

NOTES

Mechanical Properties of a Glassy Epoxide Polymer: Effect of Molecular Weight Between Crosslinks

Introduction

In two recent papers^{1,2} the characterization of the molecular weight between crosslinks of a series of amine-cured epoxide polymers was described. The present note describes room-temperature mechanical measurements on the same epoxide polymer series and discusses the results in terms of the molecular weight between crosslinks. The mechanical measurements include ultimate tensile strength, ultimate elongation, initial modulus, and notched Izod impact strength. These results are compared with previously reported dynamic mechanical measurements on the polymers.

A substantial effect of the rate of stress application on the data is observed; this should be taken into account when considering highly crosslinked glassy polymers for specific uses.

Experimental

The sample series was prepared by varying the ratio of Epon 828* to the methylene dianiline (MDA) curing agent. The amount of MDA used was -6% to $+98.6\%$ of the stoichiometric amount. The MDA was melted and mixed with the diepoxide at 100°C and then a sheet was cast on a glass plate which had been previously treated with mold-release agent. The sheets were typically $1/8$ in. thick. After curing in an air oven 45 min at 60°C , 30 min at 80°C , and finally $2\frac{1}{2}$ hr at 50°C , the samples were allowed to cool slowly to room temperature and were carefully machined to the shapes required for the mechanical tests. It had been determined previously that the curing reaction in these samples was essentially complete; some data relevant to preparation of the sample series is presented in Table I. The curing procedure is described in greater detail elsewhere.¹

The tensile properties were measured with an Instron tensile machine using the method outlined in ASTM D638-64T. The specimen geometry was that described as type I in the ASTM method, and the crosshead speed was 0.05 in./min. The tensile properties of two samples of each polymer were measured; the data were rejected if the break occurred other than in the gauge length or if there was any indication that the break was associated with a surface defect. An extensometer was used to monitor the strain. The samples were allowed to remain several days at room humidity before testing. The tests were conducted at $22 \pm 1^{\circ}\text{C}$.

The impact strength measurements were made by the method described in ASTM D256-56, method A. Five to ten specimens of each polymer were broken and the results were reported as foot-pounds of energy absorbed per inch of specimen notch depth. The standard deviation of the individual measurements from the average for a given polymer was between 0.025 and 0.030 for all but the highest excess amine levels. The samples were stored several days at $22 \pm 1^{\circ}\text{C}$ and approximately 65% relative humidity before testing.

* Trademark of Shell Chemical Co. The material is essentially the diglycidyl ether of bisphenol A.

The dynamic mechanical properties were measured with an Rheovibron viscoelastometer (Toyo Measuring Instrument Co.). The experimental procedure has been reported previously.²

Results and Discussion

The results of the tensile measurements are plotted as a function of the molecular weight between crosslinks in Figures 1, 2, and 3. The ultimate tensile strength is clearly unaffected by the distance between crosslinks. The initial modulus and ultimate elongation likewise appear to be not significantly affected, although there is some scatter in the data.

For a glassy, amorphous polymer the mechanism of deformation is thought to be predominantly the stretching of covalent and Van der Waal's bonds. Some motion of localized chain segments occurs, but there is little long-range cooperative motion of segments to relieve the stress.³ Thus, a given segment or small group of segments receives no substantial help from its neighbors on the chain, and it is unimportant whether a point many segments away is held rigid by a crosslink. The ability of the segments to endure the stress, and thus the tensile strength, is not greatly affected by the molecular weight between crosslinks, M_c . On the other hand, as crosslinks become very close

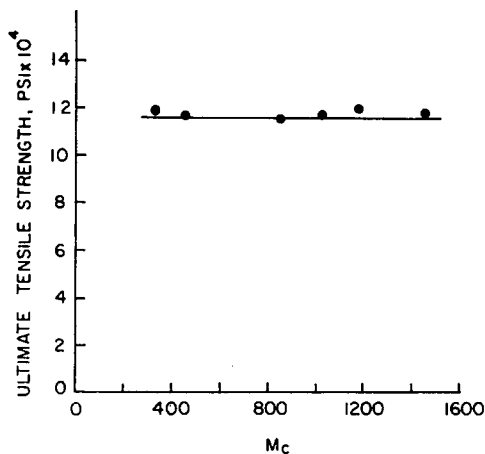


Fig. 1. Ultimate tensile strength as function of molecular weight between crosslinks, M_c .

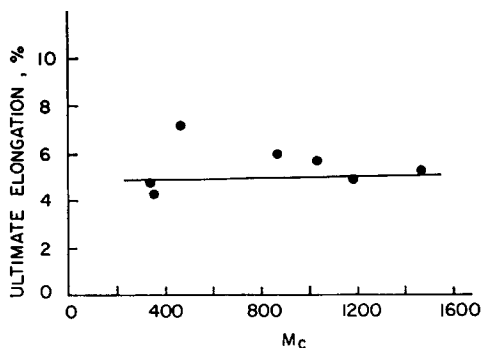


Fig. 2. Ultimate elongation as function of M_c .

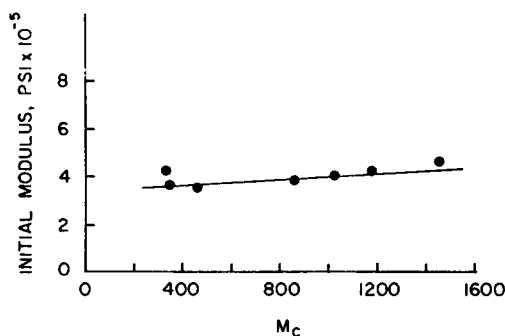


Fig. 3. Initial modulus as function of M_c .

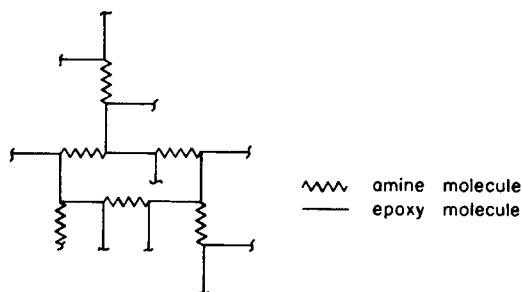


Fig. 4. Schematic representation of fully crosslinked epoxide-amine polymer.

together and their length becomes of the same general magnitude as the segment length, one might expect to see at least some effect of M_c on the tensile properties. For complete crosslinking of the present system (Fig. 4), M_c is approximately 320. However, from the data in Figures 1, 2, and 3 one observes that the tensile properties are unaffected even at this high crosslink density. This observation supports a deformation mechanism comprised of the stretching of primary and Van der Waals bonds.

One might also expect that at very high crosslink density internal stresses would be generated which would affect the tensile properties. This is apparently also not so in the present case, perhaps owing to the slow rate of cooling after crosslinking.

We know that for a low degree of cure the tensile properties of epoxide resins decrease relative to the properties at a high degree of cure. This observation is likely because of a low degree of polymerization and a large number of molecular ends which create a large amount of free volume, etc., rather than an increased molecular weight between crosslinks.

Thus far we have considered only tensile measurements in which the deformation is carried out at a very slow rate. We will next consider dynamic mechanical measurements at a frequency of 11 Hz and then, impact measurements in which the rate of loading is high.

The dynamic mechanical data, Figures 5 and 6, have been previously used to calculate M_c from the dynamic modulus 40°C above T_g .² Our present concern is with the values of $\tan \delta$, the elastic dynamic modulus E' , and the loss modulus E'' at room temperature, below T_g . Note that the value of $\tan \delta$, related to the energy-absorbing capability of the polymer ($\tan \delta = E''/E' \approx$ energy absorbed per unit of energy input, since $E' \gg E''$ at the frequency of testing), increases as the excess of amine (and the distance between crosslinks, Table I) increases. The dynamic modulus E' decreases as the amine excess

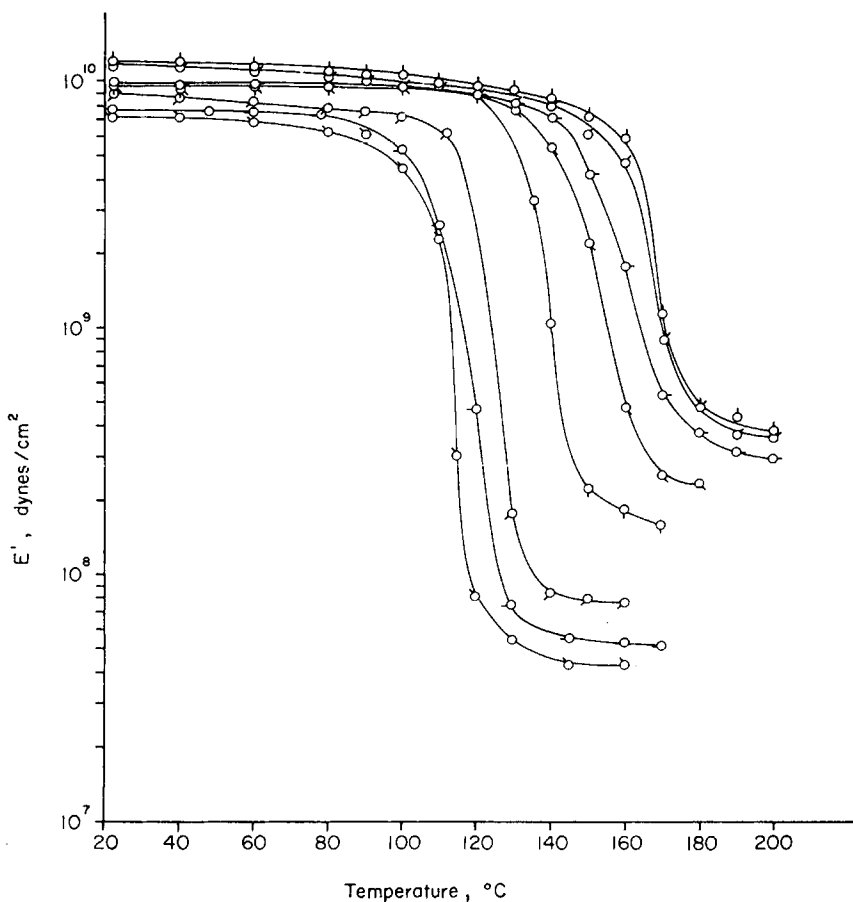


Fig. 5. Dynamic modulus E' as function of temperature: (\circ) 2.41% excess epoxy; (\odot) 5.96% excess epoxy; (\ominus) 11.64% excess MDA; (\square) 26.68% excess MDA; (\diamond) 46.20% excess MDA; (\circ) 65.61% excess MDA; (\circ) 85.04% excess MDA; (\circ) 98.57% excess MDA.

increases. One may conclude from these data that, at the loading rate corresponding to the 11 Hz frequency, the distance between crosslinks does have an effect on the material properties. The greater the distance between crosslinks, the greater the ratio of absorbed to input 11 Hz energy, and the lower the elastic modulus.

In the notched Izod impact test, the rate of loading is probably higher than in the dynamic mechanical tests, although the absolute loading rate is difficult to determine. One might expect that again the greater distance between crosslinks should give greater energy-absorbing capability and thus higher impact strength. This is experimentally observed, as seen from the data in Figure 7. As the molecular weight between crosslinks increases, there is more than a threefold increase in impact strength up to an M_c value of 1000–1100, at which time the impact strength drops rapidly. The reason for the rapid drop is not clear, although it may well be due to structural weakness associated with the small amounts of unreacted amine remaining at the high M_c values (Table I).

The reason for the observed sensitivity of the energy-absorbing capability to M_c as the rate of loading is increased is not readily apparent. One can rationalize that at the slow

TABLE I
 Sample Preparation and Characterization

Excess amine, %	Weight of amine, g	Weight of epoxide, g	Unreacted amine, ^a meq/g	M_c ^b
11.64	55.3441	192.0174	N.D.	375
26.68	62.8475	192.0000	N.D.	463
46.20	72.4717	191.9990	N.D.	662
65.61	82.0957	192.000	0.13	863
85.04	91.7270	191.8437	0.29	1032
94.84	96.5863	192.000	0.35	1183
98.57	98.4316	192.0095	0.33	1461
-2.41	48.4005	191.9993	N.D.	331
-5.96	46.7777	192.0120	N.D.	348

^a The unreacted epoxide was less than 0.07 meq/g in all cases; N.D. = not detectable.

^b Molecular weight between crosslinks from Bell.¹

loading rate of the tensile tests, both long and short sequences of backbone atoms will receive and dissipate energy, but the local energy is not great enough to break many of the Van der Waals bonds at any given time. At high rates of loading, however, the energy will be preferentially absorbed by short segments whose characteristic frequency corresponds to the rate of loading; the energy absorbed per unit time may be great enough to break the Van der Waals bonds temporarily, resulting in brief motion of segments

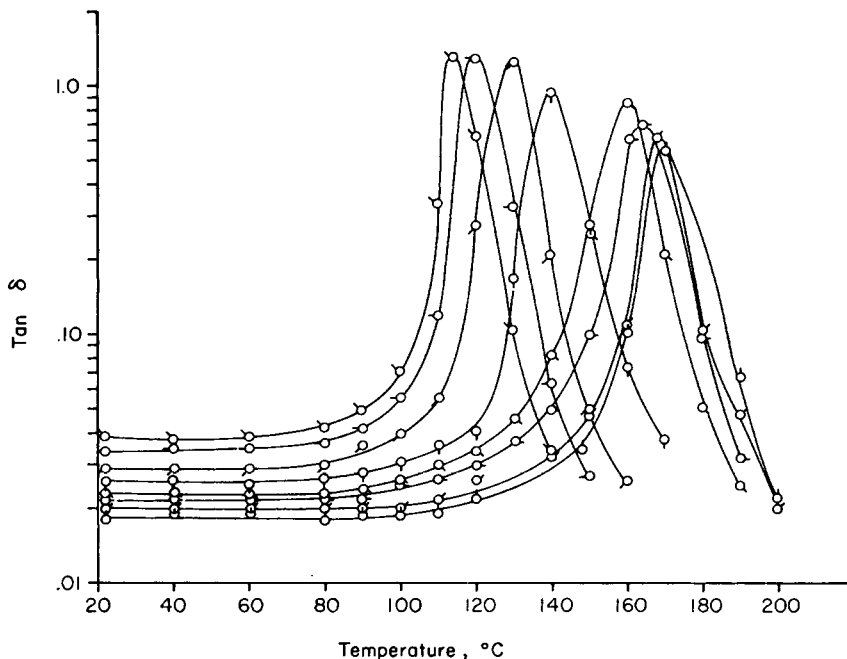


Fig. 6. $\tan \delta$ as function of temperature: (\circ) 2.41% excess epoxy; (\circ) 5.96% excess epoxy; (\circ) 11.64% excess MDA; (\circ) 26.68% excess MDA; (\circ) 46.20% excess MDA; (\circ) 65.61% excess MDA; (\circ) 85.04% excess MDA; (\circ) 98.57% excess MDA.

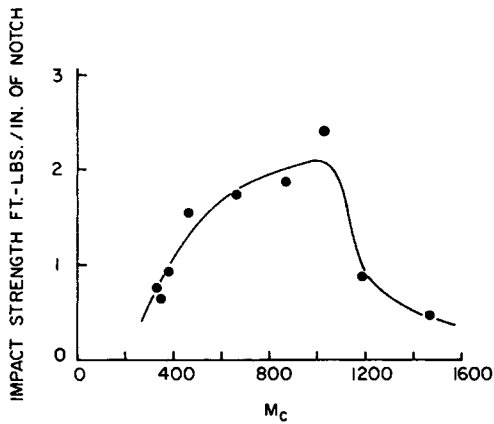


Fig. 7. Notched Izod impact strength as function of M_c .

between crosslinks. In that case the energy-absorbing capability is determined by the temporary mobility of the short segments, which is in turn influenced by the molecular weight between crosslinks.

While this view may have some merit qualitatively, it must be regarded as speculative at the present time.

References

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