

Polymer networks derived from curing of epoxidised linseed oil: influence of different catalysts and anhydride hardeners

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Abstract

Epoxidised linseed oil was cured with anhydrides. The reactions were catalysed with different types of tertiary amines and imidazoles. 2-Methylimidazole leads to very interesting properties. The effects of steric factors and of the rigidity of the diester segment formed due to the extent of conversion of anhydride groups and on the network's properties were observed. Thus, the thermosets obtained with phthalic anhydride and methyl-endomethylenetetrahydrophthalic anhydride hardeners have a lower crosslinking density than those obtained with *cis*-1,2,3,6-tetrahydrophthalic anhydride. The effects of the epoxidised triglyceride structure, made of aliphatic chains, on the network's properties were also examined. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Epoxidised linseed oil; Anhydrides; Catalysts

1. Introduction

During the last years, increasing attention has been paid to polymers obtained from renewable resources. This interest is justified by the environmental advantages of these substances, which are neutral in the carbon dioxide cycle and often biodegradable. These polymers may also constitute a new outlet for vegetable products.

Among products from agricultural resources, natural oils may constitute raw materials useful in polymer synthesis. Traditionally, unsaturated fatty acids, like linseed oil, are used in coatings and printing inks. Epoxidised oils, mainly soybean oil, are used as additives in thermoplastics to improve stability and flexibility. The feasibility of curing epoxidised natural oils for the preparation of thermosets was demonstrated [1]. These modified oils are mainly cured with cyclic acid anhydrides. With polyamine hardeners, amide formation takes place resulting in cured products of poor quality [2]. Some recent studies investigated the potential of these polymers obtained from epoxidised or maleinated oils as adhesives in the manufacture of particle boards [3] or as matrices for composites [4]. Some applications for surface coatings were also developed [5,6]. Networks suitable for such objectives are those offering high stiffness, which is achieved with a high crosslinking density. As a result, these

polymers have to be synthesised from the most unsaturated oils, e.g. soybean oil or linseed oil. For the applications of these thermosets to be successful, a complete knowledge of the mechanical and physical properties as well as thermal stability is required.

The purpose of this work is to investigate the curing mechanisms and the structure of the networks obtained with epoxidised linseed oil. Cyclic acid anhydride hardeners, tertiary amine and imidazole catalysts, usually used for the crosslinking of industrial epoxy prepolymers [2], were employed in this study. The effects of the anhydride and catalyst types and concentrations in the curing reactions were investigated using differential scanning calorimetry (DSC). The thermomechanical behaviour of the different materials formed was investigated in the glassy state and in the rubbery region using dynamic mechanical analysis (DMA).

2. Experimental

2.1. Materials

Vegetable oils are mixtures of triglycerides formed by different unsaturated fatty acids as shown in Table 1. A commercial epoxidised linseed oil (Merginate ELO 8510) was supplied by Society Harburger Fettchemie. The main fatty acid present in linseed oil is linolenic acid (C18:3) containing three carbon-carbon double bonds. ELO

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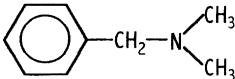
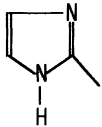
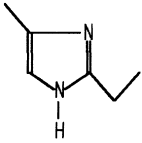
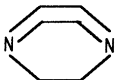
Table 1
Characteristics of some vegetable oils [7]

Type of fatty acid ^a	% Fatty acids			
	Rapeseed	Soybean	Sunflower	Linseed
C16:0	3–4	8–13	5–7	4–6
C16:1	–	<0.2	<0.4	<0.5
C17:0	–	–	<0.1	–
C18:0	1–2	2–5	4–6	2–3
C18:1	9–16	17–26	15–25	10–22
C18:2	11–16	50–62	62–70	12–18
C18:3	7–12	4–10	<0.2	56–71
C20:0	–	<1.2	<1	<0.5
C20:1	7–13	<0.4	<0.5	<0.6
C22:1	41–52	–	<1	–

^a C_x:y means that the fatty acid has *x* atoms of carbon and *y* unsaturated bonds.

contained 5.60 mmol epoxide/g as determined according procedures described by the standard NFT 51-522. On an average, an epoxidised triglyceride of linseed oil has a molecular weight of about 950 g/mol and contains about five epoxy functions. The epoxidised linseed oil is cured with different anhydrides in the presence of various catalysts such as tertiary amines or imidazoles. All the reagents, described in Tables 2 and 3, were of commercial grade with 97–99% purity and were used without further purification.

Table 2
Formulas of catalysts used in this work

Name	Formula	Supplier and purity	Molecular weight (g/mol)
Benzyltrimethylamine (BDMA)		Acros, 99%	135
2-Methylimidazole (2MI)		Acros, 99%	82
2-Ethyl-4-methylimidazole (2E4MI)		Acros, 99%	110
1,4-Diazabicyclo(2,2,2)octane (DABCO)		Acros, 97%	112

2.2. Sample preparation

The stoichiometric ratio *R* was defined as

$$R = \text{anhydride equiv/epoxy equiv}$$

$$= \text{anhydride groups/epoxy groups}$$

The samples used for the DSC experiments were prepared as follows: ELO and anhydrides were mixed at 110°C for about 15 min in the case of THPA, METH, MHHPA and MTHPA, after which the catalyst was added. The samples prepared with PA were mixed for about 15 min at 145°C, after which the catalyst was added. The samples were then quenched in cold water. The temperatures chosen for the sample preparation were just above the melting points for PA and THPA. No trace of sublimation was observed in this case. This phenomenon was then neglected in the rest of the study.

For mechanical testing, the samples were prepared as for calorimetric measurements and were cured in an aluminium mould placed in an oven under an air atmosphere. The curing cycle of each formulation was 15 h at 150°C and 1 h at 170°C. Some experiments, not detailed in this paper, show that such a cycle allows to obtain stable and maximal properties (as expected when full cure is reached) without damage connected with thermal degradation.

2.3. DSC measurements

All thermograms were obtained using a Setaram DSC92. Runs were carried out under a nitrogen atmosphere, in

Table 3
Formulas of curing agents used in this work

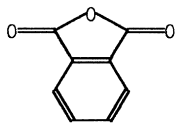
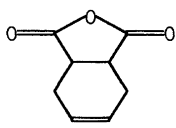
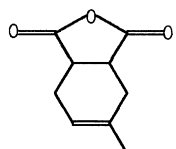
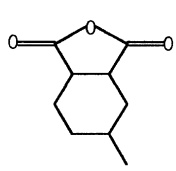
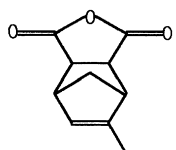
Name	Formula	Supplier and purity	Molecular weight (g/mol)
Phthalic anhydride (PA)		Acros, 99%	148
<i>cis</i> -1,2,3,6-Tetrahydrophthalic anhydride (THPA)		Acros, 99%	152
Methyl-tetrahydrophthalic anhydride (MTHPA)		Lonza, 99%	166
Methylhexahydrophthalic anhydride (MHHPA)		Lonza, 99%	168
Methyl-endomethylenetetrahydrophthalic anhydride (METH)		Lonza, 98%	178

Table 4
The different types and amounts of anhydrides and catalysts used for the curing of ELO

Experiment	Anhydride type	Stoichiometric ratio <i>R</i>	Catalyst type	Catalyst concentration (wt.%)
1	THPA	0.3	2MI	0.90
2	THPA	0.4	2MI	0.90
3	THPA	0.5	2MI	0.90
4	THPA	0.6	2MI	0.90
5	THPA	0.8	2MI	0.90
6	THPA	1.0	2MI	0.90
7	THPA	1.4	2MI	0.90
8	MHHPA	0.8	2MI	0.90
9	MTHPA	0.8	2MI	0.90
10	METH	0.8	2MI	0.90
11	PA	0.8	2MI	0.90
12	THPA	0.8	2MI	0.50
13	THPA	0.8	2MI	2.00
14	THPA	0.8	2E4MI	0.90
15	THPA	0.8	DABCO	0.90
16	THPA	0.8	BDMA	0.90

Table 5
Properties of networks prepared by curing ELO with various amounts of THPA and 0.9% 2MI

Experiment	Amount of THPA R	Flexural modulus at 30°C (MPa)	T_g (1 Hz) (°C)
1	0.3	156	34.5
2	0.4	779	48
3	0.5	1301	68
4	0.6	1744	113
5	0.8	1706	113
6	1.0	2094	112
7	1.4	2296	108.5

aluminium pans. The sample (around 25 mg) was heated from ambient temperature to 300°C at the scanning rate of 10°C/min.

2.4. Mechanical testing

The dynamic mechanical properties (DMA) of the thermosets were determined using a TA Instruments DMA2980 operating in dual cantilever mode. The applied strain was 25 μm . The sample size was $7.5 \times 3.0 \times 60 \text{ mm}^3$. The measurements were performed from -140 to 220°C at a heating rate of $3^\circ\text{C}/\text{min}$. The values of storage modulus (E'), loss modulus (E'') and $\tan \delta(E''/E')$ were followed. Usually, the frequency of deformation was 1 Hz, except for activation energy determinations.

3. Results and discussion

3.1. General properties of the networks

The different formulations studied in this paper are presented in Table 4. The mechanical and thermal properties of the networks, determined by DMA measurements at a deformation frequency of 1 Hz are presented in Tables 5–8. In these tables, the glass transition temperature (T_g) is defined as the temperature at the maximum of the $\tan \delta$ versus temperature curve. As THPA is the most economically interesting hardener, it was extensively studied. The amounts of anhydrides ($R = 0.8$) and catalysts (0.9% by weight of the reactive mixture) often employed in this work are close to those generally used for the curing of commercial epoxy resins.

The influence of R for the ELO–THPA–2MI systems is reported in Table 5. An increase in the glass transition

temperature (T_g) from 34.5°C for $R = 0.3$ up to 113°C for $R = 0.6$ is observed. Then, the T_g remains constant up to $R = 1$ and decreases weakly to 108.5°C for $R = 1.4$. This result is in good agreement with studies on epoxy resins [8–10]. According to Galy et al. [10], for $R < 1$ the unreacted epoxy functions lead to mobile pendant chain ends and account for the decrease of T_g . For $R > 1$, partly reacted hardener units increase the weight between the crosslinks and consequently the T_g is smaller.

The properties of networks prepared with different types of anhydrides are also compared in Table 6. Samples prepared with THPA, MTHPA and MHHPA exhibit similar flexural modulus between 1671 and 1726 MPa and T_g s in the range 109 – 122°C . Networks based on PA and METH differ with flexural modulus between 2000 and 1535 MPa and higher T_g with 148 and 157°C , respectively. These differences in the glassy transition temperatures for METH were also observed [8] in the case of industrial resins based on diglycidyl ether of bisphenol A (DGEBA).

The influence of the catalyst concentration for the ELO–THPA–2MI systems is reported in Table 7. An important decrease in T_g from 114.5 to 82°C and a weak reduction in flexural modulus from 1767 to 1695 MPa was observed when increasing the 2MI catalyst concentration from 0.5 to 2.0%.

The influence of the catalyst type studied for the ELO–THPA systems containing 0.9% (by weight) catalyst is reported in Table 8. The results indicate that the samples prepared with 2MI exhibit higher mechanical strength. On the other hand, formulations catalysed with BDMA show low T_g and modulus.

These changing properties have to be related to differences in the rates of conversion of anhydride groups or maybe in the network structure. The anhydride reactivities

Table 6
Properties of networks prepared by curing ELO with various type of anhydrides and $R = 0.8$

Experiment	Anhydride type	Flexural modulus at 30°C (MPa)	T_g (1 Hz) (°C)
5	THPA	1706	113
8	MHHPA	1726	122
9	MTHPA	1671	109
10	METH	1535	157
11	PA	2000	148

Table 7

Properties of networks prepared by curing the ELO–THPA system with $R = 0.8$ and various amounts of 2MI

Experiment	Amount of 2MI (wt.%)	Flexural modulus at 30°C (MPa)	T_g (1 Hz) (°C)
12	0.5	1767	114.5
5	0.9	1706	113
13	2.0	1695	82

and properties, as well as the catalyst efficiencies seem to play an important role in these phenomena. Such differences were also observed for the curing of epoxidised soybean oil [11]. Thus, a differential scanning calorimetry (DSC) study and dynamic mechanical analysis in the glassy state and in the rubbery region were done in order to determine how the different parameters influence the polymer network.

3.2. Calorimetric study of the curing reaction

3.2.1. General characteristics of the DSC thermograms

The technique of differential scanning calorimetry has been applied successfully to the study of epoxy resins [12] curing and is usually used for the determination of kinetic and thermodynamic parameters. As shown in Fig. 1, an exothermic peak is characteristic of the curing reaction. This peak is usually attributed to the epoxy/anhydride copolymerisation. The integration of this peak allows the determination of the enthalpy of polymerisation expressed in kJ/epoxy equivalent (kJ/ee) or in kJ/anhydride equivalent (kJ/ae) or in (J/g). In the case of THPA (experiments (c), (g)–(i)) and PA (experiment (f)), the melting of the anhydride is observed as an endothermic peak before the reaction peak. For THPA these two peaks (melting and polymerisation) are well separated, the endothermic peak is followed by a return to the base line. For PA the two peaks are not very well separated. As a consequence, in this case the enthalpy of polymerisation (ΔH) and the temperature of exothermic peak maximum (T_p) are probably slightly under-estimated.

In some cases, exothermic peaks have a shoulder at high temperature after the peak maximum. In the case of ELO–THPA systems catalysed with 0.9% 2MI this phenomenon is only observed for mixtures presenting a large excess of epoxy ($R < 0.4$) over stoichiometry. This is also noticed for systems crosslinked with METH (experiments (d) and (e)) and for systems catalysed with BDMA (experiment (i)) or DABCO (experiment (h)). Moreover, in the case of BDMA the second exotherm seems to be more important than the exotherm attributed to copolymerisation. According to

some authors [13,14] this second peak or shoulder at high temperature can be attributed to the epoxy homopolymerisation.

3.2.2. Influence of the epoxy/anhydride ratio

The influence of R on the reaction enthalpy was observed with THPA from $R = 0.4$ to $R = 1.4$. The systems were catalysed with 0.9% (by weight) of 2MI. In these cases the occurrence of epoxy homopolymerisation was not observed. Hence, epoxy/anhydride copolymerisation (opening of epoxy and anhydride cycles and formation of diester linkages) is the only reaction to be taken into account in the explanation of the enthalpies determined.

Calorimetric measurements (DSC) are reported in Fig. 2. The plot of the reaction enthalpy expressed in kJ/ae versus the ratio R is rather stable up to $R = 0.8$ with 61.3 kJ/ae = 49 kJ/ee. This value is in good agreement with the results obtained by others researchers [8,13] on the curing of several epoxy/anhydride systems. An important decrease of enthalpy is then observed. These results indicate that the anhydride groups have probably reacted to completion up to about $R = 0.8$. For $R > 0.8$ free THPA and/or perhaps dangling ends may be present in the network.

3.2.3. Influence of the anhydride type

The experiments were carried out for systems containing 0.9% 2MI (by weight of reactive mixture) and anhydrides with $R = 0.8$. In such conditions METH is the only anhydride where homopolymerisation is observed with a small shoulder in the exothermic peak. Hence, enthalpy of copolymerisation is probably slightly over-estimated. Only differences in enthalpies of polymerisation have to be attributed to the extent of the conversion of the anhydrides. The calorimetric measurements (DSC) are reported in Table 9. The measurements show that THPA, MHHPA and MTHPA exhibit close heats of reaction, between 42.22 kJ/ee for MTHPA and 49.00 kJ/ee for THPA. Curing of METH and PA is less exothermic, with 31.47 and 30.80 kJ/ee, respectively, indicating a weak conversion for these two

Table 8

Properties of networks prepared by curing the ELO–THPA system with $R = 0.8$ and various types of catalysts

Experiment	Catalyst type	Flexural modulus at 30°C (MPa)	T_g (1 Hz) (°C)
5	2MI	1706	113
14	2E4MI	1537	119
15	DABCO	1578	114.2
16	BDMA	1392	109

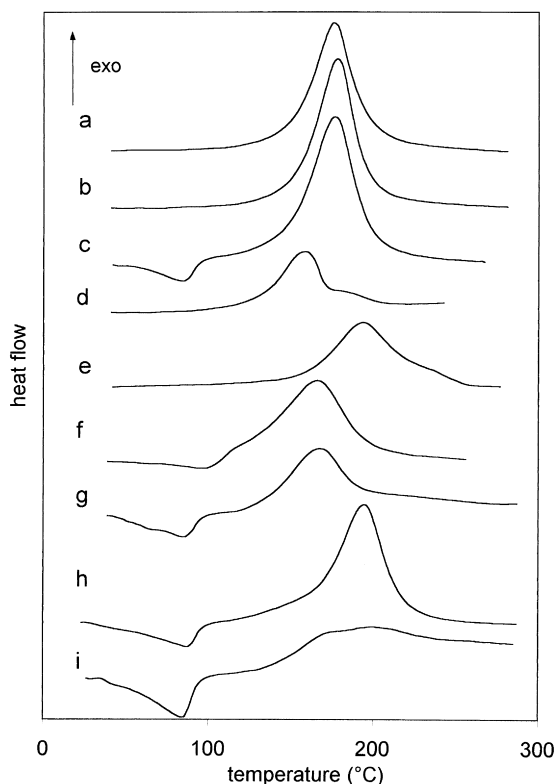


Fig. 1. Thermograms of ELO-anhydrides systems: (a) MTHPA $R = 0.8$, 2MI 0.9%; (b) MHHPA $R = 0.8$, 2MI 0.9%; (c) THPA $R = 0.8$, 2MI 0.9%; (d) THPA $R = 0.2$, 2MI 0.9%; (e) METH $R = 0.8$, 2MI 0.9%; (f) PA $R = 0.8$, 2MI 0.9%; (g) THPA $R = 0.8$, DABCO 0.9%; (h) THPA $R = 0.8$, 2E4MI 0.9%; (i) THPA $R = 0.8$, BDMA 0.9% (the scale of heat-flow was doubled for this experiment).

anhydrides. In the case of METH this low heat of reaction is associated with the highest value of the temperature of exothermic peak maximum (193.6°C), indicating a low reactivity probably due to steric factors such as the size. In the case of the ELO-PA system, the lower T_p (166.1°C) cannot be interpreted as a higher reactivity of PA because of the low extent of conversion (low value of ΔH) measured. One possible explanation could be linked to the important rigidity of the diester segment formed. It

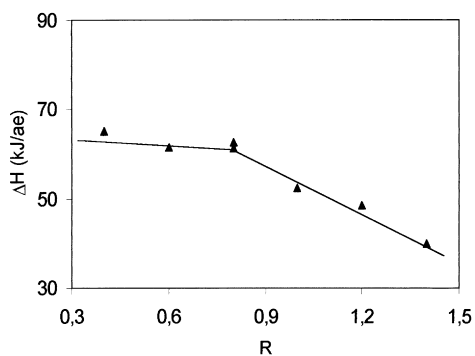


Fig. 2. Enthalpy of reaction versus R for ELO-THPA systems catalysed with 0.9% 2MI.

Table 9
DSC results of ELO-anhydrides systems

Anhydride type	ΔH (kJ/ee)	T_p^a (°C)
THPA	49.0	178
MHHPA	45.49	178.7
MTHPA	42.22	177.2
PA	30.80	166.1
METH	31.47	193.6

^a T_p : temperature of exothermic peak maximum.

comprises a carbon-carbon double bond in the case of PA and a single bond for other anhydrides. This reduces the molecular motions during cure and consequently involves an important amount of non-reacted anhydride in the network.

3.2.4. Influence of the catalysts

The initiation mechanism with tertiary amines or imidazoles has not yet been well understood and seems very complicated. For example, 2E4MI was found to be capable of reacting with epoxies [15] and might act as a crosslinking agent and not only as a catalyst. This may explain the higher T_g (119°C) found in this case. According to recent studies, the amine seems to react with an epoxide to form a complex. Some authors [16] suggested that the amine was irreversibly bound to the epoxide to form a quaternary ammonium ion. Other researchers [17] proposed a mechanism involving the release of the tertiary amine from the epoxide and the formation of a double bond at the end of the polymer chain.

The influence of the catalyst type and concentration were obtained for systems containing THPA with $R = 0.8$ in such conditions where the copolymerisation is the only reaction to be taken into account. The calorimetric measurements (DSC) are reported in Table 10. The kinetic investigations were carried out on the basis of Barrett's method [18], following the assumptions:

Table 10
DSC results on catalyst type and concentration influence on ELO-THPA systems

Catalyst	ΔH (J/g)	T_p (°C)	E_{a1} (kJ/mol)	k_0
2MI				
0.5%	323.6	184	97.6	10^5
0.9%	318.7	178	92.1	10^6
1.25%	304.6	171.5	89.9	10^4
2%	294.6	161.3	86.7	10^4
4%	181.3	147.5	66.6	10^3
2E4MI				
0.9%	291.5	194.5	81.1	10^4
BDMA				
0.9%	79.7	175.5	–	–
DABCO				
0.9%	179.5	168.4	101.5	10^8

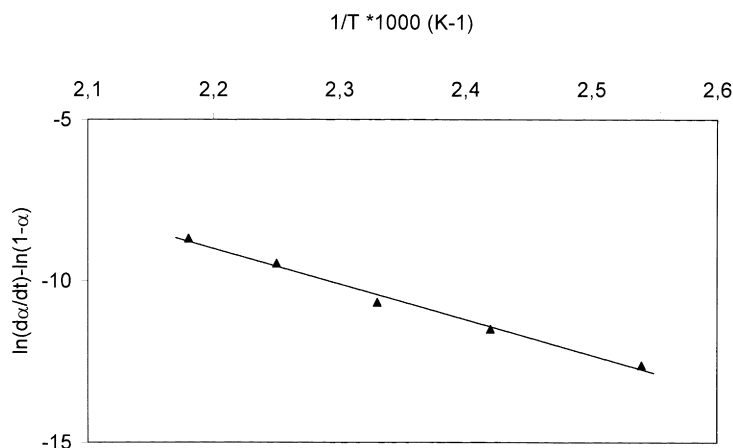


Fig. 3. First-order kinetics law regression of the anhydride conversion in an ELO-THPA system.

1. The extent of cure α is calculated as:

$$a = \Delta H / \Delta H_T \quad (1)$$

where ΔH is the partial heat of reaction (kJ/ee) and ΔH_T the total heat of reaction (kJ/ee).

2. The reaction's kinetics follow the equation:

$$d\alpha/dt = k(1 - \alpha)^n \quad (2)$$

where $d\alpha/dt$ is the reaction rate (s^{-1}), k the specific rate constant (s^{-1}), n the reaction order and t the time (s).

3. The reaction mechanism follows the Arrhenius equation:

$$k = k_0 \exp(-E_{a1}/RT) \quad (3)$$

where k_0 is the preexponential factor (s^{-1}) and E_{a1} the activation energy (J/mol).

Eq. (2) can be written as:

$$\ln((dH/dt)/(\Delta H_T(1 - \Delta H_T/\Delta H_T)^n)) = \ln k_0 - E_{a1}/RT. \quad (4)$$

A plot of the left-hand side as a function of $1/T$ enables the determination of the apparent reaction order from the best linear plot and the activation energy (E_{a1}) from the slope. Fig. 3 shows that a good fitting of the data is obtained with a first-order kinetics law for the ELO-THPA system catalysed with 0.9% (by weight) 2MI. Such a first-order law is in good agreement with several studies on epoxy resins [13,19,20]. The activation energy is 92.1 kJ/mol, this is in the range reported by other authors for epoxy-anhydride reactions [13]. This law remains valid to a maximum extent of $\alpha = 0.7$, close to the conversion at the exotherm peak maximum. For $\alpha > 0.7$ there is an important change in the kinetics law. Earlier studies on epoxy resins cured with

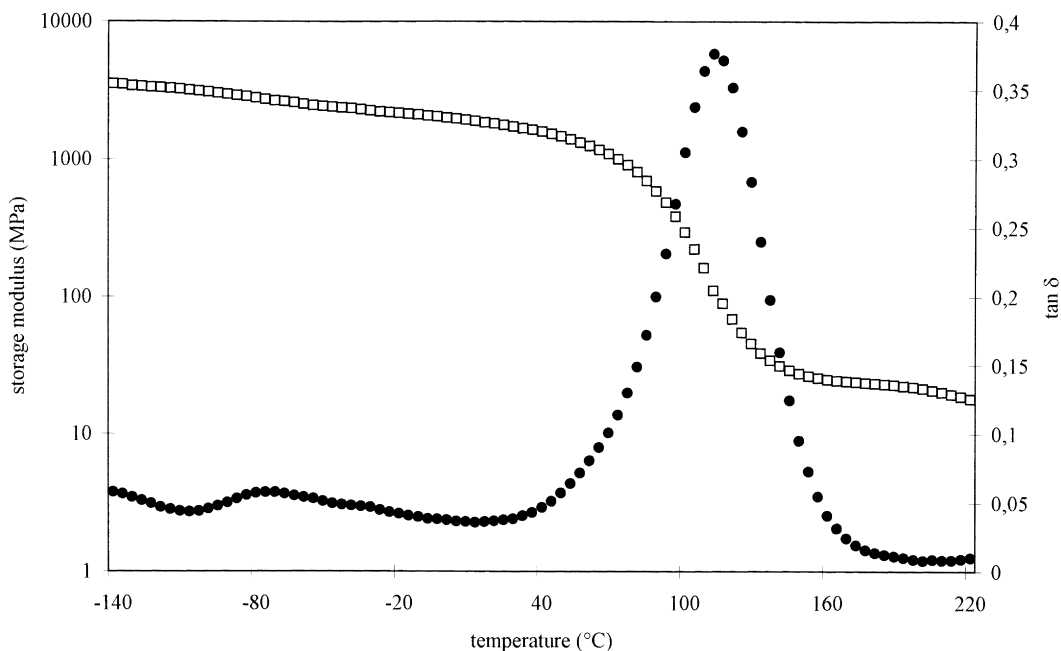


Fig. 4. Temperature dependence of $\tan \delta$ (●) and storage modulus (□) at 1 Hz for an ELO-THPA system.

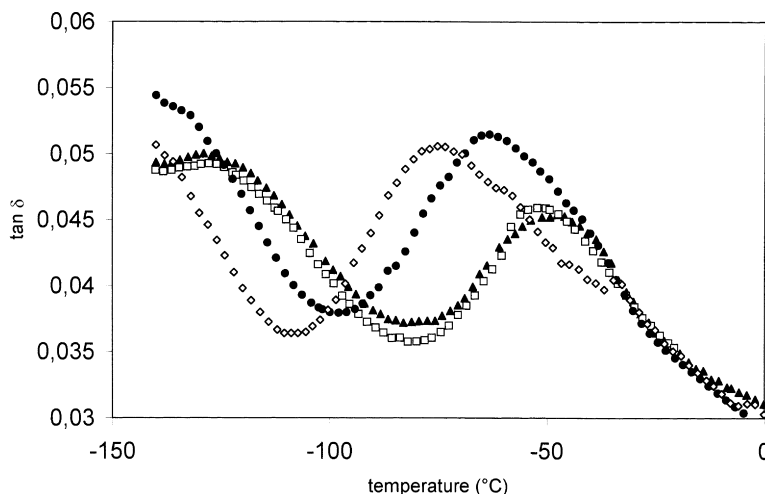


Fig. 5. $\tan \delta$ versus temperature for different frequencies: 1 Hz (\diamond); 10 Hz (\bullet); 50 Hz (\square); 100 Hz (\blacktriangle).

anhydrides [13] explained this by diffusional restrictions associated with vitrification. In our study, a first-order kinetics law was found to be valid whatever the concentration and the type of catalyst tested may be, except for benzyldimethylamine (BDMA) where the occurrence of homopolymerisation of ELO to a large extent made these experiments impossible. The results are reported in Table 10. Experiments on systems catalysed with 2MI between 0.5 and 4.0% by weight show that the enthalpy of polymerisation and activation energy decrease from 323.6 to 181.3 J/g and from 97.6 to 66.6 kJ/mol, respectively. In the meantime, the exothermic peak maximum shifts to low temperature from 184 to 147.5°C. This indicates that the higher the catalyst concentration, the faster the epoxy/anhydride copolymerisation and the lower the extent of conversion of the anhydride groups seems to be. Systems catalysed with imidazoles, especially 2E4MI, exhibit lower activation energies and preexponential factors with 81.1 kJ/mol and 10^4 s^{-1} , respectively, than systems catalysed with DABCO with $E_{a1} = 101.5 \text{ kJ/mol}$ and $k_0 = 108 \text{ s}^{-1}$ indicating easier reactions in the case of imidazoles in spite of higher temperatures of exothermic peak maximum.

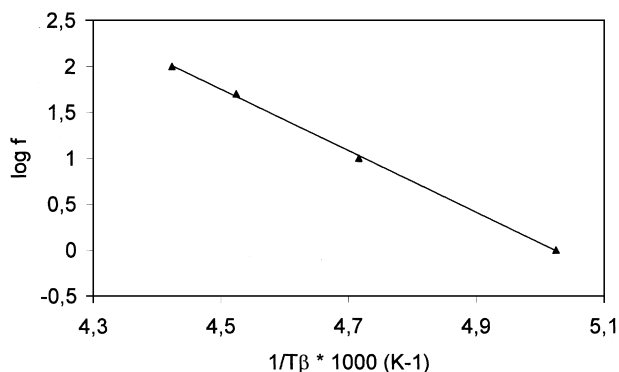


Fig. 6. $\log f$ versus $1/T$.

3.3. Investigations on the network's structure

3.3.1. General properties

A typical evolution of mechanical properties from the DMA experiments is presented in Fig. 4 for an ELO–THPA–2MI system with $R = 0.8$ and 0.9% 2MI. A decrease in the $\tan \delta$ curve from -140 to about -100°C is observed. In earlier studies, a relaxation called γ was observed in epoxy networks with a maxima in the $\tan \delta$ peak at about -190°C for networks containing at least two consecutive CH_2 units, for example in the case of aliphatic epoxies [21] or in the case of aliphatic hardeners [22]. Thus, for the ELO–THPA system such a relaxation that could be attributed to the motions of the large number of CH_2 present in the aliphatic chains of the triglyceride should be observed. In our case the initial decrease of the $\tan \delta$ curve could be linked to the end of such a relaxation. The maximum was not observed in experiments at the frequency of 1 Hz because of difficulties to reach such low temperatures as -200°C . The $\tan \delta$ curve presents two other distinct peaks. The low temperature peak centred at about -75°C , is usually noted as the secondary β relaxation. This relaxation was studied in the case of epoxy resins cured with anhydride and it was found to be due to the motion of the diester segments [23] formed between two crosslinks. The storage modulus decreases slowly through the γ and β relaxations. The peak of $\tan \delta$ that correlated with the largest fall of the storage modulus at high temperature is generally called the α relaxation and is associated with the glass transition temperature (T_g) of the thermoset. Then, in the rubbery region, the storage modulus remains rather stable from 30°C over the maximum of the α relaxation. After 200°C the storage modulus decreases again. This might be due to the fluing and/or degradation of the material.

Investigations in the glassy state were performed from -140 to 30°C at a heating rate of $3^\circ\text{C}/\text{min}$. Experiments covered the frequency range from 1 to 100 Hz. As shown

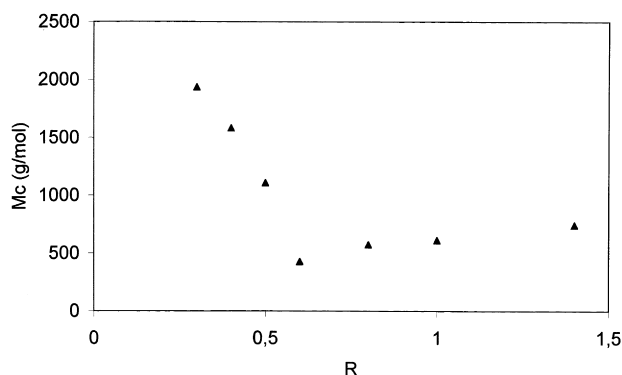


Fig. 7. Influence of THPA amount on M_c .

in Fig. 5, $T\beta$ occurs at higher temperatures with increasing frequency. This observation is the basis of the determination of the activation energy of this relaxation from the Arrhenius equation:

$$f = A \exp(-E_{a2}/RT) \quad (5)$$

where R is the gas constant (8.32 J/mol/K), T the absolute temperatures at which the maximum of $\tan \delta$ is observed (K), f the frequency (Hz), E_{a2} the activation energy (kJ/mol) and A the preexponential factor (Hz).

As shown in Fig. 6, a plot of $\log f$ versus $1/T$ enables the determination of the activation energy from the slope. The results indicate an activation energy of 63 kJ/mol. Other studies on epoxy resins [23,24] showed that the activation energy of β relaxation was dependent on the chemical structure of the curing agent. In the case of a bisphenol A type resin cured with THPA, an activation energy of 79 kJ/mol, quite close to our result, was calculated [23].

3.3.2. Influence of the anhydride amount

The value of the storage modulus (E') in the rubbery region was studied in the case of elastomers and thermosets like epoxy resins [9,25,26] and it was found to be proportional to the crosslinking density (ρ) or inverse to the molecular weight between linkings (M_c) following the

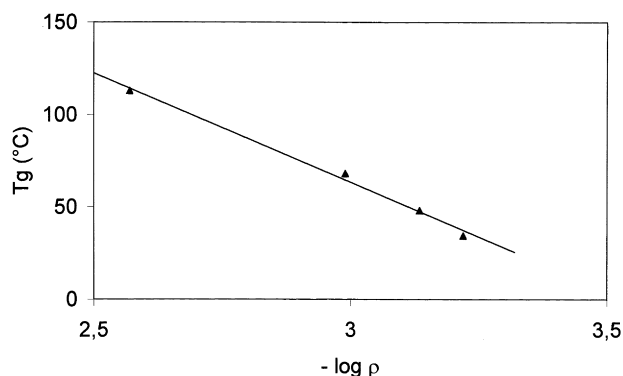


Fig. 8. Glass transition temperature (T_g) versus crosslinking density.

relationship established by Tobolsky [27]:

$$E' = 3dRT/M_c, \quad M_c = d/\rho \quad (6)$$

where d is the density (g/cm^3), R the gas constant (8.32 J/mol/K) and T the absolute temperature (K).

The evolution of the molecular weight between linkings with R , calculated in the rubbery region at a temperature where E' is almost stable is presented in Fig. 7. It was determined in the case of an ELO–THPA system catalysed with 0.9% 2MI. First, we can see a decrease in M_c from 1939 to 429 g/mol for $R = 0.3$ to $R = 0.6$. This evolution of M_c with R involves a decrease in the chain's mobility. This is in good agreement with the important increase of T_g observed in experiments 1–7 (see Table 4). After $R = 0.6$, M_c increases weakly. Although this increase might be due to experimental errors, it could also be attributed to the formation of dangling ends. Such a hypothesis must be confirmed with an accurate structural analysis.

A relationship between T_g and the crosslinking density ρ (ρ has been calculated from Eq. (6)) was studied in the case of epoxy resins [28] and it was found to follow the relation:

$$T_g = K_1 \log K_2 \rho \quad (7)$$

where K_1 characterises the degree of restraint of the molecular motion near the crosslink, K_1 decreases when the restraint increases. K_2 depends on the strength of interactions and on the rigidity of the main chain. In the case of ELO–THPA systems, as shown in Fig. 8, relation (7) was found to be valuable up to $R = 0.6$ with $K_1 = 118.3$ and $\log K_2 = 3.53$. These values are similar to those obtained from the diglycidyl ether of bisphenol A cured with aliphatic polyamines [28], indicating a low rigidity of the main chain and weak restraint of molecular motions. This result is consistent with the structure of triglyceride made of aliphatic chains.

3.3.3. Influence of the anhydride types

The molecular weights between crosslinks have been calculated for various thermosets using the same model as described previously. The molecular weights between crosslinks (see Table 11) are similar for THPA, MHHPA and MTHPA, between 574 g/mol for THPA and 669 g/mol for MTHPA systems and higher for METH and PA systems with, respectively, 870 and 883 g/mol. These results seem to indicate that in spite of high T_g s, networks obtained with PA and METH present weaker crosslinking densities as those obtained with THPA, MHHPA and MTHPA.

3.3.4. Influence of the catalyst concentration

The influence of the catalyst's concentration is reported in Table 12. The results show that M_c increases with the catalyst's concentration from 393 g/mol for 0.5% 2MI to 1059 g/mol for 2.0% 2MI. This indicates that the catalyst concentration has a determining influence on crosslinking density. These results are in good agreement with the

Table 11

Molecular weight between crosslinks (M_c) for networks prepared by curing ELO with different types of anhydrides ($R = 0.8$) and 0.9% (by weight) 2MI

Experiment	Anhydride type	E' (rubber) (MPa)	M_c (g/mol)
5	THPA	22.9	574
8	MHHPA	21.9	584
9	MTHPA	19.8	669
10	METH	15.6	870
11	PA	14.4	883

decrease of T_g and flexural modulus with increasing catalyst concentration.

3.4. General discussion

For the curing of ELO, the use of imidazole catalysts was found to be more interesting than tertiary amines. Thus, the resulting networks exhibit higher extents of conversion of anhydrides and stiffness.

The influence of the anhydride structure on crosslinking density and extent of reaction was also examined. Steric hindrance for METH is expected to result in low crosslinking densities. This must be connected to the epoxy ring's position having a low accessibility inside a chain and close together. An important rigidity of the diester segment formed for PA leads to a weak crosslinking density by restriction of the molecular motions.

The importance of the triglyceride structure, made of aliphatic chains, on the network's properties was explained with a relationship established between T_g and the crosslinking density.

An ELO–THPA–2MI system was particularly studied in this paper. The dependence of the thermomechanical and calorimetric behaviours of this system upon anhydride stoichiometric ratio and catalyst concentration has been observed. We have shown that THPA reacts to completion to about $R = 0.8$. The increase of R to 0.8 causes an increase in crosslinking density (d/M_c), the consequence is a decrease in chain mobility and consequently an increase in T_g and stiffness. Further investigations may be undertaken to confirm the occurrence and the influence of dangling ends and free anhydride in the network particularly at high anhydride ratios ($R > 0.8$). The rise in catalyst concentration induced a decrease in activation energy, peak temperature, extents of conversion of THPA and T_g . When varying the

Table 12

Molecular weight between crosslinks (M_c) for networks prepared by curing ELO with THPA ($R = 0.8$) and different amounts of 2MI

Experiment	Amount of 2MI (wt.%)	E' (rubber) (MPa)	M_c (g/mol)
12	0.5	33.1	393
5	0.9	22.9	574
13	2.0	12.0	1059

catalyst concentration the polymerisation propagation mechanism may change. The increase of catalyst amount is expected to induce an important number of propagation sites. This explains the lower activation energy and the T_p found. But, the increasing number of growing polymer bulks might also involve a fast gelling of the system causing important diffusional restrictions of the reagents. Consequently, the extent of conversion of the anhydride functions is low. On the other hand, when the catalyst concentration decreases, the polymerisation reaction takes place in a fewer sites. The few number of growing polymer bulks do not hinder the diffusion of the reagents. The extent of conversion of anhydrides and consequently network properties are then higher.

4. Conclusions

The structure and formation of the network derived from curing of epoxidised linseed oil were investigated. This work showed the good agreement and the complementary results obtained with the two methods employed (DSC and DMA) in spite of different curing conditions, in two isothermal steps in the case of DMA measurements and with an heating rate for DSC measurements.

The results explained the distinctive features of these polymers. They also allow to fit the formulations to the applications expected for these epoxy resins having a high agricultural resources content. Amongst the possible applications of these polymers, their use in combination with natural fibres in composites may be of a great environmental interest.

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