Polymer Bulletin 24, 421–427 (1990)

Polymer Bulletin

Low-temperature thermal conductivity of diolmodified epoxies

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SUMMARY

The thermal conductivity at low temperatures (between 0.5 K and 100 K) was measured for diolmodified epoxies. Diglycidyl ether of bisphenol A (DGEBA) was modified for this purpose by aliphatic diols with the structure $HO-(-CH_2-)_n-OH$ in the presence of catalyst (either N,N-dimethyl benzylamine or magnesium perchlorate). Sample series with diols of n=4,8 and 12 were synthesized and measured. The results at $T<20K$ shows a clear dependence of the thermal conductivity values on the chain length of the diols. The increasing amount of diol in the epoxies cause a larger change on these values in the same temperature range.

INTRODUCTION

In general the use of measurements of the thermal conductivity to investigate the properties and modifications of structure of amorphous solids is well known (1). For polymeric materials the earliest investigations were carried out to estimate and explain their utility as insulating materials (2). In the last years more publications deal with a systematic study of thermal property changes due to changes on the structure of polymers (3-5). On the other hand, the study of epoxy-resin structure and modifications is of increasing interest. One of the central tasks of epoxy research is to flexibilize the hard and brittle basis resin of DGEBA to its aromatic structure (6). One way to achieve this is to crosslink DGEBA with aliphatic diols in the presence of catalysts. Studies on the crosslinking behaviour of these epoxy systems were carried out by Tänzer et al. (7-10). In an attempt to characterize the effects of changing chemical structure of networks in a systematic way on the thermal conductivity the following studies were undertaken.

EXPERIMENTAL

Synthesis

Diglycidyl ether of bisphenol A (DGEBA), obtained from VEB Leuna chemical plants (Epilox A-17-00), recrystallized from acetone-methanol was modified with aliphatic diols with the

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structure $HO-(-CH_2-)_n-OH$. Diols with n=4,8 and 12 as commercially available products were used. As catalysts we used either a basical one, N,N-dimethyl benzylamine (DMBA), or a Lewis acid, magnesium perchlorate ($Mg(ClO_4)_2$); both of them as commercially available products without further purification. We synthesized three series of samples (table 1).

Table 1 : Composition of the epoxies

Molar ratio DGEBA:diol = 1:0.25		
Sample series 1 (5 mol% DMBA)		Sample series 2 (3 mol% $Mg(ClO_4)_2$)
Sample no.	Dioltype	Sample no.
1.4	Butane-1,4-diol	2.4
1.8	Octane-1,8-diol	2.8
1.12	Dodecane-1,12-diol	2.12
Sample series 3	: Dioltype = Butane-1,4-diol (3 mol% $Mg(ClO_4)_2$)	
Sample no.		Molar ratio DGEBA:diol
2.4.2		1:0.5
2.4.3		1:0.75
2.4.4		1:1

For sample series 1 the components were stirred till homogeneity at T=330 K (about 30 min). The mixture was than placed on the sample holders and cured at T=320 K for 48 h. This "low" curing temperature was chosen to inhibit side reactions and to contribute to a regular formation of the network structure, since it is known that the crosslinking behavior of these systems shows superimposed reaction orders between 340 K and 440 K and since many different starting steps appear with an increasing reaction temperature (10). For sample series 2 the components were stirred at T=370 K till homogeneity, this procedure takes between 1 and 2 hours. The mixture was then placed on the sample holders and was cured at T=390 K for 48 h. Investigations of the cure kinetics show that the reaction mechanism for these systems is nearly independent of curing temperature (9). For sample series 3 only the amount of butane-1,4-diol was changed. The curing procedure is the same as for sample series 2.

Thermal conductivity methods

The steady-state technique was employed to measure the thermal conductivity (λ) in the temperature range between 2 and 100 K. A conventional cryostat described in (11) using two-bath arrangement with liquid nitrogen, hydrogen and helium as refrigerants was used. The temperature differences over the measuring distance (about 10 mm in length on a sample bar) were determined with a Gold-Iron/chromel-thermocouple. Measurements in the range 0.5 to 2 K were made in a ^{3}He-cryostat. The method used was a two-heater bar arrangement (12). Matsushito radio resistors wich had been calibrated against Germanium resistors were used as a thermometer.

RESULTS AND DISCUSSIONS

Figure 1 shows the thermal conductivity λ versus temperature T on a log-log plot for sample series 1. The thermal conductivity of all samples shows the plateau between 3 and 20 K typical of glassy materials. Below 3 K the thermal conductivity decreases and above 20 K increases with the temperature. From the curves it can be seen that below 20 K the thermal conductivity of each sample is clearly different. It can be said with confidence that the thermal conductivity increases with the length of the diol chain. The same behaviour is evident in sample series 2 (fig. 2). Furthermore the extent of the plateau region increases with the length of the diol chain. This is illustrated in table 2 based on graphical approximations. The differences in the values of the thermal conductivity at the plateau region for each sample series seem to be an effect of the different crosslinking densities of the samples.

Table 2 : Characterization of the epoxies

Sample no.	γ 10^{-4} mol/cm^3	T_g K	Plateau-width (approx.) K	λ (plateau) 10^{-3} W/cmK
1.4	9.4	373	9.1	0.91
1.8	7.4	354	11.6	1.01
1.12	4.0	338	14.6	1.08
2.4	12.6	398	7.9	0.73
2.8	8.3	377	-	0.94
2.12	4.6	331	10.3	1.01
2.4.2	12.1	361	(>10)	0.91
2.4.3	8.6	336	(>14)	1.11
2.4.4	4.3	327	(>17)	1.24

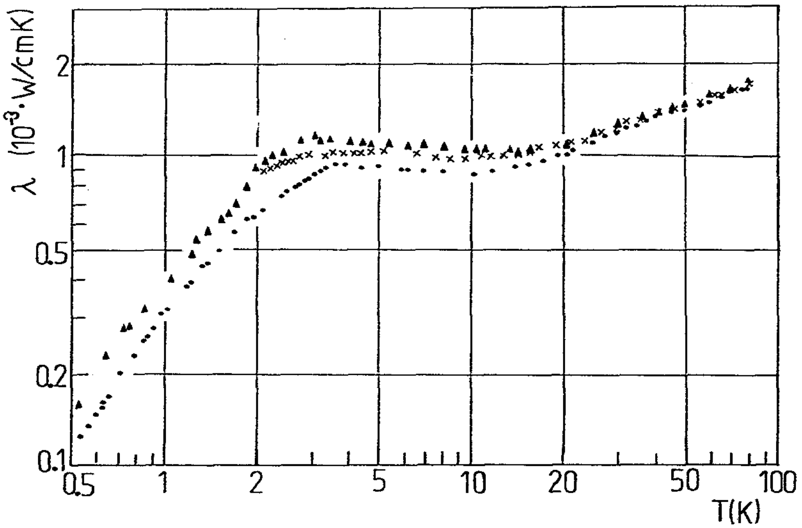

Fig.1 : Thermal conductivity vs. temperature, a log-log plot for sample series 1
1.4 - ● / 1.8 - x / 1.12 - ▲

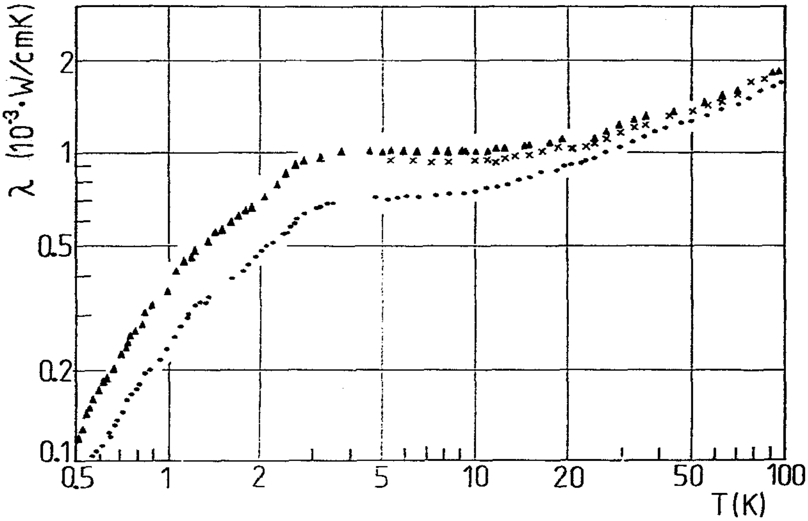

Fig.2 : Thermal conductivity vs. temperature, a log-log plot for sample series 2
2.4 - ● / 2.8 - x / 2.12 - ▲

In table 2 the crosslinking densities (γ) of the samples are listed as estimated from compression measurements (13). The glass-transition temperature (T_g) from DSC-measurements (13) is also listed. Normally T_g will be shifted to lower temperatures with decreasing crosslinking densities. A view of these parameters in comparison with the plots of thermal conductivity vs. temperature shows that the thermal conductivity under 20 K is lower for the more highly crosslinked samples.

These results are in agreement with the investigations of Nicholls and Rosenberg (4) on epoxies hardened with diamines of different chain length and with investigations on epoxies with different crosslinking densities (14).

A comparison between sample series 1 and 2 with each other shows that the thermal conductivity below 20 K for the samples with the same diol chain length for series 2 is even lower than for series 1. To facilitate the comparison the average values of the thermal conductivity at the plateau region are listed in table 2. This can be explained in terms of the different crosslinking densities of the two series, due to the different crosslinking behaviour caused by the catalysts (10). The different behavior could lead to the formation of more free chain ends in DMBA-catalysed epoxies as estimated by ultrasonic investigations (15); and this can be responsible for the lower crosslinking densities of sample series 1. It is interesting to note, that just for the DMBA-catalysed epoxies a ligth maximum-minimum-behavior appears at the plateau region. The same behaviour was reported for epoxies hardened with non-stoichiometric quantities of hardener (16).

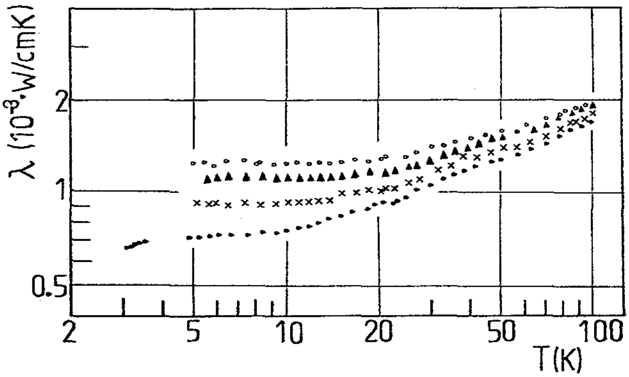

Fig. 3 : Thermal conductivity vs. temperature, a log-log plot for sample series 3
2.4 - ● / 2.4.2 - x / 2.4.3 - ▲/ 2.4.4 - o

Fig. 3 shows the plots of the thermal conductivity vs. temperature for sample series 3 and sample no. 2.4. One major difference to the behaviour of sample series 1 and 2 can be noticed. The variation of the thermal conductivity among the samples from one sample to another for the complete temperature range is much larger for this series than inside the sample series 1 and 2. For example, the difference of the crosslinking density between sample no.2.4 and 2.12 ist almost the same as between sample no. 2.4 and 2.4.4. But the differences between the same samples concerning the thermal conductivity average values at the plateau between 2.4 and 2.4.4 are approx. 80% larger than between 2.4 and 2.12 (table 2). This cannot result from differences in crosslinking densities alone. Studies of the reaction of DGEBA with butane-1,4-diol (8) show that for this system only 25% of the stoichiometrically necessary amounts of diol will be chemically incorporated in the network. That means that the increasing amounts of diol in the sample series 3 leads, on the one hand, to a lower crosslinking density due to larger DGEBA -diol sequences between crosslinks and probably increasing a mounts of free chain ends; on the other hand it leads to increasing amounts of diol as non-reactive plasticizer inside the epoxies. These amounts of non-reactive diol can be responsible for the additional increase on the thermal conductivity of sample series 3.

CONCLUSIONS

Low-temperature thermal conductivity measurements proved to be a suitable method for the investigation of the modification of structure of epoxies. Structural changes of the epoxies due to modification leads to changes on the thermal conductivity at temperatures $T < 20$ K . With increasing diol chain length the value of the thermal conductivity and the extent of the plateau increase. The $Mg(ClO_4)_2$-catalysed epoxies show lower thermal conductivities than the DMBA-catalysed ones, due to the higher crosslinking densities. The increasing amount of diol on the epoxies causes an additional increase of the thermal conductivity, due to the existence of diol as a non-reactive plasticizer on the network structure.

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Accepted June 23, 1990 C