

Thermal Conductivity of Epoxy Resins Cured with Aliphatic Amines

Katsuhiko KANARI and Takeo OZAWA

Electrotechnical Laboratory, Tanashi, Tokyo, Japan.

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ABSTRACT: The thermal conductivity of epoxy resins cured with various aliphatic amines is measured from room temperature to 150°C. The thermal conductivity increases with rising temperature below the glass transition temperature, T_g , and levels off or decreases with temperature above T_g . It is observed that the thermal conductivity increases linearly with increasing crosslink density as estimated from the measurement of shear modulus in the rubbery state, and that its negative temperature coefficient decreases with increasing crosslink density in the rubbery state. An empirical equation is also derived for the thermal conductivity, λ , of amorphous polymers;

$$-\Delta\left(\frac{1}{\lambda} \frac{d\lambda}{dT}\right)T_g=0.66$$

The left side of the equation is estimated for the samples as well as for other various amorphous polymers, and they are both in agreement with the constant of the equation.

KEY WORDS Epoxy Resin / Thermal Conductivity / Temperature Dependence / Glass Transition Temperature / Thermal Expansion Coefficient / Crosslink Density / Shear Modulus /

Various properties of high polymers have been extensively investigated, while there remain unsolved problems of thermal conductivity, especially that of crosslinked polymers. The thermal conductivity is one of important properties in a scientific sense as well as from a practical viewpoint. For instance, the thermal conductivity is one of properties indispensable for the thermal design, using polymeric insulating materials of various electric and electronic products, such as devices encapsulated in resin, and the relation between the thermal conductivity and the structure is of scientific interest.

The relation between the thermal conductivity and crosslink density of amorphous polymers has only been studied by Ueberreiter, *et al.*,¹ Hattori,² Kline, *et al.*,³ Yamamoto, *et al.*,^{4,5,6} and Berman, *et al.*⁷ The quantitative value of the thermal conductivity of cross-linked polystyrene and poly(methyl methacrylate) below the glass transition temperature, T_g , has been observed only by Yamamoto, *et al.*^{4,6}

The thermal conductivity of an epoxy resin was also measured in relation to its cross-link density, and a clear dependence was observed

above T_g . On the other hand, the relationship of T_g with the difference between the temperature coefficient of the thermal conductivity below T_g and that above T_g was measured. The relationship was observed experimentally for the epoxy resin and some other polymers. These results are reported in this paper.

EXPERIMENTAL

Materials

The epoxy resin used was "Epon 828" of Shell Chemical Co., and the epoxide equivalent was measured and found to be 172. The curing agents were ethylene diamine (EDA), diethylene triamine (DETA) and triethylene tetramine (TETA), all of which are GR grade. GR grade phenyl glycidyl ether (PGE, monoepoxide) made by Shell Chemical Co. and the same grade of *n*-octyl amine (OA, monoamine) were used in order to modify the cross-linking structure.

The samples are listed in Table I. The samples containing OA are made by mixing the constituents, then after degassing, leaving the mixture at room temperature for 24 hr. It was cured at

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Table I. The constitution, the density and the crosslink density of the samples

Sample no.	Diamine	Molecular ratio to Epon 828			Density, g/cm ³	Number of cross-linked chain per 1 cm ³
		Diamine	OA	PGE		
E-0.8	EDA	0.40	0	0	1.196	2.00 × 10 ²¹
E-1.0	"	0.50	0	0	1.198	2.06 "
E-1.2	"	0.60	0	0	1.197	1.94 "
D-0.8	DETA	0.32	0	0	1.193	2.04 "
D-1.0	"	0.40	0	0	1.194	2.24 "
D-1.2	"	0.48	0	0	1.195	2.17 "
T-0.8	TETA	0.27	0	0	1.190	1.63 "
T-1.0	"	0.33	0	0	1.188	1.76 "
T-1.2	"	0.39	0	0	1.189	1.64 "
EO-2	EDA	0.33	0.33	0	1.148	1.21 "
EO-3	"	0.25	0.50	0	1.132	0.76 "
EP-5	"	0.53	0	0.12	1.199	1.80 "
EP-10	"	0.57	0	0.26	1.201	1.50 "
EP-15	"	0.60	0	0.38	1.201	1.18 "

50°C for 8 hr. followed by post-curing at 115°C for 24 hr; this procedure is adopted to prevent OA from evaporating. The samples containing PGE are made by leaving the mixture at room temperature for 24 hr again after degassing, curing at 60°C for 8 hr. and post-curing at 150°C for 24 hr; this procedure is also adopted also to prevent PGE from evaporating. The other samples are manufactured by curing the mixture at room temperature for 24 hr followed by post curing at 150°C for 24 hr.

Apparatus

The thermal conductivity was measured by time-integration of the temperature gradient within the specimen for a transient period, which is reported elsewhere.⁸ Briefly, two specimens sandwiching a central heater are inserted between two metal plates uniformly maintained at a constant temperature. The temperature gradient within the specimens was measured and compared with that within another pair of dummy specimens of the same material. The graph of the temperature gradient showed a peak due to the heat evolved in the central heater and the thermal conductivity was obtained from the peak-area, the dimensions of the specimen and the heat evolved in the central heater. The apparatus was put in a vacuum chamber where the pressure was maintained below 10⁻⁴ Torr. Silicone high vacuum grease (Dow Corning Corp.) was used as an oil film. The length of the specimens was

50 mm, the width 50 mm and the thickness 2mm.

The shear modulus was measured with a Clash-Berg testing apparatus; the specimen of 6.4 mm × 3 mm × 38 mm being immersed in a silicone oil bath maintained at a constant temperature, and the shear modulus estimated from the distortion 10 sec. after applying the stress. The specific volume was measured by weighing a specimen in a silicone oil bath maintained at a constant temperature.

RESULTS AND DISCUSSION

A typical result is shown in Figure 1. A similar temperature dependence is also observed for the resin containing OA and PGE (Figures

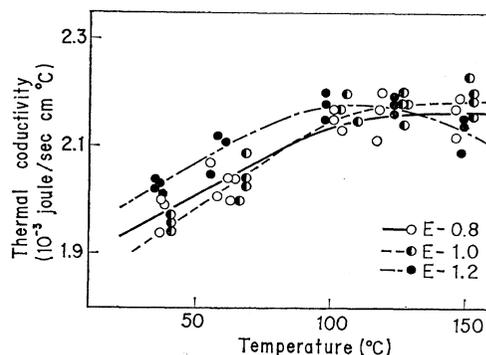


Figure 1. Temperature dependence of thermal conductivity for typical epoxy resins.

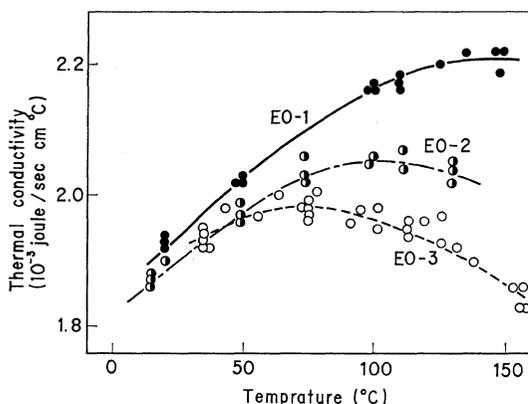


Figure 2. Temperature dependence of thermal conductivity for epoxy resins containing *n*-octyl amine as a modifier.

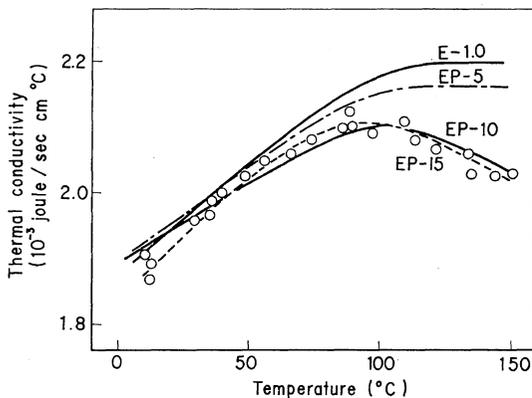


Figure 3. Temperature dependence of thermal conductivity for epoxy resins containing phenyl glycidyl ether as a modifier. The plots for EP-15 only are shown.

2 and 3). The observed thermal conductivity is almost in agreement with the other reported ones,^{3,9,10,11} though their curing agents differ from those in this report. Generally, the thermal conductivity of amorphous high polymers increases with rising temperatures below T_g , and decreases above T_g . This dependency is also observed in epoxy resins. The temperature where the thermal conductivity levels off or becomes a maximum corresponds to T_g which is measured from the inflection point in the plot of the specific volume vs. the temperature.

The thermal conductivity above T_g seems to

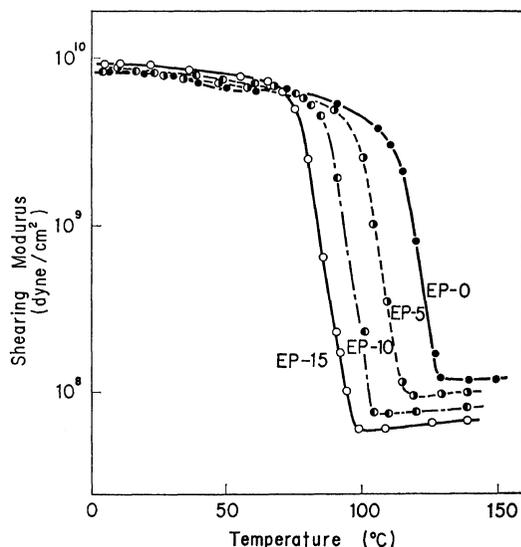


Figure 4. Temperature dependence of shear modulus for an epoxy resin.

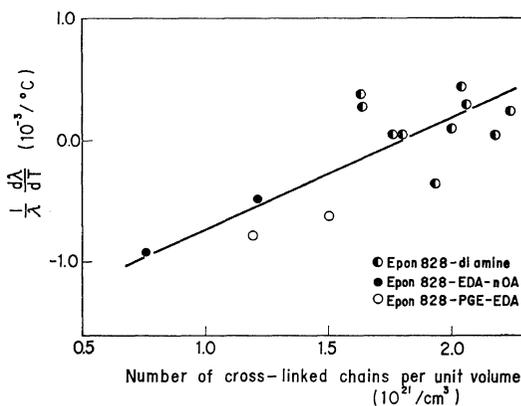


Figure 5. Plot of temperature coefficient of thermal conductivity above the glass transition temperature versus crosslink density.

increase with increase in the crosslink density. Moreover, the temperature dependency above T_g seems to be in some way related to the crosslink density. The crosslink density is then estimated from the measurement of the shear modulus in the rubbery state. A typical result of the measurement of the shear modulus is reproduced in Figure 4. The shear modulus increases with temperature in the rubbery state; this fact implies that the theory of the rubber

elasticity holds in that state and that the shear modulus is equal to the product of the absolute temperature, the Boltzmann constant and the number of network chains in a unit volume effective to the rubber elasticity. By using this relationship, the crosslink density, *i.e.*, the number of network chains in a unit volume, is estimated and tabulated in Table I. In Figure 5, the temperature coefficient of thermal conductivity, $1/\lambda(d\lambda/dT)$, above T_g is plotted against the crosslink density, where λ and T are the thermal conductivity and the temperature, respectively. The negative temperature coefficient observed decreases with increasing crosslink density. Thus, the temperature coefficient of thermal conductivity have a linear relationship to the crosslink density, although some scattering of the points is seen.

This relationship between the thermal conductivity and the crosslink density and the relationship shown in Figure 5 were observed qualitatively by Hattori,² Kline, *et al.*,³ and Yamamoto, *et al.*⁴ Hattori² reported the thermal conductivity of polyester polymerized from ethylene glycol and maleic acid and cross-linked by combining it with styrene. He observed that the thermal conductivity and its temperature dependency for a hard specimen are less than those for a soft specimen. Kline, *et al.*,³ measured the thermal conductivity of epoxy resin cured with metaphenylene diamine. They reported that the thermal conductivity becomes high after post-curing. They also observed that the temperature of the maximum thermal conductivity of a sample of constitution of equal equivalent is higher than that of the other sample of unequal equivalent, and that the temperature dependence above T_g is smaller in the former sample than in the latter one. Yamamoto, *et al.*,⁴ also observed a similar relationship between the temperature coefficient and the content of cross-linking monomer for poly(methyl methacrylate) cross-linked with triallylcyanurate. On the other hand, Ueberreiter, *et al.*,¹ reported a complicated relationship between the temperature dependence and the crosslink density for polystyrene cross-linked with divinylbenzene.

T_g is also clearly related to the crosslink density, as is shown in Figure 6, where the T_g observed from the temperature dependence of

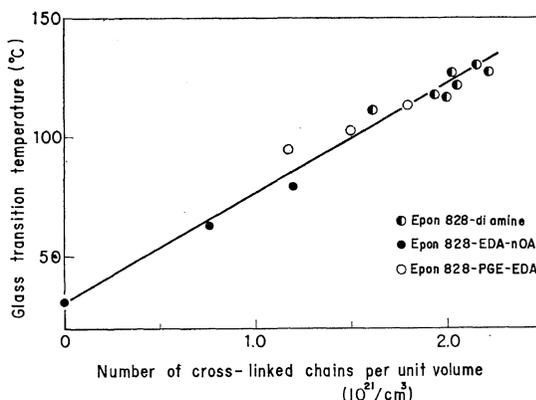


Figure 6. Plot of the glass transition temperature vs. crosslink density.

the specific volume is plotted against the crosslink density. The clear linear relation can be observed. This fact is in accordance with the theory of Fox, *et al.*,¹³ although Shibayama¹⁴ proposed another relationship between T_g and the crosslink density, ρ , *i.e.*,

$$T_g = K_1 \ln \{K_2(1 + \rho/\rho_0)\} \quad (1)$$

where K_1 and K_2 are constants and ρ_0 is the quantity which evaluates the entanglement effect of molecular chains when no cross-linking bonds exist.

Simha and Boyer¹⁵ derived the following experimental equation for various amorphous high polymers;

$$T_g \cdot \Delta\alpha = 0.113 \quad (2)$$

where α is the thermal expansion coefficient and Δ represents the difference in a certain quantity between above T_g and below T_g . From the thermal expansion coefficient, which is obtained by the measurement of the specific volume and tabulated in Table II, the values of the left side of eq 2 are calculated and listed in Table II, and the average value is 0.112 ± 0.025 , which is in very close agreement with the constant in eq 2.

On the other hand, Eiermann¹⁶ proposed on the base of his theory of an elementary thermal resistance model that the difference in the temperature coefficient of thermal conductivity around T_g is proportional to $\Delta\alpha$, *i.e.*,

Table II. The glass temperature, the thermal expansion coefficient, the temperature dependency of the thermal conductivity, and their relation

Sample no.	Number ^a	T_g, K	$\alpha \times 10^5$		$(1/\lambda)(d\lambda/dT) \times 10^3$		$T_g \Delta\alpha$	$-d\left(\frac{1}{\lambda} \frac{d\lambda}{dT}\right)T_g$
			$T < T_g$	$T > T_g$	$T < T_g$	$T > T_g$		
E-0.8	2.00×10^{21}	390	29.5	48.7	1.5	0.1	0.075	0.55
E-1.0	2.06	396	18.0	55.4	1.8	0.3	0.148	0.65
E-1.2	1.94	391	23.3	57.5	0.9	-0.7	0.134	0.61
D-0.8	2.04	400	22.7	59.0	1.7	0.4	0.145	0.52
D-1.0	2.24	401	21.8	49.1	1.2	0.2	0.109	0.40
D-1.2	2.17	403	22.5	43.9	1.4	0.1	0.086	0.52
T-0.8	1.63	385	31.3	55.4	1.7	0.4	0.094	0.49
T-1.0	1.76	388	29.5	58.7	1.6	0.1	0.113	0.59
T-1.2	1.64	383	31.4	58.0	1.9	0.4	0.103	0.56
EO-2	1.21	353	21.8	52.2	1.3	-0.5	0.107	0.60
EO-3	0.76	336	20.3	50.8	0.8	-0.9	0.102	0.57
EO-5	1.80	387			1.8	0.1		0.67
EP-10	1.50	376			1.0	-0.6		0.61
EP-15	1.18	368			1.0	-0.8		0.69
Average							0.112 ± 0.025	0.56 ± 0.07

^a Number of cross-linked chains per 1 cm³.**Table III.** The observed relation of $-d\left(\frac{1}{\lambda} \frac{d\lambda}{dT}\right)T_g$ for various polymers

Substance	T_g, K	$-d\left(\frac{1}{\lambda} \frac{d\lambda}{dT}\right)T_g$	ref
Silicone rubber	183	0.53	17
Natural rubber	203	0.33	17
Vukollan	233	0.37	17
Poly(isobutylene)	200	0.19	17
Poly(vinyl chloride) (40%) ^a	243	0.41	17
" (20%) ^a	283	0.34	17
" (10%) ^a	313	0.40	17
"	337	0.30	18
Poly(methyl methacrylate)	373	0.41	16
"	373	0.67	20
MMA+TAC (1-5%) ^b	370	0.41	4
" (7%) ^b	377	0.35	4
" (10%) ^b	380	0.31	4
Poly(ethyl methacrylate)	341	0.37	21
Poly(butyl methacrylate)	290	0.52	21
Polystyrene	354	0.33	22

^a The content of plasticizer.^b Copolymer of methyl methacrylate (MMA) and triallyl cyanurate (TAC).

$$d\left(\frac{1}{\lambda} \frac{d\lambda}{dT}\right) = -5.8 \Delta\alpha \quad (3)$$

Combining eq 2 and 3, we have

$$-d\left(\frac{1}{\lambda} \frac{d\lambda}{dT}\right)T_g = 0.66. \quad (4)$$

The experimental results shown in Table II are in very close agreement with the above relation proposed by the authors, and the average value of the left side in eq 4 is 0.56 ± 0.07 . This relationship shown in eq 4 is examined for other amorphous polymers, and the results are tabulated

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in Table III. The relation holds for various amorphous polymers.

Now, let us consider quantitatively the relationship between the thermal conductivity and the crosslink density. The thermal conductivity depends greatly on the crosslink density above T_g , while little dependence is observed below T_g . As is mentioned above, T_g changes with the crosslink density. The comparison is then made between the thermal conductivity of the various samples at the temperature where the ratio between the absolute temperature of T_g and the temperature measuring the thermal conductivity is constant. In Figure 7 is shown the

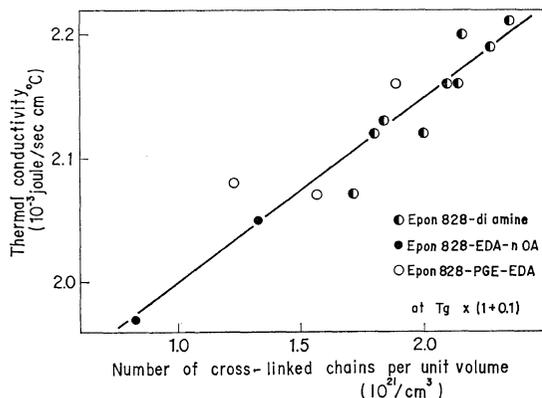


Figure 7. Relationship between thermal conductivity and crosslink density in the rubbery state.

relationship between the thermal conductivity and the crosslink density at the temperature 10% higher than T_g , ($1.1 \times T_g$), *i.e.*, in the rubbery state. The thermal conductivity increases linearly with increasing crosslink density. The thermal conductivity without cross-linking obtained by extrapolation of the straight line is lower by about 15% than the maximum thermal conductivity observed on the sample cured with DETA. At the temperature of $0.8 \times T_g$, *i.e.*, in the glassy state, the similar relation can also be observed, and the difference between the maximum value and that without cross-linking is about 5%. The relationships at different temperatures are represented in Figure 8, and the slope of the line increases with increasing temperature.

The similar relationship was observed by Yamamoto, *et al.*,^{4,6} for poly(methyle meth-

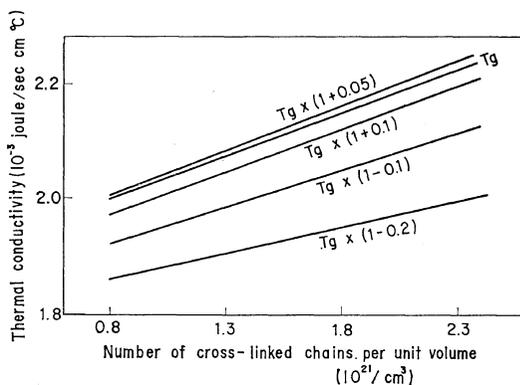


Figure 8. Relationship between thermal conductivity and crosslink density at the different temperatures indicated in the figure.

acrylate) cross-linked with triallyl cyanurate and polystyrene cross-linked with divinyl benzene below T_g , and Yamamoto⁵ derived a theoretical relationship in accordance with the experimental results by extending Eiermann's elementary thermal resistance model.¹⁶ However, his theory and experimental relations are restricted to the temperature range below T_g . In fact, the linear relationship found below T_g is also observed above T_g .

REFERENCES

1. K. Überreiter and E. Otto-Laupenmuhlen, *Kolloid-Z.*, **133**, 26 (1953).
2. M. Hattori, *Kobunshi Kagaku (Chem. High Polymers)*, **19**, 32 (1962).
3. R. P. Krehling and D. E. Kline, *J. Appl. Polym. Sci.*, **13**, 2411 (1969).
4. W. Knappe and O. Yamamoto, *Kolloid-Z. Polym.*, **240**, 775 (1970).
5. O. Yamamoto, *Polymer J.*, **2**, 509 (1971).
6. O. Yamamoto and H. Kambe, *ibid.*, **2**, 623 (1971).
7. B. L. Berman, R. P. Madding and J. R. Dilling, *Phys. Lett.*, **30A**, 315 (1969).
8. T. Ozawa, *Japan. J. Appl. Phys.*, **6**, 1455 (1967); T. Ozawa, and K. Kanari, *Polym. Lett.*, **5**, 767 (1967).
9. D. E. Klein, *J. Polym. Sci.*, **50**, 441 (1961).
10. W. Knappe, *Kunststoffe*, **51**, 707 (1961).
11. L. N. Cherkasova, *Zh. Fiz. Khim.*, **33**, 1929 (1959).
12. D. Katz and A. V. Tobolsky, *Polymer*, **4**, 417 (1963).

13. T. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955).
14. K. Shibayama, *Kobunshi Kagaku (Chem. High Polymers)*, **18**, 183 (1961); *idem.*, *ibid.*, **19**, 219 (1962); *idem.*, *ibid.*, **20**, 587 (1963).
15. R. Simha and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).
16. K. Eiermann, *J. Polym. Sci., Part C*, **6**, 157 (1964).
17. K. Eiermann and K. H. Hellwege, *ibid.*, **51**, 99 (1962).
18. R. P. Sheldon and S. K. Lane, *Polymer* **6**, 77 (1965).
19. K. Eiermann, *Kunststoffe*, **65**, 335 (1965).
20. R. H. Shoulberg and J. A. Shetter, *J. Appl. Polym. Sci.*, **6**, S 32 (1962).
21. W. Knappe, P. Lohe, and R. Wutschig, *Angew. Chem.*, **7**, 181 (1969).
22. A. D. Pasquino and M. N. Pilsworth, *Polym. Lett.*, **2**, 253 (1964).