

Epoxy Thermosetting Systems Based on Cycloaliphatic Diamines

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Synopsis

We have investigated the reaction kinetics of a liquid prepolymer DGEBA with isophorone diamine (IPD) and menthane diamine (MNDA). IPD is 10 times more reactive than MNDA. With mixtures of these two hardeners we have the possibility to control the reactivity of the curing agent and the pot life of the system. The kinetic results can be described with a single conversion temperature-phase diagram and interpreted with the classical autocatalytic epoxy-primary and secondary amine hydrogens addition. The differences between IPD and MNDA can be explained by the steric hindrance around the amine group of MNDA and also by the difficulty to obtain pure MNDA without oxidation.

INTRODUCTION

A current problem with epoxy systems used in high performance coatings, adhesives, potting, and encapsulating compounds is their pot life. Once the liquid prepolymer is mixed with the curing agent, it must be used immediately or stored at low temperature.

Isophorone diamine (IPD) and menthane diamine (MNDA) are isomers (Table I), and are at once aliphatic and cycloaliphatic amine. Donnellan and Roylance¹ have shown that for MNDA the primary amine hydrogens react slowly at room temperature to form a linear polymer. They assume that the secondary amine hydrogens do not react at room temperature because they are much less reactive due to the steric hindrance of the nearby methyl groups.

The present work investigates the reaction kinetics of a liquid epoxy prepolymer diglycidyl ether of bisphenol A (DGEBA) with IPD, MNDA, and mixtures of the two amines. So we think that we have the possibility of controlling the kinetics and the pot life of the epoxy systems.

EXPERIMENTAL

Materials. The epoxy prepolymer used in this study consist of a commercial diglycidyl ether of bisphenol A and commercial isophorone diamine and 1.8 diamino-*p*-menthane (Table I). Purity was more than 98%, DGEBA and IPD were used without further purification, and MNDA was distilled.

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TABLE I
Formulars and Characteristics of Different Materials Used^a

Name ^a	Origin	Molecular weight	Functionality	Structure
(a) Diglycidyl ether of bisphenol A DGEBA	Dow Chemical DER 332	342	2	
(b) Isophorone diamine IPD	Vebe-Chemie AG	170	4	
(c) 1,8-Diaminomenthane MNDA	Aldrich	170	4	

^a IUPAC name: (a) diglycidyl ether 4,4'-dihydroxydiphenyl 1-2,2 propane; (b) 3-amino-methyl 3-5-5 trimethylcyclohexylamine; (c) 4(2-amino) propyl-1-methylcyclohexylamine.

The epoxy prepolymer E—E is considered to be difunctional and the diamine curing agent tetrafunctional

$$\begin{array}{c} \text{A} \quad \quad \quad \text{A} \\ \diagdown \quad \quad \diagup \\ \text{---} \\ \diagup \quad \quad \diagdown \\ \text{A} \quad \quad \quad \text{A} \end{array}$$

So the stoichiometric ratio is defined by $r = \{A\}/\{E\}$ (Table II).

Apparatus. A differential scanning calorimeter, Mettler TA 3000, has been used to characterize the glass transition temperatures T_g and heats of reaction of the unreacted and partially cured samples. A rheometer, model Contraves, was used to monitor the viscosity of the resin system as a function of time at 25°C. Gel permeation chromatography (GPC) was used to determine the molecular weight of the polymer formed by the reaction of DGEBA with IPD and MNDA at 25°C. We employed the Waters Model 244 chromatograph with tetrahydrofuran (THF) as solvent. We used four styragel separating columns: 1000, 500, 100, and 100 Å pores size.

RESULTS AND DISCUSSION

Kinetics Results

A DSC scan to 250°C at 10 K/min of a freshly mixed sample of the resin system DGEBA + IPD and DGEBA + MNDA with $r = 1.0$ is shown on Figure 1. The two exothermic peaks on Figures 1(a) and 1(b) represent the primary and secondary amine hydrogens reactions. IPD is more reactive than MNDA.

DSC has been used with some assumptions by a number of workers¹⁻³ and recently by us⁴ to study the kinetics of epoxy curing reactions without

TABLE II
Different Systems Studied with the Ratio $r = 1.0$

No.	% IPD	% MNDA
1	100	0
2	50	50
3	25	75
4	10	90
5	0	100

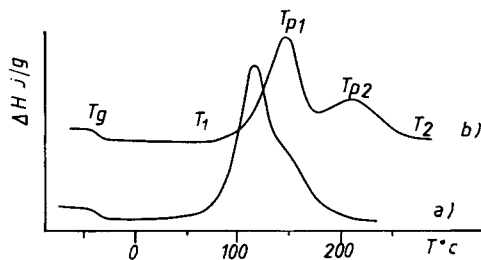


Fig. 1. DSC plots of freshly mixed system: (1) DGEBA + IPD, $r = 1.0$; (b) DGEBA + MNDA, $r = 1.0$. Heating rate $q = 10$ K/min.

attempting to determine the reaction order. The relation between the heating rate q and the peak exotherm temperature T_p is of the form:

$$\ln q = -\frac{E_a}{RT_p} + B$$

where q is the heating rate (K/min), T_p is the absolute peak exotherm temperature, B is a constant related to an Arrhenius frequency factor, and R is the gas constant. The activation energy E_a can be obtained from the slope of a plot $\ln q$ vs. $1/T_p$.

Dynamic DSC scans were run at $q = 2.5, 5, 7,$ and 10 K/min. The plot of $\ln q$ vs. $1/T_p$ for the two peaks of MNDA and the principal one of IPD is shown in Figure 2. The activation energies determined from the slope are quite similar, $E_a = 62 \pm 2$ kJ/mol (14.8 kcal/mol). These values are rather higher than the result found by Donnellan and Roylance¹ for MNDA (but unknown peak) but are in good concordance with the value found by Horie et al.⁵ and by Riccardi et al.⁶ for ethylenediamine and for the autocatalytic mechanism ($E_a = 14$ kcal/mol).

The area of the first exotherm increases when $r > 1.0$ and the second one practically disappears for $r > 2.0$. So we can say that the first peak is due to the reaction of the primary amine hydrogens and the second peak to the reaction of the secondary one:

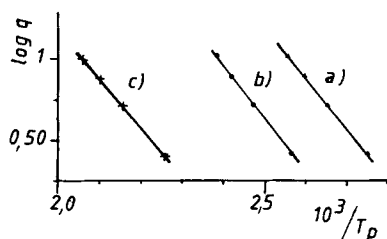
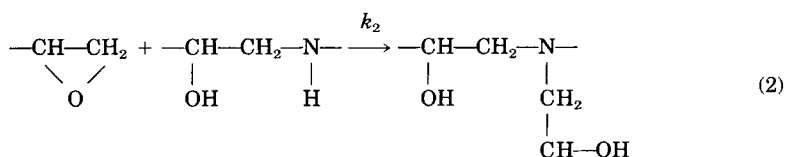
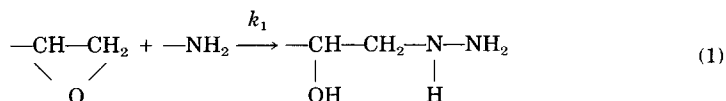


Fig. 2. Arrhenius plot of $\ln q$ vs. $1/T_{\max}$: (a) DGEBA + IPD, $r = 1.0$, first peak, $E_a = 61$ kJ/mol; (b) DGEBA + MNDA, $r = 1.0$, first peak, $E_a = 63$ kJ/mol; (c) DGEBA + MNDA, $r = 1.0$, second peak, $E_a = 63$ kJ/mol.

The hydroxyl groups —CH— catalyze these two reactions.



The second DSC peak of the MNDA-epoxy system at high temperature is ascribed to the reaction between secondary amine hydrogens and epoxy group. It is supported by the fact that we have the same activation energy for the two DSC peaks, and IR analysis on DSC samples show no evidence of ether group due to the epoxy-OH reaction. But this will not be the case for large samples, for an isothermal cure in the temperature range 230–250°C, etherification but also degradation reactions can be observed in these cases.

DETERMINATION OF T_g

After the first one, a second DSC scan at $q = 10$ K/min allowed us to determine the glass transition temperature (T_g) and the heat capacity change ΔC_p at T_g for the polymer network. In a recent work⁴ we found that the maximum attainable T_g coincides with the stoichiometric composition for different curing agent among which IPD.

On Figure 3 we compare the results for IPD and MNDA. For MNDA the crosslink density is maximum, T_g maximum and ΔC_p minimum for $r = 1.2$. This cannot be due to a catalytic mechanism leading to an homopolymerization of the epoxy groups because in such case there is a maximum for a ratio $r < 1.0$.⁴ Because of the steric hindrance of the methyl group adjacent to the amine group, the secondary amine hydrogens of MNDA have some difficulties in reacting to 100%. So, to compensate this low reactivity, it is necessary to introduce a large amount of amine hydrogens. Another reason could be the difficulty to obtain pure MNDA without any oxidation. Just after a distillation, MNDA is colorless, but in a few minutes when we want to use it, it is yellow. These explanations are in excellent agreement with the heat reaction measurements because $\Delta H_0(\text{IPD}) = 485$ J/g is higher than $\Delta H_0(\text{MNDA}) = 350$ J/g.

If we look at the values, the maximum in T_g for IPD (155°C) is superior to the maximum for MNDA (150°C), and, contrary to our expectation, the minimum in ΔC_p for IPD is also superior to the minimum for MNDA.

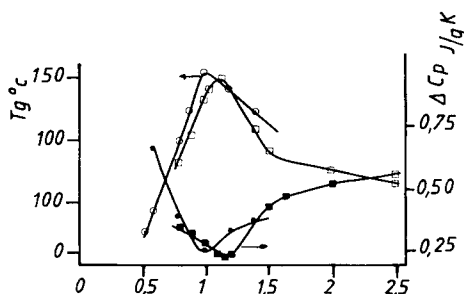


Fig. 3. Effect of the stoichiometric ratio on the temperature of the glass transition T_g and on the heat capacity change ΔC_p at T_g ($q = 10$ K/min). (a) DGEBA + IPD: (○) T_g and (●) ΔC_p ; (b) DGEBA + MNDA: (□) T_g and (■) ΔC_p .

EVOLUTION OF THE RESINS SYSTEMS (1) AND (5) IN A CONVERSION-TEMPERATURE PHASE DIAGRAM

When an epoxy system cures, two principal structural transitions may occur: gelation and vitrification. Gelation marks the transition from a liquid to a rubbery state, since the crosslinked network has elastic properties not present in the low molecular weight linear or branched prepolymers. Vitrification involves a transition from the liquid or rubbery state into the glassy state as a consequence of an increase in molecular weight before gelation or an increase in crosslink density after gelation. As long as the extent of cure remains below the gel point, the epoxy system remains processable and fusible. Gelation takes place when $p_{gel} = 0.577$ for the reactivity ratio $k_2/k_1 = 1$, and increases to 0.618 when $k_2/k_1 \rightarrow 0$. This indicates the gelation phenomena depends only slightly on temperature, as long as the reaction mechanism (i.e., addition or etherification) is not a function of temperature.

(a) We studied the evolution of the resins systems (1) and (5) at room temperature (RT = 25°C) for the ratio $r = 1.0$.

During the course of the reaction, samples are made and analysed by DSC. On each sample, from the first scan made, we were able to determine its $T_{g(t)}$ and then the heat ΔH_t of the residual reaction. As we have only one mechanism of reaction, the degree of conversion can be expressed by $p = (\Delta H_0 - \Delta H_t)/\Delta H_0$, where ΔH_0 is the heat of reaction for complete cure of a freshly mixed sample ($t = 0$). A second scan measures the $T_{g\infty}$ which is constant for a given system; in this case, we have $T_{g\infty}$ (system 1) = 155°C and $T_{g\infty}$ (system 5) = 135°C.

In the course of time, we notice the disparition of the first peak corresponding to the primary amine hydrogens. When $T_{g(t)}$ becomes higher than the curing temperature, the thermogram show endothermic peaks which are more or less pronounced, characterizing the physical aging⁷⁻⁹ of the system (in this case the annealing temperature $T = 25^\circ\text{C}$, is just below the T_g). Contrary to the affirmation of some authors,¹ this peak is not related to a residual melting of the prepolymer DGEBA.

At the same time as the DSC analysis, the samples were dissolved in THF

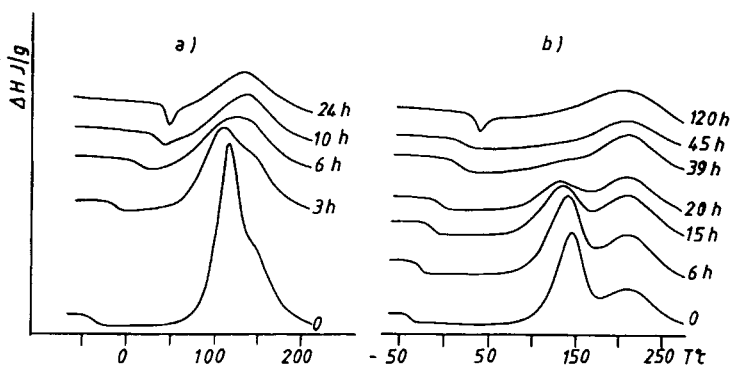


Fig. 4. DSC plots of epoxy systems after a curing time t at room temperature (RT = 25°C) $q = 10$ K/min; (a) DGEBA + IPD, $r = 1.0$; (b) DGEBA + MNDA, $r = 1.0$.

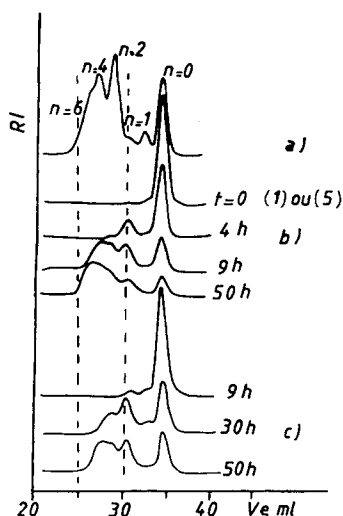


Fig. 5. Molecular weight distribution of epoxy systems after a curing time t at RT = 25°C: (a) DGEBA, $\overline{M}_n = 880$ for a comparison; (b) DGEBA + IPD, $r = 1.0$; (c) DGEBA + MNDA, $r = 1.0$.

and injected in GPC (Fig. 5). From the height of the peak h_i of the DGEBA prepolymer $n = 0$, we can compute a second degree of conversion $p' = (h_0 - h_i)/h_0$. This peak h_i decreases with time, and products of higher molecular weight are formed and compared with the chromatogram of a solid prepolymer DGEBA (Fig. 5). Simultaneously, we continuously measured the viscosity evolution of the systems. The results are shown in Table III.

Initially, values of p and p' for IPD are close. After 30% of conversion p' becomes higher than p . This is consistent since those two parameters do not represent the same phenomena; p' only measures the disparition of the prepolymer DGEBA and not the consumption of epoxy groups. But initial values of p and p' are not closed for MNDA; $p > p'$ before 30% of conversion suggests that chain extending reactions are more probable with MNDA.

Samples with IPD cured less than 7 h are completely dissolved in THF. But if we want to dissolve the samples cured for 7 h or longer, insolubles are formed, indicating that a gel fraction exists in the system. On the other hand, after 50 h of reaction, the whole polymer with MNDA is still dissolved; a gel fraction appears only after 100 h (4 days).

Figure 6 shows the evolution of the degree of conversion p and the viscosity η with time. With IPD, the viscosity increases rapidly between the seventh and the eighth hours, thus at the same time as the gel fraction is observed. A same increase in viscosity is noticed with MNDA, between 18 and 25 h, a long time before insolubles are formed.

The degree of conversion increases very quickly with IPD (system 1), the point $p = 50\%$ is reached just before 7 h. For 7–8 h, p goes from 50 to 55% (during this time the insoluble fraction appears and $\eta \rightarrow \infty$). The theoretical degree of conversion at the gel point for such a system is $57.7\% < p < 61.8\%$ ¹⁰ for $k_2 \leq k_1$. Then a stable value p is reached around 66% with a value of $T_{g25^\circ\text{C}} = 48^\circ\text{C}$, 23°C higher than the curing temperature. We can

TABLE III
Kinetics Results at Room Temperature for Systems (1) and (5)^{a, b}

	t_h	0	1	2	3	3.5	4	4.5	5	7	10	15	23.5
IPD	η (Pa s)	0.9	1.5	3	8	15	25	45	75	5000			
	T_g (°C)	-42	-38	-35	-25	-15	-12	-8	-2	16	28	35	48
	p (%)	0	1.2	5	15	22.3	27.5	34	38	54	57	61	66
	p' (%)	0	1.5	5	17.5	25	32	40	46.5	66.5	70.5	75	78
	t_h	0	1	3.5	5	6.5	8	9	10	11	13	15	23
MNDA	η (Pa s)	0.9	1	1.6	2.3	3.8	5.7	8.2	11.4	16.4	36.3	75	4500
	T_g (°C)	-43	-42	-38	-35	-32	-29	-27	-25	-23	-21	-18	-9
	p (%)	0	1.1	4.8	8	11	12.8	15	17	19	22.5	25.8	38
	p' (%)	0	0.5	1	1.5	2	3	5.5	8.5	11.5	17.5	23.5	46.5
	$p/1.2$	0	0.8	4	6.7	9.2	10.7	12.5	14.2	15.8	18.8	21.5	31.7
													31.7
													39.8
													47.5
													50
													55

^a $p = (\Delta H_0 - \Delta H_t)/\Delta H_0$ measured by DSC, with ΔH_0 (IPD) = 485 J/g and ΔH_0 (MNDA) = 350 J/g.

^b $p' = (h_0 - h_t)/h_0$ measured by GPC (refractive index detector) from the DGEBA, $n = 0$ peak.

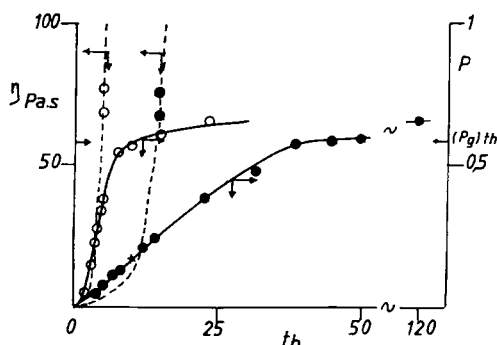


Fig. 6. Evolution with the curing time of the viscosity (---) and degree of conversion (—) for epoxy systems cured at $RT = 25^{\circ}\text{C}$: (○) DGEBA + IPD, $r = 1.0$; (●) DGEBA + MNDA, $r = 1.0$.

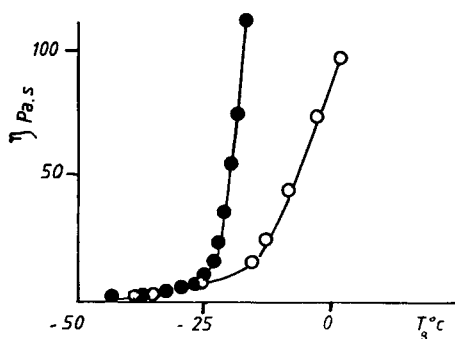


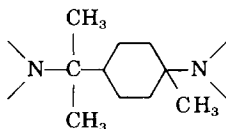
Fig. 7. Comparison of the evolution of the viscosity of the two systems (1) and (5) with the $T_{g(t)}$: (○) IPD; (●) MNDA.

notice that the increase in viscosity corresponds not only to the formation of the gel but also to a value of T_g close to the curing temperature. The experimental gelation point, which is close to its theoretical value when considering experimental errors, would be confounded with the transition from the liquid state to the glassy state at RT: $T_{g, \text{gel}}$, the temperature at which both gelation and vitrification simultaneously occur, equals $25 \pm 3^{\circ}\text{C}$ for system (1).

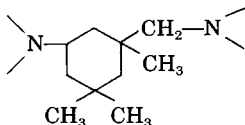
With MNDA (system 5) the reaction is much slower, $p = 50\%$ is reached after 34 h, $p = 60\%$ after 50 h with $T_g = 12^{\circ}\text{C}$. The reaction goes on, and at $t = 100$ h the degree of conversion is stable at 66% with $T_{g25^{\circ}\text{C}} = 32^{\circ}\text{C}$; the two results obtained with IPD and MNDA are comparable for p_{∞} but not for $T_{g25^{\circ}\text{C}}$. With MNDA during the period 50–100 h, we noticed that Δp only equals 6% but $\Delta T_g = 20^{\circ}\text{C}$. A slight variation of p induces a large variation of T_g . Always with MNDA the gel fraction is formed later and only for p close to 65%, which is superior to $p_{\text{gel, th}}$. Surprisingly, the viscosity increases at low values of p , around 30% and at T_g values close to -12°C , far below RT. Figure 7 representing η vs. T_g shows the high viscosity of system (5) during the reaction.

To explain this result, we can precise that even though IPD and MNDA

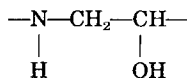
are isomers, there are important differences in their conformations. With MNDA the chain has the following form:



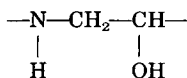
so that it is more rigid because the aliphatic cycle will allow a larger number of intermolecular interactions and a better compacity than with IPD where the chain is:



Primary and secondary amine hydrogens have different reactivity, $k_1 > k_2$ (Figs. 1 and 4). With IPD the gel point is still found at $p = 55\%$, so close to its theoretical value. The difference between the two amine hydrogens reactivities is greater with MNDA. We can tell from the values of the activation energies that both systems are autocatalyzed: during the reaction $>NH + \text{epoxy}$, the $-\text{OH}$ groups are catalyst.^{5,6} With the primary amine hydrogens $-\text{NH}_2$, we have a trimolecular reaction, which can be bimolecular with



We can think that linear molecules $-(\text{DGBA}-\text{MNDA})-$ are formed at the beginning of the reaction; but after 50 h, as the system has a high viscosity, a bimolecular reaction between epoxy and



is not null anymore, and the gel point is reached, including a gel fraction. For system (5) the ratio k_1/k_2 is very high at the beginning, but, as it may certainly be related to the viscosity of the reactive system, it decreases during the reaction.

Finally we can notice that values of the degree of conversion p are determined from heat reaction measurements, since $p = (\Delta H_0 - \Delta H_t)/\Delta H_0$, with the assumption that $\Delta H_t = 0$ implies a total reaction. This may not necessarily be true. Effectively, to explain the MNDA behavior, we supposed that some secondary amine hydrogens $>NH$ do not react. The value of $\Delta H_0 = 350 \text{ J/g}$ used to compute p would be underestimated and p values overestimated. Considering the fact that T_g goes through a maximum for $r = 1.2$, we can divide the computed values of p by 1.2. So for $p = 66\%$ we

would obtain a new value $p = 55\%$, and gelation of both systems (1) and (5) cured with IPD and MNDA would start at the same value of p .

(b) To finish off this kinetics study at RT, we measured both p and T_g at different curing temperature. Results are shown in Table IV.

To be sure to have p_x and T_{g_x} at a given curing temperature T_c , we take measurements at large t_x . So we were able to plot a conversion temperature phase diagram,^{6,11} showing the different states which may appear during the curing (Fig. 8).

We can explain the higher curve of system (5) based on MNDA with the

TABLE IV
Kinetics Results at Different Curing Temperatures for Systems (1) and (5)^a

Amine	No.	T (°C)	t_h	T_g (°C)	p (%)
IPD $r = 1.0$	2	140	3	155	100
	3	110	21	140	96
	4	90	—	120	91
	5	70	—	103	85
	6	60	—	98	80
	7	50	—	80	75
	11	25	—	45	66
	13	15	70	40	65
	17	-18	250	-22	77
MNDA $r = 1.0$	1	150	21	133	100
	3	110	—	132	a)
	4	90	—	115	a)
	5	70	—	90	94
	7	50	—	50	83
	8	40	21	25	71
	9		120	63	81
	10	28	120	42	72
	11	25	50	12	60
	12		100	32	66
	13	15	70	5	53
	14		240	27	64
	15	5	75	-20	25
	16		240	10	53

^a p cannot be measured by DSC in these cases; $p \cong 96-100\%$.

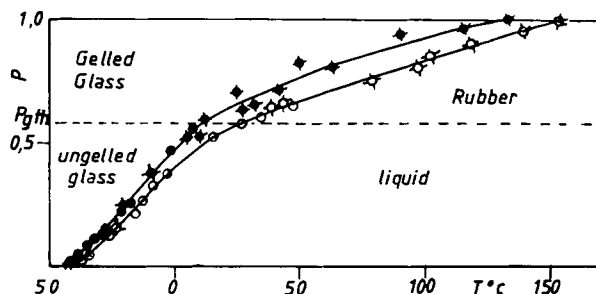


Fig. 8. Conversion phase diagrams for epoxy thermosetting systems ($r = 1.0$): (○) IPD and (●) MNDA cured at RT = 25°C and at different time t . (—○—) IPD and (—●—) MNDA cured at different temperatures T_c and at t_x .

systematic underestimation of ΔH_0 and overestimation of p : dividing p by 1.2 would give a curve for system (5) similar to the curve representing system (1) based on IPD. On the other hand, the dispersion of the experimental points is more important with MNDA.

The curves can be assimilated to two straight lines. Between $t = 0$ and t_{gel} the slope is twice as much as the slope after t_{gel} . This means that, for a given Δp , T_g increases twice as quick after the gel point. To explain this result, we can consider that, before the gel point, an increase in T_g is due to an increase in molecular weight, and, after p_{gel} , the T_g increase is due to the crosslinking.

The diagram has to be completed with the plot of T_g vs. the curing temperature T_c (Fig. 9). We judged interesting to plot the results obtained by Enns and Gillham¹² with the system based on Epon 828 (DGEBA, $n = 0.2$) and another aliphatic amine, the bis(*p*-aminocyclohexylmethane) called PACM, and also the 4,4-diaminodiphenylsulfone (DDS). In all cases T_g is higher than T_c . The difference $T_g - T_c$ increases slightly with T_c from 20°C at $T_c = 25\text{--}35^\circ\text{C}$ at $T_c = 100^\circ\text{C}$. This reported difference can be the result of the scanning method used to determine T_g (10 K/min). Results of Enns and Gillham¹² for PACM are similar to our results obtained with system (1) based on IPD (except at $t = 0$, the authors may have chosen the T_g value of the prepolymer DGEBA alone, at the place of the T_g of the freshly mixed system). It is only at the end of the reaction that differences exist between the two systems, since $T_{g^{\infty}}$ is higher with PACM. We can also consider the few points obtained with DDS as the extension of the same curve.

With MNDA, T_g is also superior to T_c but the experimental curve is slightly below the previous straight line. This is consistent with the explanation given earlier about the T_g variation as a function of the stoichiometric ratio r (Fig. 3). We have to precise that values of samples 7, 8, 11, 13, and 15 for which $T_g < T_c$ were not used to plot the curve of system (5) based on MNDA, since it is obvious that the reaction times were too short, $t < t_{\infty}$. This shows again that the reaction with MNDA is very slow and that we have to wait a very long time to get a maximum degree of conversion. This explains the possibility of oxidation at higher temperature.¹³

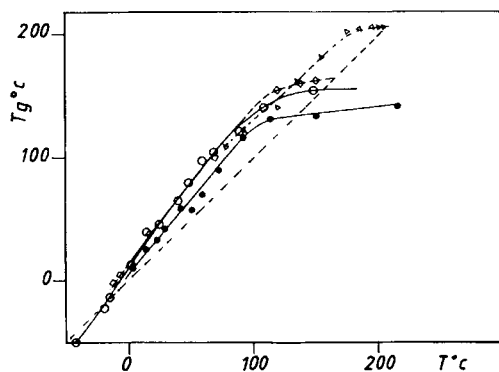


Fig. 9. Evolution of $T_{g^{\infty}}$ vs. cure temperature T_c for different epoxy systems: (○) IPD; (●) MNDA; (□) PACM¹²; (△) DDS.¹²

CONTROL OF AN EPOXY SYSTEM EVOLUTION AT ROOM TEMPERATURE

Several reactive blends have been made with the two curing agents having different reaction rates. For the system based on IPD, the introduction of more MNDA increases the pot life of the reactive system at room temperature.

We studied the evolution of systems (2), (3), and (4) as we did with systems (1) and (5) by DSC. Figure 10 shows the evolution of p with the reaction time (t) for the five systems. In all cases p begins to increase linearly and then becomes asymptotic at a 66% conversion. This point is reached after a certain time depending on the MNDA concentration. The variation of the initial slope dp/dt vs. the IPD concentration is quasi linear (Fig. 11), and indicates that IPD is around 10 times more reactive than MNDA.

The experimental values can also be plotted on a conversion temperature phase diagram (Fig. 12). We noticed that at the beginning, points representing blends (2), (3), and (4) follow those of system (5) and then go through the gelation point on the plot representing system (1) based on IPD.

Likewise, T_g of the tridimensional network follows an additive law, going from 153°C for system (1) to 135°C for system (5) (amine-to-epoxy ratio $r = 1.0$).

CONCLUSION

We have investigated the reaction kinetics of a liquid epoxy prepolymer DGEBA with two aliphatic-cycloaliphatic diamines, IPD and MNDA. IPD

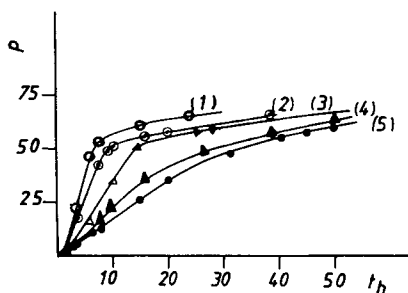


Fig. 10. Evolution with the curing time of the degree of conversion for epoxy systems (1), (2), (3), (4), and (5) cured at RT = 25°C.

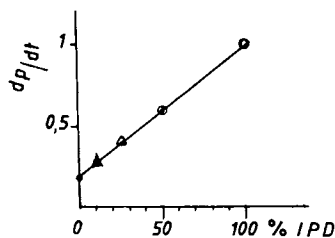


Fig. 11. Effect of IPD concentration on the initial rate of the reaction.

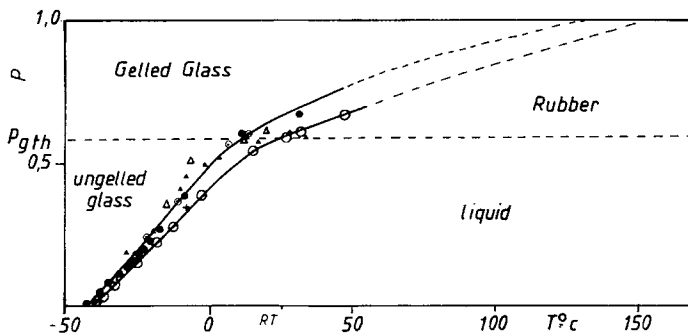


Fig. 12. Conversion temperature phase diagrams for DGEBA, $n = 0$ thermosetting systems cured at $RT = 25^\circ\text{C}$ and at different time t : (○) system (1); (●) system (5); (◐) system (2); (△) system (3); (▲) system (4).

is 10 times more reactive than MNDA. At room temperature, a gel fraction appears after 7 h with IPD and 100 h with MNDA. With IPD, $T_{g,\text{gel}}$ equals $25 \pm 3^\circ\text{C}$. The kinetics results can be described with a single conversion temperature phase diagram. The activation energies of the epoxy primary and epoxy secondary amine hydrogen reactions are in good concordance with an autocatalytic mechanism.

T_g obtained at t_∞ for a curing temperature T_c is always $20\text{--}35^\circ\text{C}$ higher than T_c . For completely cured systems the maximum attainable T_g coincides with the stoichiometric composition for IPD and with $r = 1.2$ (an excess of hardener) for MNDA. This result can be explained by a difficulty for MNDA secondary amine hydrogens to react, or by a difficulty in obtaining pure MNDA without oxidation.

With mixtures of these two hardeners, IPD and MNDA, we have the possibility of controlling the reactivity of the curing agent and the pot life of the system.

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