Transitions in Epoxy-Diamine Networks

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SUMMARY

A comparison has been made of relaxation regions determined using a torsion pendulum and transition regions using an infrared spectrophometer of a series of epoxy-α,ω-diamine networks. This has allowed assignment of the mechanical relaxations to discrete portions of the molecular framework. It appears that the hydroxyl groups do not significantly affect the mechanical relaxations in the cross-linked network.

INTRODUCTION

A previous paper [1] shows the mechanical loss spectrum for a series of networks formed from the diglycidyl ether of 2,2-bis(4'-hydroxyphenyl)-propane (I) and a series of α,ω-diaminoalkanes containing 2, 3, 4, 5, 6, 8, 10, and 12 methylene units.

A further paper [2] shows the variation of the hydroxyl stretching frequency in the infrared spectra of the same materials from 60-160°C. The present work extends the IR results down to -100°C and allows the mechanical and spectral results to be compared.

EXPERIMENTAL

The resin used was Epon X22 supplied by Shell Chemical (Australia) Pty. Ltd. It had a melting point of 42-43°C and contained 0.043% chlorine. Samples were prepared by mixing the resin and the stoichiometric amount of amine at 60°C, sandwiching a small amount between potassium bromide disks and curing for 20 hr at 60°C, followed by 2 hr at 200°C. Samples are referred to by a code number of "C" followed by the number of methylene units in the alkylidene chain of the diamine, e.g., the system cured with hexamethylene diamine is referred to as "C6."

The low temperature IR cell consisted of a heated block surrounded by a reservoir of liquid nitrogen. The temperature could be controlled to within ±0.2°C. Spectra were determined on a Perkin-Elmer 521 spectrophometer.

RESULTS AND DISCUSSION

Figure 1 shows the results for the wavenumber of the position for the hydroxyl stretching peak as a function of temperature for systems C2, C3, C5, C6, and C10 from -100 to 160°C. It will be seen that systems C3, C5, C6, and C10 show transitions of the hydroxyl group in the region -10 to 50°C and around the glass transition temperature. The C2 system shows an additional transition near -25°C.

Table 1 summarizes results of mechanical and spectral investigations. Mechanical results in the table refer to the temperatures of the maxima in plots of loss modulus (G″) against temperature, and spectral results refer to the points of inflection of the wavenumber for hydroxyl absorption against temperature plots.

THE NATURE OF THE HYDROGEN BOND

As the IR spectra showed no absorption peak near 3600 cm^{-1} it can be concluded that the majority of the hydroxyl groups are bonded to some extent over the temperature range examined. It has been suggested [2] that, due to the low concentration of hydroxyl groups and the restricted motion of the polymer molecules, hydrogen bonds between sections of the molecule separated by one or more of the diphenylpropane units (long range bonds) are unlikely.
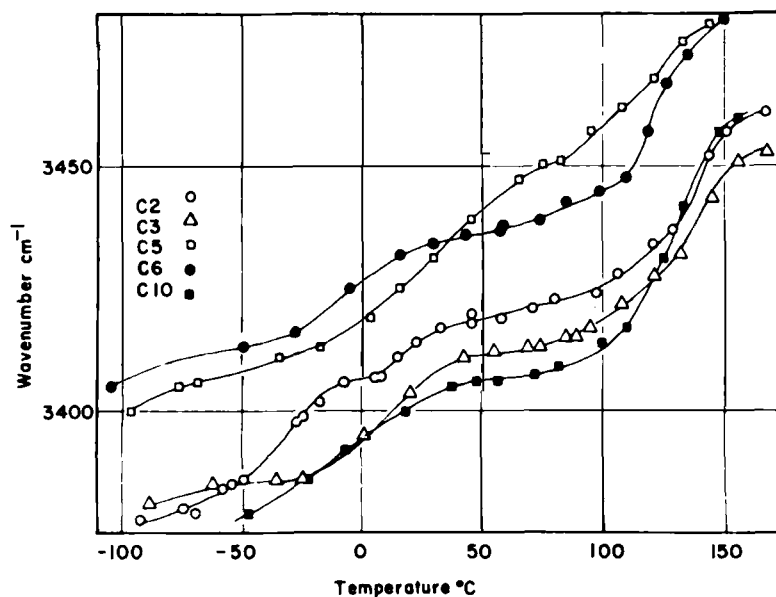
Fig. 1. The wavenumber of the hydroxyl stretching peak as a function of temperature for epoxy resin (I) cured with α,ω-diaminoalkanes.

In order to investigate this more fully a network was prepared using epoxy resin (I) and N-methylethylene diamine. Figure 2 shows the hydroxyl stretching frequency as a function of temperature for this sample and for the C2 and C5 systems.

If the polymer derived from unsubstituted ethylene diamine contained a significant number of long-range hydrogen bonds, decreasing the functionality of the diamine, and hence the cross-link density, would be expected to result in more efficient packing of the less sterically hindered and more mobile chains resulting in the formation of stronger hydrogen bonds. It is observed that decreasing the functionality of the diamines results in a shift of the graph to higher wavenumber indicating the presence of markedly weaker hydrogen bonds. The resin concentration in the trifunctional C2 system is similar to that of the C5 system which forms, however, markedly stronger bonds than the substituted C2 system. Consequently, the steric requirements of the bulky immobile diphenylpropane unit cannot be the main cause of the weakening of the bond between the tri- and tetrafunctional C2 systems. It is suggested, therefore, that the network does not contain a significant number of interchain hydrogen bonds.

Table 1. Temperature of Mechanical Relaxations and Hydroxyl Transitions for a Series of Epoxy-Diamine Networks

System	Mechanical[a,b]				Spectral[a,b]		
	Polymeth	Glyc. A[c]	Glyc. B	T_g[d]	Glyc. A'	Glyc. B'	T_i[e]
C2	<-125	-55	30	150	-30	12.5	140
C3	<-125	-55	30	127	Nil	13	134
C4	<-125	-60	30	126	ND[f]	ND	125
C5	<-125	-50	30	122	Nil	30	122.5
C6	<-125	-60	25	119	Nil	-12	120
C8	<-125	-55	30	109	ND	ND	126
C10	<-125	-60	35	103	Nil	-15	129
C12	<-125	-60	30	98	ND	ND	137

a All temperatures in degrees centigrade.
b Relaxations and transitions are grouped according to assignment (see below).
c Glyc. = glycidyl.
d Glass transition temperature defined by the temperature at which $G' \cong 10^9$ as loss maximum not determined.
e The main hydroxy transition in the region of T_g.
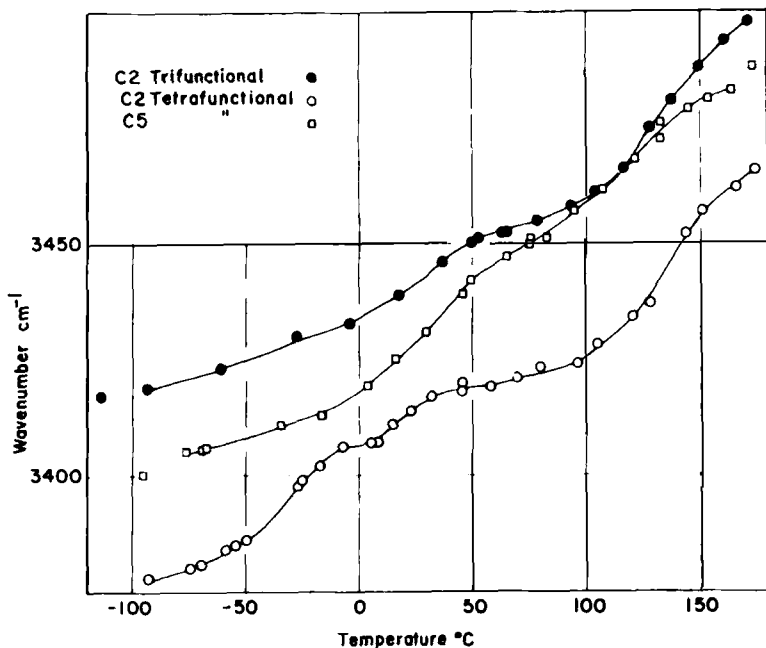f Not determined.

Fig. 2. The wavenumber of the hydroxyl stretching peak as a function of temperature for epoxy resin (I) cured with ethylene diamine, N-methyl ethylene diamine, and pentamethylene diamine.

This conclusion is in agreement with the observation that for C8, C10, and C12 systems the polymer can undergo the glass transition with the associated major change in molecular freedom without significantly affecting the hydroxyl absorption frequency.

Figure 3 shows the structure of the polar region of the network.

Several short range bonds may be postulated within this system:

Type A. Between the hydroxyl group and the nearest nitrogen.

Type B. Between the hydroxyl group of the α-chain and the oxygen of the hydroxyl group of the β-chain.

Type C. Between the hydroxyl group and the nearest aryl-alkyl ether oxygen.

Type D. Between the hydroxyl group of the α-chain and the nitrogen joining the α' and β' chains.
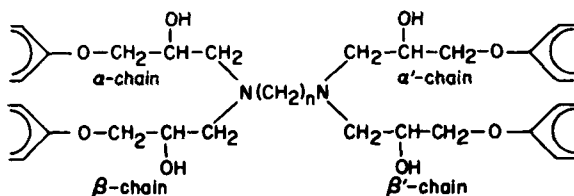
Fig. 3. The polar section of the epoxy-diamine network.

Hydrogen bonds of Types A, B, and D cannot describe all of the bonds formed and it is postulated that residual hydroxyl groups form Type C bonds.

Hydroxyl transitions can occur either within one bond type if the equilibrium distance between donor and acceptor groups changes or from one type to another.

Transition regions will be discussed in turn.

THE GLASS TRANSITION REGION

Mechanical Relaxations

A number of workers have studied the dynamic mechanical properties of epoxy resins. Their results have been reviewed [1]. The major loss peak normally occurs over 100°C for widely differing derivatives of 1, for example, systems cured with aliphatic diamines [1], aromatic diamines [3, 4, 7], anhydrides [4, 5], and linear systems formed by condensation of 1 with 2,2-bis(4'-hydroxyphenyl)propane [6]. In these studies the diphenylpropane unit could not be associated with any of the minor relaxation regions in the polymer. Changes in the structure and arrangement of the propane group bridging the aromatic groups results in large changes of T_g but not of other loss peaks [4]. The use of epoxy resins without rigid aromatic rings, such as 1,4-butane diglycidyl ether, has been shown to reduce T_g to 0-10°C without affecting other relaxations [7].

It is postulated that the glass transition is initiated by the onset of mobility within the bulky diphenylpropane units.

Spectral Transitions

Spectral results near the glass transition temperature have been considered in detail [2].

It was postulated that for the C3, C4, and C5 systems a stress is imposed by the methylene units of the diamine on the nitrogen bridge, forcing the close approach of the hydroxyl groups of the α and β chains, which consequently form a stable Type B hydrogen bond. Increase of the number of methylene units decreases the stress and decreases the strength of the hydrogen bond. At T_g, the aromatic portions of the molecule become free to move, relaxing the stress and causing the hydrogen bond to weaken markedly or to rearrange to give Type C bonds.

For the C6, C8, C10, and C12 systems the stress imposed by the alkylidene chain is insufficient to force the close approach of the hydroxyl bonds and a bond of Type A forms between the hydroxyl and the neighboring nitrogen atom. Increase of the number of the methylene groups in the diamine results in an increase of the freedom of the nitrogen atom and an increase in the strength of the hydrogen bond. The onset of mobility of the phenyl units at T_g has little effect on the hydrogen bond which persists until thermal energy becomes sufficient to initiate the transition.

The C2 system presents an anomaly. It is of generally similar shape to the C3, C4, and C5 systems but is shifted to higher wavenumber and lies between C3 and C4. The effect of ring size on the stability of intramolecular hydrogen bonds in model compounds has been reviewed [8]. There is a marked decrease in the strength and stability of bonds which result in formation of a ring with six intervening groups between the donor hydroxyl and the acceptor, compared to the equivalent system with five such groups. The C2 system alone can form a bond of Type D with five intervening groups. The equivalent system for C3 would contain six groups and would be comparatively unstable.

TRANSITIONS NEAR +25°C

Mechanical Relaxations

A loss peak has been observed in the region 25-50°C in systems with epoxy resin I cured with aliphatic diamines [1], with aromatic diamines [3, 4, 7], with anhydrides [4, 5], and in linear systems formed by condensation of I with 2,2-bis(4'-hydroxyphenyl)propane [6]. Variations of the exact placing of the peak may be ascribed to the differences between the frequencies used in the dynamic experiments used to define the loss peak. It has been shown [1] that the height of the loss modulus (G'') peak is proportional to the weight of the resin component in the cured system. Kline [3] has shown that the height of the mechanical loss peak is

enhanced by the presence of aluminum filler which has been shown [9, 10] to interact strongly with the hydroxyl groups. May and Weir [4] have shown that the height of this peak is enhanced by the use of purified resin. It has been postulated, therefore, that the peak at $25°C$ is due to a relaxation of the glycidyl portions of the network carrying the hydroxyl group involved in the hydrogen bonding.

Spectral Transitions

The systems C2, C3, and C5 show hydroxyl transitions and mechanical relaxations in the region 10-30°C. The systems C6 and C10 show hydroxyl transitions near -5°C and mechanical relaxations near 25°C. This suggests that the mechanical loss peak for C2, C3, and C5 involves a relaxation of the group carrying the hydroxyl group which initiates a hydroxyl transition but that for the C6 and C10 systems the equivalent hydroxyl transition can occur before the whole glycidyl group relaxes.

It is suggested that this hydroxyl transition is associated with a change in the mean position of the strongly bonded hydroxyl group without change of the bond-type. In the case of C6 and C10 this occurs independently of the relaxation of the glycidyl group, whereas for C2, C3, and C5 the restrictions placed on the hydroxyl group do not permit this transition until the relaxation of the glycidyl group carrying the donor hydroxyl group occurs.

RELAXATIONS NEAR –40°C

Mechanical

The relaxation at –40°C has been observed for all systems based on epoxy resin I [1, 3-6] and the height of the loss modulus peak appears to be directly related to the concentration of I in the cured resin [1]. Epoxy resins based on 1,4-butane diglycidyl ether (II) and fluorinated derivatives of I and II and cured with aliphatic and aromatic curing agents have been studied by Dammont and Kwei [7] and also show a relaxation in this region. It has been concluded that this relaxation is associated with the glycidyl group. The present work shows that no significant variation of the hydroxyl stretching frequency occurs over the same temperature range.

It is concluded, therefore, that this relaxation is not associated with the hydroxyl group forming the dominant hydrogen bond and is probably due to the glycidyl groups involved in the weaker subsidiary hydrogen bonds to the ether oxygens (Type C).

RELAXATIONS BELOW -100°C

Mechanical relaxations near -120°C have been observed in many systems based on epoxy resins I or II or their fluorinated derivatives cured with materials containing alkylidene chains [1, 7, 11]. Distinct peaks have been observed with systems containing four or more methylene units in the curing agent [1, 11] or in the resin [7]. It has been shown [1] that the value of the loss modulus (G″) at -120°C is linearly related to the weight of aliphatic diamine in the cured polymer for all systems from C2 to C12, which suggests that all systems containing alkylidene chains have some loss mechanism in this region. A number of polymers containing unsubstituted alkylidene chains [12], including polyethylene, polyalkylidene oxides, polyalkylidene terephthalates, and polyalkylidene polyamides, all show a relaxation in this region. It is concluded that this may be ascribed to a relaxation involving methylene units.

No spectral results were obtained in this region.

THE HYDROXYL TRANSITION FOR THE C2 SYSTEM ABOUT -30°C

The tetrafunctional C2 system alone shows an hydroxyl transition near -30°C. This system is unique in having the shortest alkylidene chain and in being able to form a stable hydrogen bond of Type D across the ethylene group. It can be seen from Fig. 2 that the trifunctional methylated C2 system does not show a similar transition, although construction of models shows that there is no steric reason why Type D bonds should not form in this case. The transition, therefore, may be associated with the high steric stress introduced by the tetrafunctionality and the short length of the ethylene group. It is suggested that at low temperatures the steric requirements of the molecule in the tetrafunctional case force the system to form a Type B bond between the hydroxyl groups on the α and β chains. It can be seen that at low temperatures the infrared absorption for this bond occurs at a frequency consistent with the variation between C3 and higher systems. As the temperature increases, the glycidyl groups not involved in this hydrogen bond relax near -50°C, allowing a rearrangement of the hydrogen bond to form a Type D bond unique to the C2 system and causing a general shift to higher wavenumber, resulting in the anomalous position of the C2 system with respect to the C3 and higher systems. The higher transitions are not significantly affected and the general shape of the wavenumber vs temperature relationships are similar to those of the Type B bonds which contain a similar size ring formed by the hydrogen bond.

The variation in wavenumber between the tetrafunctional and the trifunctional cases is consistent with the decrease in steric crowding allowing the hydroxyl and nitrogen groups to adopt equilibrium positions further apart.

CONCLUSIONS

A comparison of a study of the effect of temperature on the dynamic mechanical properties and the absorption in the IR due to the hydroxyl group has allowed a detailed assignment of relaxation regions in the mechanical loss spectrum and has given information on the role of hydrogen bonding on the mechanical properties. Generally hydrogen bonding has negligible influence on the dynamic mechanical properties of the highly cross-linked system, although in some cases the mechanical relaxation may initiate transitions of the hydrogen bond.

The mechanical loss peaks may be ascribed to relaxations in the diphenylpropane nucleus (the glass transition temperature near or over 100°C at 1 cps), to relaxations within glycidyl groups having strong short range hydrogen bonds (near 25°C at 1 cps), to relaxations of weakly bonded glycidyl groups (near -50°C at 1 cps), and to relaxations of alkylidene chains (near -125°C at 1 cps).

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