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THE α RELAXATION IN EPOXY RESINS

G. A. POGANY
Shell Research Limited, Carrington Plastics Laboratory, Urmston, Manchester, England

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Abstract—Purified diglycidyl ether of Bisphenol A, crosslinked with polyamines in different ratios, has been used to investigate the effect of chemical structure and crosslink density on the modulus (G) and on the glass transition temperature (T_g). Bulky groups in the resin increase T_g more than they increase G either in the glassy or in the rubbery state. The rubber elasticity theory seems to be applicable even to these highly crosslinked systems.

INTRODUCTION

THE RELAXATION which involves a change in the properties of the resin from the glassy to the rubbery state is called the α relaxation.(1) It is associated with the onset of co-operative motion of a large number of molecular segments.(2) The effect of chemical structure on the α relaxation in epoxy resins has been investigated by Nowak and Steinbacher,(3) Kaelble,(4) Blinne and Möller,(5) Jellinek(6) and Katz and Tobolsky.(7) They used different resin systems and drew the general conclusions that the stiffer and bulkier the crosslinking molecule, the higher the glass transition temperature (T_g) of the resin.

With one exception,(7) however, no serious attempt has been made to investigate the effect of structure on the rubbery modulus G_r. With the same exception, all other workers used commercial resins of unknown purity and an arbitrary cure schedule. It was therefore necessary to carry out a comprehensive study of the various parameters which influence the α relaxation in epoxy resin.

The present paper is based on measurements of the viscoelastic properties of epoxy resins in the α region. The specimens have been cast from specially purified monomer and have been fully cured above their respective T_g, the importance of which will be discussed separately.(8) The main purpose of this paper is to examine the effect of chemical structure and crosslink density on T_g and on the rubbery modulus G_r in epoxy resins.

DESCRIPTION OF TECHNIQUE AND SPECIMEN PREPARATION

(*a*) *The experimental technique*

Measurements were carried out with a torsion pendulum employing free vibration at 0·67 c/s frequency. The specimen was rigidly clamped at its lower end, while a steel tube leading to the inertia arm was attached to its upper end. The moment of inertia of the system could be increased by placing pairs of steel ball bearings on the inertia arm at various positions. The weight of the tube and arm was counter-balanced by a lever mechanism, which supported the arm by a wire.

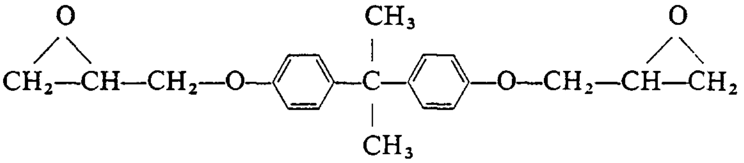
Initially use was made of a single wire which had enough tensile strength to support the assembly. It was found, however, that the rigidity of this wire was comparable to the rigidity of the specimen when it was in the rubbery region and this led to inaccuracies. Subsequently this single wire was replaced by a composite of 16 thin wires with the same total cross-section area. As the tensile strength of a wire is proportional to the second power and its rigidity to the fourth power of the radius, the change resulted in a great reduction of rigidity without any loss of tensile strength.

The specimen was protected by a copper tube, which was immersed in a thermostat. The shear modulus G and the logarithmic decrement δ of the specimens were determined between −180° and +250°. A more detailed description of the techniques and of the methods of calculation can be found elsewhere.(9)

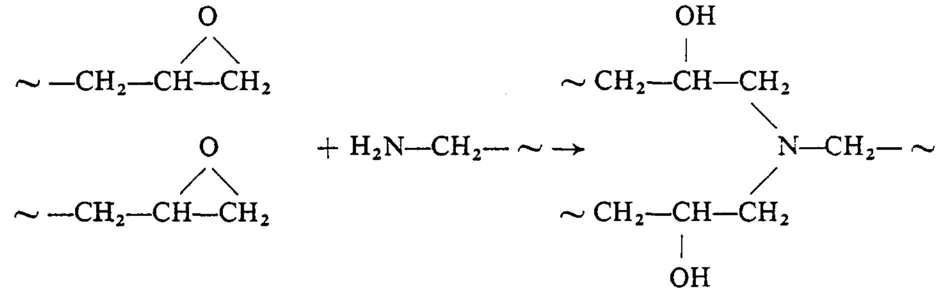
(*b*) *The monomer and curing agents*

The epoxy monomer used in this investigation was the purified diglycidyl ether of bisphenol A. The curing agents used were aliphatic and aromatic polyamines (see Table 1).

It is known(10) that during the uncatalysed cure of epoxy monomers by polyamines the only reactions which take place are those between the epoxy and amine groups. This makes the system very suitable for studying the effect of crosslink density on various properties.



Diglycidyl ether of bisphenol A



Reaction between epoxy and amine groups

(*c*) *Casting and curing of specimens*

All the specimens cast during the investigation are listed in Table 1. The term "phr" refers to parts wt. per 100 parts wt. of basic epoxy monomer. The resin was stirred both during and after the slow addition of the curing agent in a glass beaker. The mixture was transferred into another beaker and the residues on the side of the first were scraped into the second under continuous stirring, to overcome any preferential wetting of the glass by one of the components. The mixture was poured into an aluminium container to the depth of a few millimetre and allowed to cure.

After 1 week curing at room temperature, the container was heated for the time and at the temperature recommended by the resin manufacturers to complete cure.

All specimens were machined out of the cured block to an approximate size of 10 × 1 × 0·15 cm and the actual size carefully measured to the nearest 0·001 cm. Finally all specimens were heated above their respective T_g in the torsion pendulum, until the measured values of G_r were reproducible.

TABLE 1. THE LIST OF CASTINGS FROM DIGLYCIDYL ETHER OF BISPHENOL A

Specimen number	Curing agent used			Temp. of mixing (°C)
	Composition	Code	phr	
1	Diethylene triamine	DETA	4	25
2	Diethylene triamine	DETA	8	25
3	Diethylene triamine	DETA	10	25
4	Diethylene triamine	DETA	12	25
5	Diethylene triamine	DETA	14	25
6	Diethylene triamine	DETA	16	25
7	Diethylene triamine	DETA	20	25
8	Ethylene diamine	EDA	9·0	25
9	1,3 Diamino propane	PDA	10·9	25
10	1,4 Diamino butane	DAB	12·9	25
11	1,5 Diamino pentane	DAP	15·0	25
12	1,6 Diamino hexane	DAH	17·1	50
13	Diamino diphenyl methane	DDM	28·7	100
14	Diamino diphenyl sulphone	DDS	40	140

THE EFFECT OF CHEMICAL COMPOSITION ON THE α RELAXATION

The effect of chemical structure on T_g and on G_r has been investigated by using the same epoxy monomer with different crosslinking agents. These crosslinking agents contained either aromatic or aliphatic units, and in the case of the latter, their length has been varied. The crosslink density within the same resin composition was controlled by the curing agent concentration which was maintained at stoichiometric ratios.

(*a*) *The chemical composition of the crosslinking molecule*

The effect of three crosslinking agents have been compared: DETA (an aliphatic polyamine) DDM (an aromatic diamine) and DDS (another aromatic diamine). All resins were cast using stoichiometric compositions details of which are given in Table 1 (specimens 4, 13 and 14).

Plots of the moduli against the temperature of these three resins after complete cure are compared in Fig. 1. The values for the glass transition temperature were taken as the peaks of the damping curves (not shown) and are tabulated in Table 2 together with values of the unrelaxed moduli G_u at 25° and the relaxed or rubbery moduli G_r at 200° (extrapolated as in Fig. 4).

It can be seen that T_g is highest when the crosslinking molecules consists of mainly aromatic groups. The rubbery modulus, however, is highest in the case of the aliphatic amine, and there is little difference in the unrelaxed moduli of the three resins at 25°.

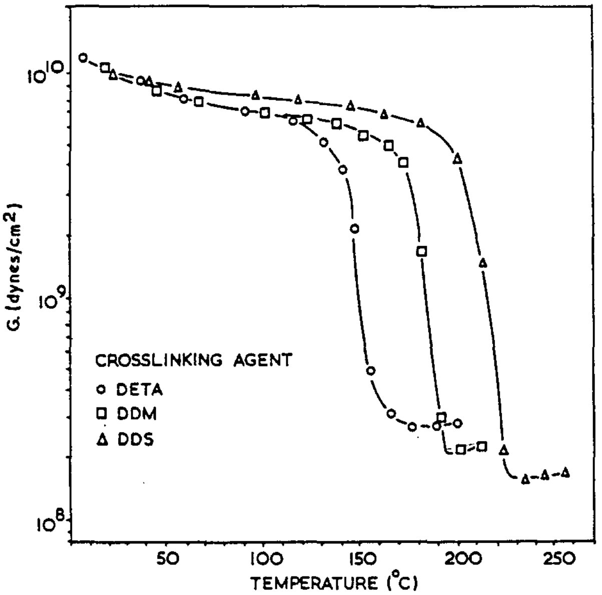


FIG. 1. Effect of the crosslinking agent composition on the modulus–temperature relationship for the resin.

TABLE 2. T_g, G_u AND G_r IN EPOXY RESINS CAST WITH DIFFERENT POLYAMINES USING STOICHIOMETRIC RATIOS

Crosslinking molecule and formula		G_u at 25°C $\times 10^{-10}$ dynes/cm²	G_r at 200°C $\times 10^{-8}$ dynes/cm²	T_g (°C)
1,6 Diamino hexane	NH_2—$(CH_2)_6$—NH_2	0·85	1·70	123
1,5 Diamino pentane	NH_2—$(CH_2)_5$—NH_2	1·00	1·80	130
1,4 Diamino butane	NH_2—$(CH_2)_4$—NH_2	0·90	1·60	132
1,3 Diamino propane	NH_2—$(CH_2)_3$—NH_2	0·95	2·00	142
Ethylene diamine	NH_2—$(CH_2)_2$—NH_2	1·00	2·00	145
Diethylene triamine	NH_2—$(CH_2)_2$—NH—$(CH_2)_2$—NH_2	1·00	2·60	155
Diamino diphenyl methane	NH_2—⌬—CH_2—⌬—NH_2	0·95	2·00	184
Diamino diphenyl sulphone	NH_2—⌬—SO_2—⌬—NH_2	0·95	1·40	220

(*b*) *The length of an aliphatic crosslinking molecule*

Katz and Tobolsky[(11)] investigated the effect of different crosslinking molecules by examining the series of ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine. There was no appreciable difference in the modulus–temperature curves of any of these resins.

In that series, however, after each $(CH_2)_2$ unit there was an NH group, which resulted in a crosslink. To eliminate this middle crosslink, a series of α,ω-diamines have been examined with the general structure of

$$H_2N\text{—}(CH_2)_n\text{—}NH_2$$

where "*n*" has been caried from 2 to 6. (See Table 1, specimens 8, 9, 10, 11 and 12.)

Figure 2 shows the modulus G of these polymers as a function of the temperature. For clarity, only two limiting curves ($n = 2$ and $n = 6$) have been connected by lines as all the other points would fall between them. The effect of changing "n" from 2 to 6 reduces T_g by about 25°, with a corresponding reduction in the moduli in both the glassy and rubbery regions. The values for T_g have again been taken as the peaks of the damping curves (not published here) and included in Table 2 together with the values of G_u and G_r.

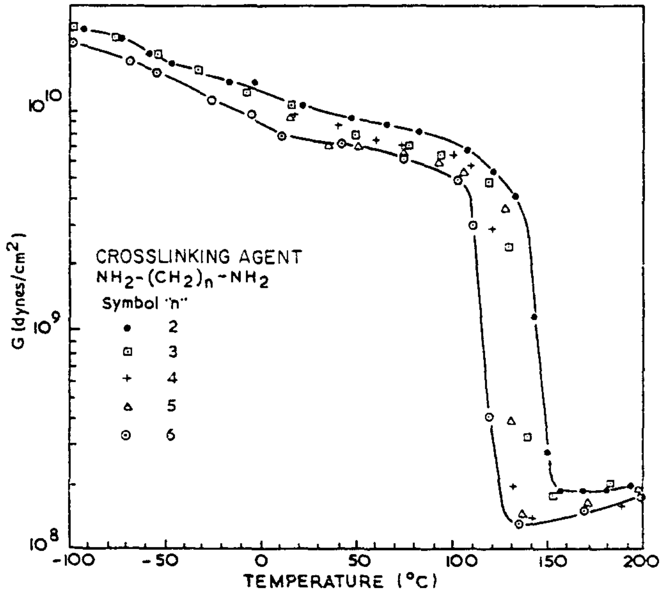


FIG. 2. Effect of the length of the crosslink on the modulus–temperature relationship for the resin.

It can be seen from Table 2 that the effects of chain stiffness on T_g is more significant than its effects on G_u or G_r. The fact that chain stiffness influences T_g is known for many linear polymers.(12) This investigation provides evidence that stiffness of segments have similar influence on the T_g of crosslinked resins.

A somewhat similar experiment has been conducted by Kwei(13) who used 1,9-diaminononane, 1,6-diaminohexane, ethylene diamine and diethylene triamine curing agents. Kwei observed a qualitatively similar effect to that reported in this paper, his actual values of T_g however, are in error. This is because his resins were cured at a maximum temperature of only 70°, which is not enough to complete the cure.(8) What Kwei in fact observed was an upward shift of the glass transition temperature owing to the heat of the experiment itself. Of course, solvent extraction could not reveal the degree of undercure as most molecules were already connected to the network.(8)

The undercure in Kwei's experiment can also explain the anomalous results of his measurements of moduli. The reported fall of modulus at the so-called T_g is of the order of ½ decade only and the so-called rubbery moduli do not increase with the temperature. It is unfortunate that Kwei stopped his experiments at about 110° just short of the true glass transition.

It is concluded that the temperature at which a polymer chain can relax depends on all the restrictions in the way of its relaxation. These restrictions may not influence G_u or G_r which, by definition, are measured at temperatures where mobility is either negligible or already large.

THE EFFECT OF CROSSLINK DENSITY ON THE α RELAXATION

The crosslink density in the amine cured epoxy resin can be controlled by the curing agent concentrations.

Five resins have been prepared using diethylene triamine (DETA) in different ratios. These ratios were 4, 8, 10, 12 (stoichiometric amount) 14, 16 and 20 per cent DETA. (See Table 1, specimens 1 to 7.) Figure 3 shows the resultant G of five of these resins as a function of the temperature.

T_g is the highest for the stoichiometric composition (12 per cent DETA), and excess of either component reduces the temperature of the inflexion point of the modulus curve. This is in line with the observed effect of curing agent concentration on other physical properties.(14) The rubbery modulus G_r also changes with the amount of crosslinking agent, being highest at the stoichiometric composition. Similar results

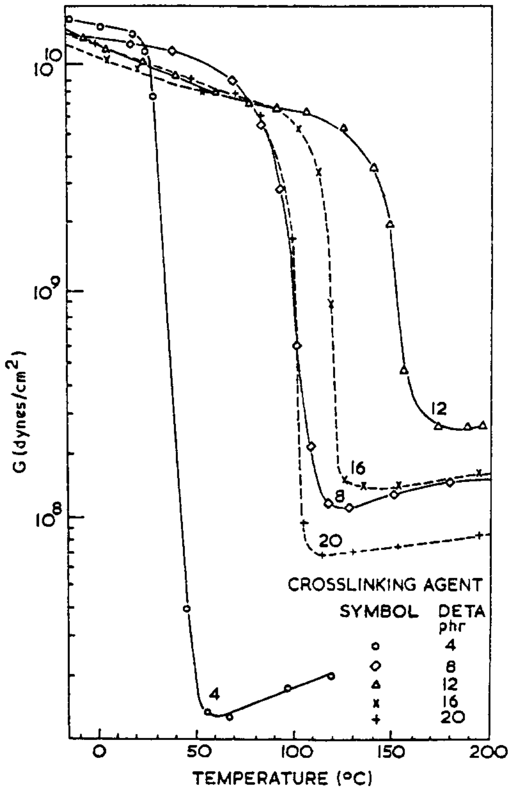


FIG. 3. Effect of the crosslinking agent concentration on the modulus–temperature relationship for the resin.

have been obtained when curing agent DDM (diamino diphenyl methane) has been used in excess to the stoichiometric amount.

(*a*) *The relationship between crosslinking density and G_r*

The crosslink density can be defined by M_c, the molecular weight between crosslinks. This is related to G_r by the classical equation of rubber elasticity.(15)

$$G_r = NkT = \rho\, RT/M_c \qquad (1)$$

where G_r is the shear modulus,
N the number of chains per unit volume,
k the Boltzmann constant,
ρ the density,
M_c the number average chain mol. wt.
R and T have their usual meanings.

G_r is therefore a linear function of the absolute temperature and should be zero at 0°K; Eqn. (1) is valid only if there is a Gaussian distribution of chain segments between crosslinks, a condition which is fulfilled only if there is a large number of rotating links between crosslinks.

The value of M_c in a fully crosslinked epoxy resin made from diglycidyl ether of bisphenol A and DETA should be the mol. wt. of the epoxy monomer, i.e. 340. This ignores the two CH_2 units between the nitrogens of the amine and considers one amine molecule as a single point of crosslink. The number of rotating links is only 12, and on this basis the quantitative relationship of Eqn. (1) is not expected to be valid in this resin.

The rubbery moduli G_r for the various resins have been plotted against the absolute temperature in Fig. 4 and the results are reasonably consistent with the concept that the relationship is linear and that the lines go through the origin. The reason for small discrepancies is that at the elevated temperatures the resins degrade, and this increases G_r as will be demonstrated in another publication.(19)

The theoretical value of G_r in the fully crosslinked resin (12 DETA) at 200° as calculated from Eqn. (1) is $1{\cdot}33 \times 10^8$ dyn/cm^2. The measured value is $2{\cdot}60 \times 10^8$ dyn/cm^2, i.e. 1·95 times greater, which is in good agreement with the value measured by Katz and Tobolsky(7) of 1·87 times for the same resin.

TABLE 3. A COMPARISON OF RESINS MADE WITH DIFFERENT AMOUNTS OF DIETHYLENE TRIAMINE

Specimen number	DETA conc. phr	$G_r \times 10^{-8}$ dynes/cm^2 at 200°C	M_c calculated from G_r	T_g °C
1	4	0·20	2320	45
2	8	1·42	322	100
3	10	1·88	243	115
4	12	2·60	176	155
5	14	2·32	197	148
6	16	1·50	300	117
7	20	0·82	550	105

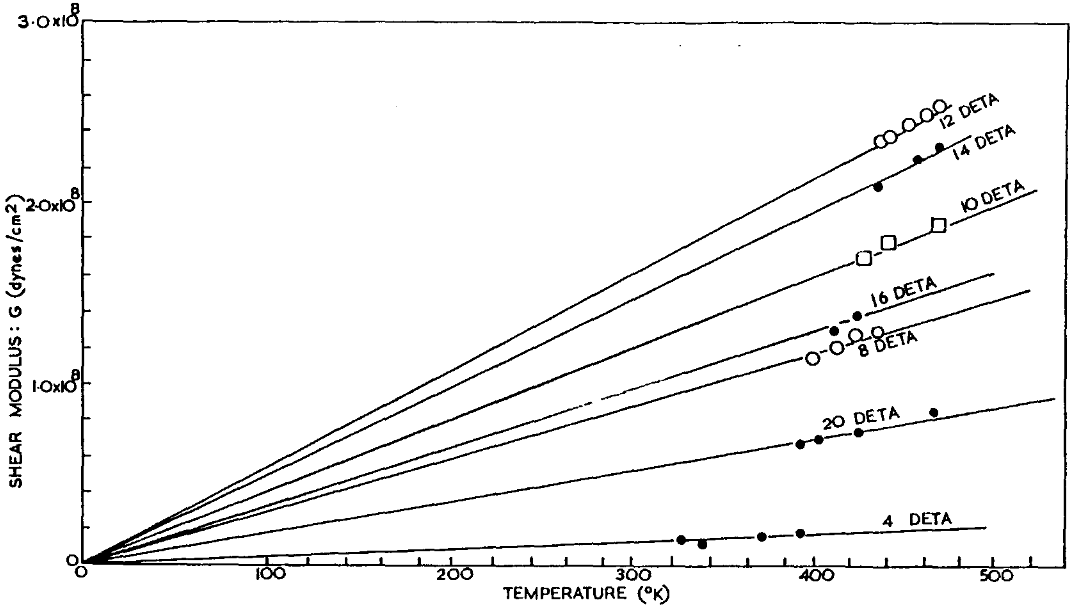


FIG. 4. Modulus–temperature relationship for different resin compositions in the rubbery region.

Katz and Tobolsky(11) found reasonable agreement between the measured and calculated values of G_r for another crosslinked resin where the number of units between crosslinks was reduced to 10. However, the measured moduli were greater than that of the theoretical. Table 3 shows the measured dependence of G_r and M_c on the curing agent (DETA) concentrations. The measured values of the temperature of the α peaks are taken to be T_g and are also included in the Table for later use. The values of M_c calculated from the measured values of G_r should be compared with the actual values of M_c in the resins, however, in a loosely crosslinked resin, M_c is not readily available. It would be of interest to establish the statistically most probable network of these systems.

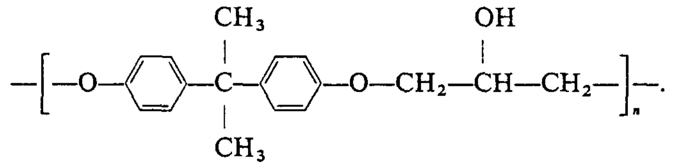
(b) The relationship between crosslink density and T_g

The rubber elasticity theory provides an excellent quantitative relationship between crosslink density and G_r, but there is to date no satisfactory theory relating T_g to crosslink density. An empirical relationship was first found by Ueberreiter and Kanig,(16) and later confirmed by Fox and Loshaek,(17) who observed an increase in T_g with an increase in crosslink density.

In a more recent paper, Heinze *et al.* presented experimental data on changes in T_g with increased crosslink density in rubber.(18) At first, there is little increase in T_g with a reduction in chain length between points of crosslinks. If, however, the chain length is reduced below 50 carbon atoms, T_g begins to rise more and more with crosslinking.

In the above paper the crosslinks were introduced into already high mol. wt. linear polymers, which is not the case in epoxy resins. A direct comparison of T_g and M_c in the series of epoxy resins examined is complicated by the fact that both polymerization and crosslinking progress simultaneously. It is necessary therefore first to establish what would be the value of T_g in the uncrosslinked homopolymer of the epoxy monomer at infinite mol. wt.

A commercially available polymer with a similar structure is Phenoxy resin® having the form



With a mol. wt. of approximately 25,000, this polymer can be considered a non-crosslinked homopolymer of the epoxy nonomer. G and δ of a compression moulded specimen has been measured at different temperatures (not shown here) and 100°, the temperature of the α peak, is taken as T_g of the homopolymer.

The relationship between T_g and the crosslink density (M_c) can now be examined in Fig. 5. Values of T_g, the temperature of the α peak in the resins with different degrees of crosslinks, are taken from Table 3. Since actual values of M_c are not known the values calculated from the measured values of G_r (also in Table 3) are used. T_g of the non-crosslinked homopolymer is taken to be 100° as discussed before. The lightly crosslinked resin with 4 phr DETA, has been omitted from the curve. This

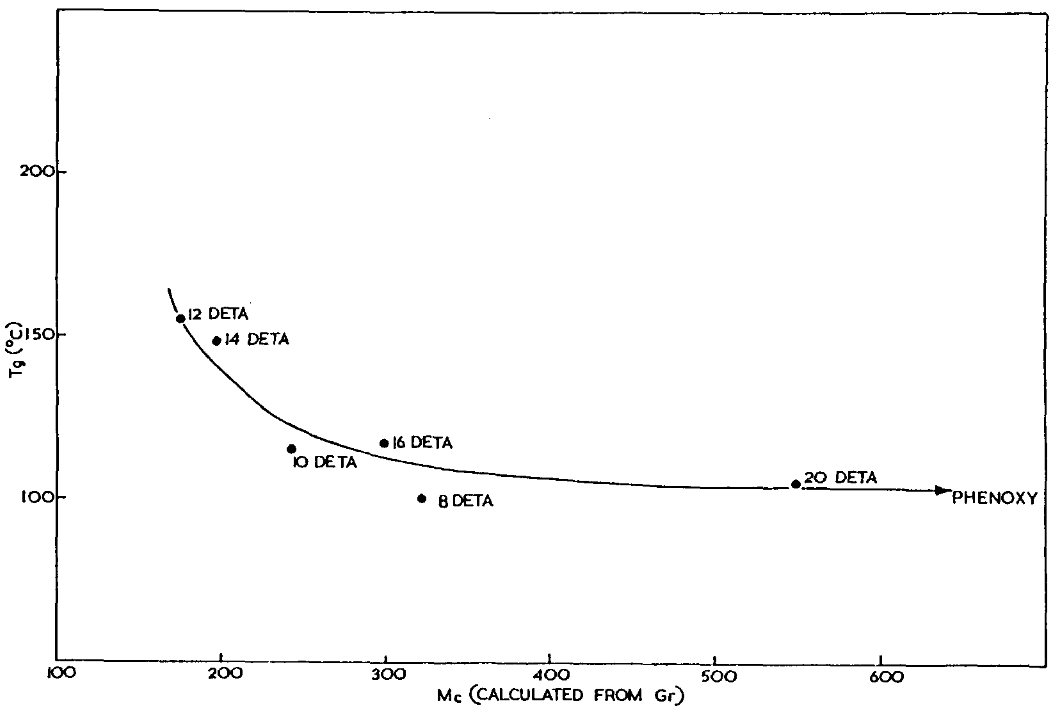


Fig. 5. Relationship between T_g and M_c in resins made from diglycidyl ether of bisphenol A by amine cure.

resin has its T_g nearer to the melting point of the monomer than to the T_g of the homopolymer, because it has a large number of unreacted epoxy monomers and a low degree of polymerization.

The relationship between T_g and M_c, as presented in Fig. 5, is similar to that reported by Heinze *et al.* for rubber,(18) i.e. small amount of crosslinks have little effect on T_g until M_c is reduced below a critical value. The critical value of M_c in this case appears to be ~ 300, which is very close to 340, the theoretical M_c in the fully crosslinked resin.

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Résumé—L'éther diglycidylique purifié du bisphénol A, réticule avec des polyamines en différentes proportions a été utilisé pour étudier l'effet de la structure chimique et de la densité de pont sur le module (G) et la température de transition vitreuse (T_g). Des groupements volumineux fixés sur la résine accroissent T_g plus qu'ils n'accroissent G que ce soit à l'état vitreux ou caoutchoutique. La théorie de l'élasticité caoutchoutique semble être applicable même à ces systèmes fortement réticulés.

Sommario—Etere diglicidile purificato di bisfenolo A a legame incrociato con poliammine in rapporti differenti, è stato usato per studiare l'effetto della struttura chimica e della densità del legame, sul modulo (G) e sulla temperatura di transizione vetrosa. Gruppi centrali nella resina aumentano T_g più di G sia allo stato vetroso che gommoso. La teoria dell'elasticità della gomma sembra essere applicabile anche a questi sistemi con molti legami incrociati.

Zusammenfassung—Gereinigter Diglycidyläther von Bisphenol A, vernetzt mit Polyaminen in verschiedenem Verhältnis, wurde verwendet, um den Einfluß der chemischen Struktur und der Vernetzungsdichte auf den Modul (G) und auf die Glasübergangstemperatur (T_g) zu untersuchen. Sperrige Gruppen in dem Harz erhöhen T_g stärker als G, sowohl im glasähnlichen als auch im kautschukartigen Zustand. Die Theorie der Kautschukelastizizät scheint selbst auf diese hoch vernetzten Systeme anwendbar zu sein.