noted for linear polymers as well (PETRIE 1972).

Model inhomogeneous networks, conditioned by slow cooling from 150°C to room temperature, also display an endothermic peak in the region of the glass transition, as shown in Figure 5. The presence of a higher endotherm near 115°C is independent of DSC heating rate and seems to be a unique property of the inhomogeneous networks, since it is observed neither in the crosslinked nor in the linear polystyrene. At present, no explanation of this observation is available.

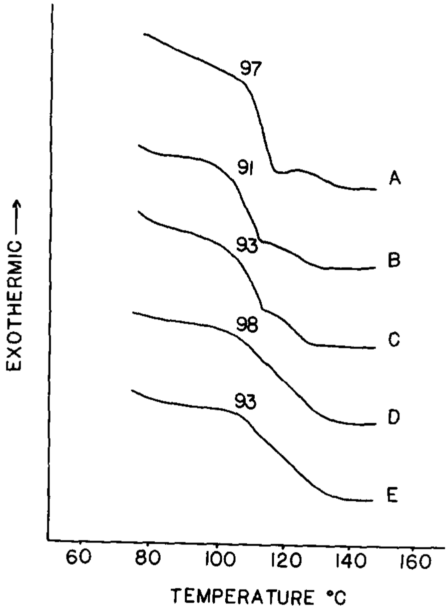

Figure 5. DSC scans of polystyrene model polymers at 20°C per minute, showing values of T_g (°C) obtained from extrapolation to 0°C per minute heating rate. A. 25% microgel and 75% in-situ polymerized styrene; B. 25% microgel, 25% linear polystyrene, 50% in-situ polymerized styrene; C. 50% microgel, 50% in-situ polymerized styrene; D. poly(styrene-co-divinylbenzene) microgel containing 5% dvb; E. 50% linear polystyrene, 50% in-situ polymerized styrene.

Conclusions

A convenient method for the preparation of model glassy inhomogeneous polymer networks has been demonstrated in which the variables of nodule size, size distribution, concentration and degree of matrix interpenetration may be controlled precisely over broad ranges. Once prepared, the networks may be studied for a variety of properties and may be employed to check the techniques used to characterize network inhomogeneities in glassy thermosetting resins. Fracture studies indicate that nodule concentration is quite important in determining the fracture toughness, but that nodule size, in the range of 80 to 180 nm diameter, has no significant effect over a wide concentration range. While the model network system differs from epoxies in the details of polymer backbone structure, it does clearly demonstrate the probable consequences of the hypothetical inhomogeneities often described in the literature for epoxies. Further studies are needed using the range of variables in structure accessible in the model system to validate low-angle x-ray and thermal transition evidence for inhomogeneous networks.

Acknowledgement

Support by the Air Force Office of Scientific Research and the Owens-Corning Fiberglas Corporation is gratefully acknowledged.

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Accepted May 19, received Springer-Verlag May 26, 1982 *K*