

Dynamic thermomechanometry of networks from acrylated epoxy resins

Giampaolo Giuliani and Aldo Priola

Assoreni, Polymer Research Laboratories, S. Donato Milanese, 20097, Italy

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Dynamic thermomechanical analysis of networks from acrylated DGEBA type epoxy resins, crosslinked through u.v. induced polymerization, was performed to elucidate the effect of the functionality and functionality distribution of the oligomers on the network properties. Partially acrylated and propionated DGEBA resins were employed in which the acrylic functionality was changed in the range 2–1 double bonds per mole of the resin. The dynamic storage modulus, measured with a Rheovibron instrument, was found, in the high temperature region ($>150^{\circ}\text{C}$), to follow the classical laws of rubber elasticity when the proper number of elastic effective chains was taken into account. The glass–rubber transition temperature was found to decrease linearly as a function of the fraction of free chain ends. The influence of the presence of CBr_4 as a chain transfer agent on the network properties was also preliminarily investigated.

Keywords Dynamic thermomechanical analysis; acrylated epoxy resins; u.v. curing; functionality distribution; chain transfer agents

INTRODUCTION

The study of structure–property relationships of networks obtained from the bulk polymerization of polyreactive oligomers is of considerable interest both from the fundamental and practical point of view. By changing the nature of oligomers, the type and the number of reactive functions, it is possible to obtain networks with different characteristics and applications. The work in this field was recently reviewed by Berlin¹.

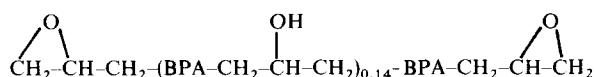
Particularly interesting are polymerizable oligomers with reactive double bonds in the end positions, which can be converted easily to networks in which the distance between the network junctions depends on the molecular weight of the original oligomers.

In this work we have examined networks obtained from acrylated epoxy oligomers having the same molecular weight and chemical composition but different functionality and functionality distribution, with the aim of investigating the effect of these parameters on the network properties. The curing reaction was performed by u.v. irradiation in the presence of a photoinitiator. We have used a network characterization technique based on dynamic thermomechanical measurements. The influence of the presence of a chain transfer agent on the properties of the network has also been preliminarily examined.

EXPERIMENTAL

Materials

Four epoxy-acrylated resins have been prepared by acrylating a commercial sample of bisphenol-A-diglycidyl-ether (DGEBA) having the following composition:



The resins have been prepared by reacting DGEBA either with an equivalent quantity of acrylic acid with respect to the content of epoxy groups, or with an acrylic and propionic acid mixture with an increasing quantity of propionic acid up to the 1/1 molar ratio with respect to the acrylic acid.

The acrylation reaction was carried out in bulk, at 100°C , by using benzyl-dimethylamine as a catalyst (1.5% by weight with respect to the epoxy resin) and continuing the reaction until an acid number <2 was obtained. Due to the statistic character of the reaction, the products obtained by using an acrylic and propionic acid mixture consist of a mixture of bi-acrylated, mono-acrylated and non-acrylated molecules. For example, in the case of the reaction with a 1/1 molar mixture of acrylic and propionic acid, the reaction mixture will contain 50% mono-acrylated, 25% bi-acrylated and 25% non-acrylated molecules. Pure non-acrylated product obtained by reacting DGEBA with propionic acid was also prepared.

Curing

The resins, mixed, when not otherwise specified, with 5% by weight of a photoinitiator (Irgacure 651, benzyl-dimethylketal) were coated on sheets of sanded steel or tin. The coated sheets were irradiated by using IST.200/1 Labor Hildebrand equipment with a 80 W cm^{-1} medium pressure mercury lamp, at a distance of 11 cm. The samples were passed under the lamp twenty times with a belt speed of 24 m min^{-1} ; in these conditions the sample's hardness attained the asymptotic maximum value.

Conversion measurements

Acrylic double bond conversion during the u.v. crosslinking reaction was controlled by means of i.r. measurements. The direct measurement of the conversion was carried out on very thin films cast on NaCl glass. After irradiation the value of the absorbance band at 1633 cm^{-1} (due to the acrylic double bonds) was less than 5% of

the initial value. The acrylic double bond conversion for thicker films was controlled through i.r. measurements on the products ground and pressed with KBr. Such measurements have revealed in every case a decrease of the acrylic double bond concentration to values less than 10% of the initial value.

Testing methods

The dynamic mechanical properties were measured with a Rheovibron Instrument DDV II. T_g was obtained from the maximum $\tan \delta$ curve. The gel percentage was determined by the weight difference after 24 h immersion in CHCl_3 . König hardness, impact flexibility and adhesion were measured according to the FN Unichim 91, FIM 6226, ASTM 3002 Standards.

RESULTS AND DISCUSSION

The samples used in the experiments are shown in Table 1; the mean functionality is defined as the mean number of acrylic double bonds per molecule. The mean functionality was changed in two ways; varying the molar acrylic acid/epoxy group ratio at which the synthesis was carried out (type I resins, samples A, B, C, D, E and F) or blending sample A with a zero functional product (type II resins, samples G, H, I, L and M).

Figure 1 shows the results obtained by the Rheovibron analysis for sample B. The loss factor $\tan \delta = E''/E'$ shows two peaks: one, with its maximum value at $\sim -50^\circ\text{C}$, due to local motions², the other at $\sim 130^\circ\text{C}$, due to the glass-rubber transition.

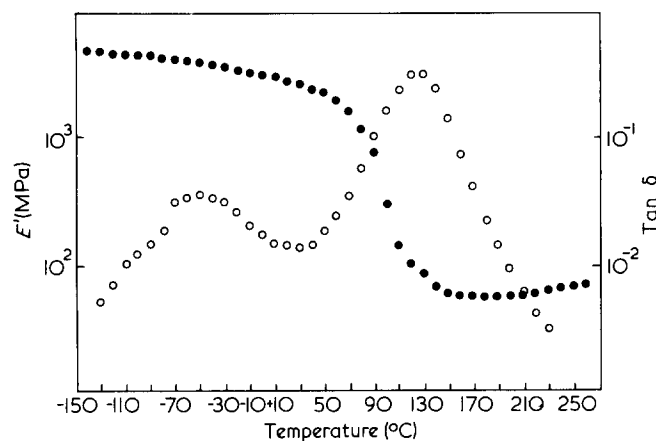


Figure 1 Dynamic modulus E' (●) and $\tan \delta$ (○) at 110 Hz as a function of the temperature. Acrylated DGEBA resin with $f = 1.85$

This last assignment is substantiated by the decrease of the storage modulus E' by a factor of 10^2 in the same temperature region. Above 160°C the modulus increases slightly with the typical behaviour of a rubber network.

The temperature of the rubber-glass transition T_g and the value of the dynamic storage modulus in the rubbery region E_r are two parameters sensitive to the network topology. The glass transition of a crosslinked polymer was generally found to be that of the linear parent polymer increased by a contribution proportional to the crosslink density³.

Conversely, with reference to an ideal network, the glass transition temperature of a real network, which contains free dangling ends, is decreased by a factor proportional to the number of the chain ends⁴.

As far as the elastic modulus is concerned, the relationship with the parameter ζ which characterizes the network structure on the basis of rubber elasticity theory, is⁵:

$$E = 3\zeta RT$$

The parameter ζ can be equal to the crosslink density ν or related to it through a factor depending on the junction's functionality. However, if the junction functionality is constant, the modulus is proportional to the crosslinking density ν .

In Table 2 the values of the dynamic moduli measured in the rubbery region at 150°C and the glass transition temperatures of the different samples are reported. It is evident that both the moduli and glass transition temperatures decrease by decreasing the mean functionality of the samples.

In order to apply the above mentioned relationships between the network parameters (ν and the number of chain ends) and the experimental values of T_g and E_r , a model network shown in Figure 2 was used. In this model the chain resulting from the acrylic double bond polymerization is viewed as a network junction. The length of the chain segment between the two acrylic functions is the length of the elastically effective segment. Intramolecular reactions (i.e. between two acrylic double bonds belonging to the same oligomer molecule) are not taken into account in this model.

According to the reported model, only the molecules with functionality 2 are elastically effective and increase the modulus: the mono-functional molecules are connected to the network but do not contribute to the elastic modulus. Their effect is that of decreasing T_g by adding more free volume to the polymer. The molecules

Table 1 Composition and mean functionality of the resins used

Type I resins	Acrylate epoxy resins					
	A	B	C	D	E	F
Molar ratio acrylic epoxy	2/2	1.85/2	1.80/2	1.75/2	1.5/2	1/2
Mean functionality	2	1.85	1.8	1.75	1.5	1
Type II resins	Blends of A with the propionated resin					
	G	H	I	L	M	
% A	90	80	75	65	50	
Mean functionality	1.8	1.6	1.5	1.5	1	

Table 2 Dynamic moduli in the rubbery region and glass transition temperatures

Sample	f^*	E_r' (MPa)	T_g (°C)	Sample	f^*	E_r' (MPa)	T_g (°C)
A	2	80	135	G	1.8	60	115
B	1.85	65	125	H	1.6	—	100
C	1.8	55	115	I	1.5	40	95
D	1.75	55	115	L	1.3	30	85
E	1.5	40	95	M	1	15	80
F	1	13	60				

* f = mean functionality

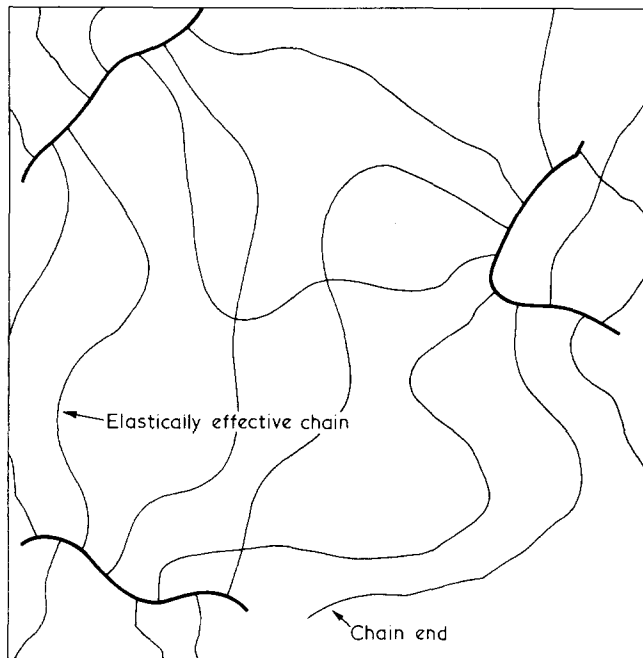


Figure 2 Model of an acrylated DGEBA network

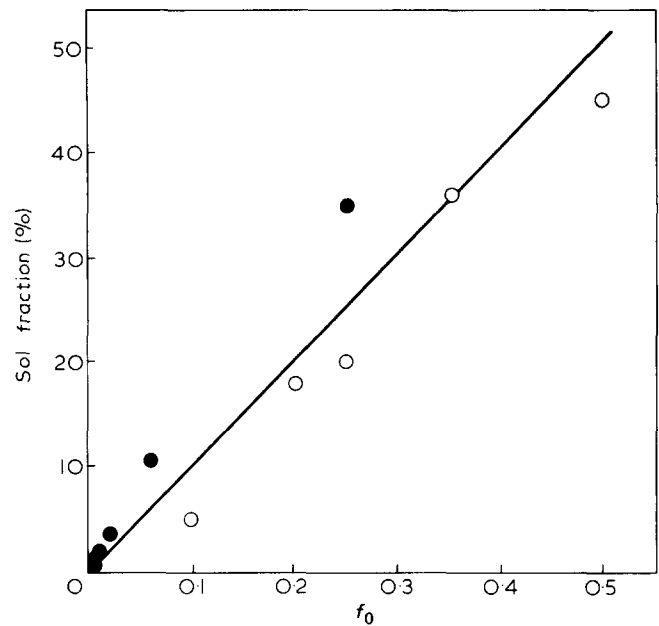
Table 3 Functionality distribution in the samples used

Sample	f_2	f_1	f_0	Sol. fract. (%)
A	1	0	0	<5
B	0.86	0.14	0	<5
C	0.81	0.18	0.01	<5
D	0.75	0.23	0.02	<5
E	0.56	0.38	0.06	11
F	0.25	0.50	0.25	35
G	0.9	0	0.1	5
H	0.8	0	0.2	18
I	0.75	0	0.25	20
L	0.65	0	0.35	36
M	0.50	0	0.50	45

with zero functionality only act as a plasticizer. The functionality distribution was calculated, for samples A, B, C, D, E and F (type I resins) on the basis of a random distribution among the molecules, for samples G, H, I, L and M (type II resins) on the basis of the composition, and the results are displayed in Table 3 as a fraction of molecules with functionality 2 (f_2), 1 (f_1) and 0 (f_0).

If the Figure 2 model is a good approximation to the networks obtained after complete curing of these resins:

- (i) the sol fraction should be equal to f_0 ;


 Figure 3 Sol. fraction as a function of the number f_0 of molecules with $f = 0$. Type I resins ●; type II resins ○

- (ii) E_r should be proportional to f_2 ;

- (iii) the decrease of T_g should be proportional to the number of free ends, $f_1 + 2f_0$.

In Figures 3, 4 and 5 the experimental data are reported for the two types of resins. Figure 3 data show that the sol fraction is close to f_0 , taking into account the measurement accuracy which is ± 0.05 . This allows exclusion of the occurrence of significant amounts of grafting reactions in the systems.

Figure 4 shows that the rubber modulus, relative to the modulus of the bi-acrylated molecules, is proportional to the fraction of bi-acrylated molecules for type I resins. Type II resins behave in a different manner; generally they show lower moduli.

Finally the T_g of all the samples is linearly related to the quantity $f_1 + 2f_0$, with exception of sample M (Figure 5). In conclusion, the network obtained from type I resins seems not to be too far from the model drawn in Figure 2, while type II resins behave in a more complex manner.

In Table 4 and Figure 6 the results of tests performed on coated steel plates are shown. As the mean functionality decreases, impact flexibility and adhesion increase, while hardness decreases.

Large differences are observable, at the same functionality, between type I and type II resins: the former are characterized by higher hardness and mechanical properties.

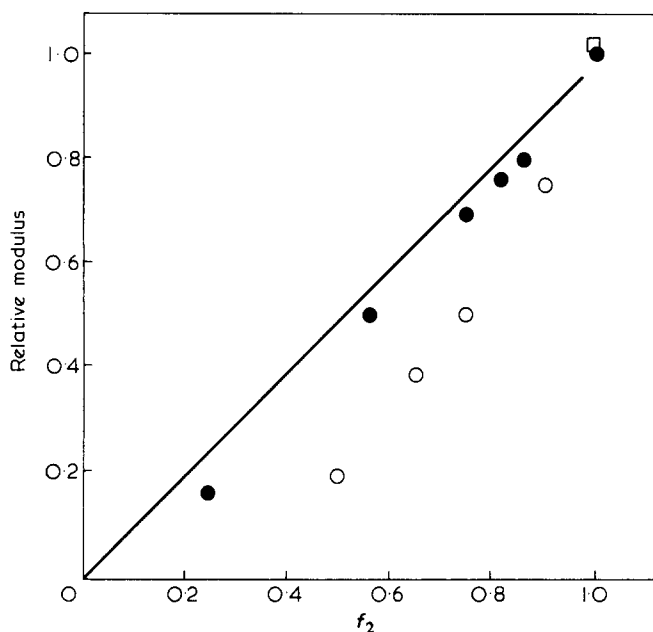


Figure 4 Relative rubber modulus as a function of the fraction of molecules with $f = 2, f_2$. Symbols as in Figure 3

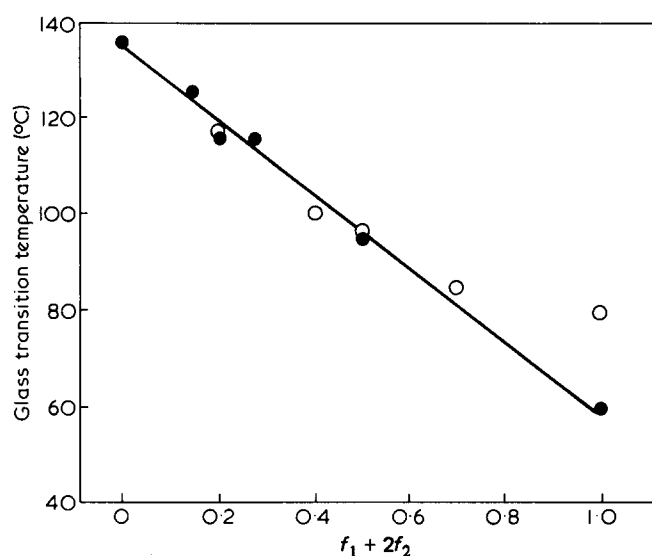


Figure 5 Glass transition temperature as a function of the number of chain ends, $f_1 + 2f_2$. Symbols as in Figure 3

In the model of Figure 2, the chain resulting from the acrylic double bonds is considered as a network junction. It would be interesting to study the effect of changing the length of the chain on the network properties. This study can be performed through the use of 'chain transfer' agents which, under certain experimental conditions, can control the kinetic chain length of the polymerization. A study of the effect of chain transfer agents on the properties of radiation cured acrylourethane oligomers, was previously reported by Walsh⁶. With this aim, we performed some preliminary experiments on bi-acrylated DGEBA resins using CBr_4 as a chain transfer agent.

The effectiveness of CBr_4 is well known⁷. Test experiments of polymerization of n-butyl-acrylate in dioxane solution in the presence of azo-bis-isobutyronitrile showed that, if CBr_4 is added in the quantity of 10% by weight, oligomers are obtained with Br bonded in a quantity corresponding to one molecule of CBr_4 for each oligomeric chain. Sample C was added with 10% by weight of CBr_4 and irradiated as usual. The gel content was found to be >95% as in the sample without CBr_4 , and the bromine content of the gel fraction 9.3%.

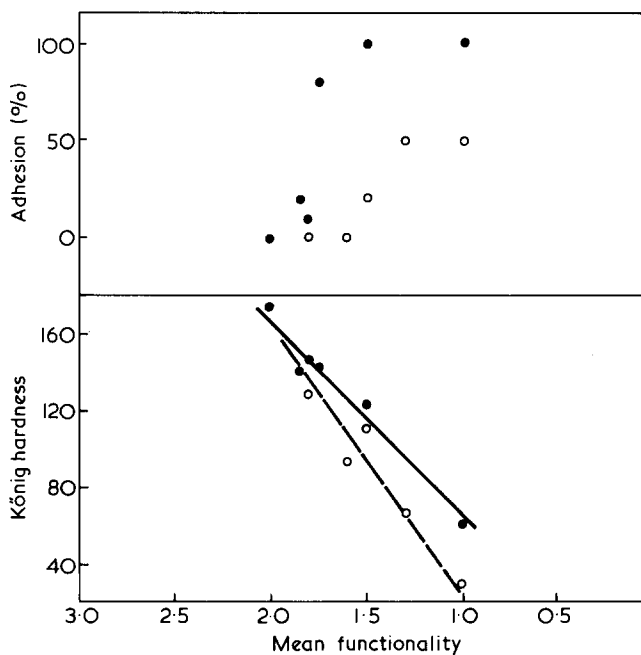


Figure 6 König hardness and adhesion, as a function of the mean functionality. Symbols as in Figure 3

Table 4 Properties of epoxy-acrylated resins with different mean functionality

Type I network	A	B	C	D	E	F
Mean functionality	2	1.85	1.80	1.75	1.50	1
König hardness	174	140	146	143	123	61
Impact flexibility (%)	0.5	0.5	0.5	0.5	1	60
Adhesion (%)	0	20	10	80	100	100
Type II network	G	H	I	L	M	
Mean functionality	1.80	1.60	1.50	1.30	1	
König hardness	129	94	111	67	31	
Impact flexibility (%)	0.5	0.5	0.5	1	5	
Adhesion (%)	0	0	20	50	50	

Table 5 Effect of the presence of a chain transfer agent on the properties of the network

Sample	T_g (°C)	E_r (MPa)	Sol. (%)
C	115	55	<5
C + 10% CBr ₄	90	20	<5

This last result indicated that practically all the CBr₄ added is bonded to the network. On the basis of the bromine content the mean length of the chains has been found to be equal to 12 acrylic units. The characteristics of the network are compared with those of the parent network C in Table 5. The wide differences in the value of T_g and E_r provide evidence of the effect of the chain length on the network properties.

We are working along this line in our laboratory by also using different chain transfer agents with the aim of clarifying the relationships between the length of the chain and the network properties.

CONCLUSIONS

The main conclusions of our work can be summarized in this manner:

(1) From the dynamic thermomechanical measurements two parameters are obtained, glass transition temperature and modulus in the rubber region, which are related to the topology of the network. The properties of bi-acrylated DGEBA networks, crosslinked with u.v. radiation, depend on the mean functionality of the molecules and on their functionality distribution; at an equal mean functionality, networks built using only molecules with $f=2$ or $f=0$ show mechanical properties lower than those built using molecules with a random distribution of 2, 1 and 0 functionalities.

(2) Chain transfer agents can modify the network topology determining the length of the acrylic chains, and thus changing the network properties.

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