

Influence of Different Imidazole Catalysts on Epoxy-Anhydride Copolymerization and on Their Network Properties

NELLY BOUILLON, JEAN-PIERRE PASCAULT, and LAN TIGHZERT, *Laboratoire des Matériaux Macromoléculaires, UA CNRS n° 507, Institut National des Sciences Appliquées de Lyon, 20, Avenue A. Einstein, 69621 Villeurbanne Cedex, France*

Synopsis

The copolymerization of nadic and methyltetrahydrophthalic anhydrides and diglycidyl ether of bisphenol A (DGEBA) with various stoichiometric ratios [$r = 2[\text{anhydride}]/[\text{DGEBA}]$] and with different concentrations of several imidazoles has been studied. These results are compared with those obtained with a tertiary amine such as benzyldimethylamine, a well-known efficient catalyst of epoxy-anhydride copolymerization. Thermal and hydrothermal behaviors of these networks also have been examined.

INTRODUCTION

Thermosets based on crosslinked epoxies are used extensively as structural adhesives, matrix materials for fiber-reinforced composites, coating, and potting compounds. The properties of the cured epoxy prepolymers depend on their composition, the structure of the epoxy prepolymer, and the conditions and course of the curing process.

Until now, many researchers have studied the mechanism of curing using a tertiary amine as catalyst of the epoxy-anhydride reaction,¹⁻⁶ but the obtained network has a slightly low glass transition temperature. Imidazoles, especially 2-ethyl-4-methylimidazole (2,4-EMI), have been shown to be effective initiators for the homopolymerization of epoxy prepolymers. The final networks exhibit excellent chemical resistance and electrical characteristics.⁷⁻¹¹

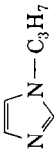
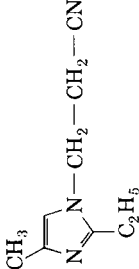
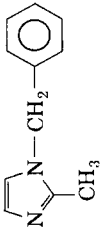
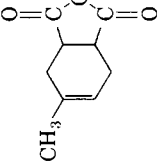
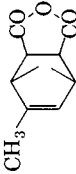
The purpose of this work is to investigate various formulations with different ratios (anhydride)/(epoxy) and catalyzed with several imidazoles and to compare them with a tertiary amine. The thermal and hydrothermal characteristics of these networks are also compared.

MATERIALS AND TECHNIQUES

A commercial epoxy prepolymer (DER 332) supplied by Dow Chemical and consisting largely of pure diglycidyl ether of bisphenol A (DGEBA $n = 0.03$) was cured with pure methyltetrahydrophthalic (MTHPA, Aldrich) and nadic (MNA, Aldrich) anhydrides, in the presence of various catalysts such as benzyldimethylamine (BDMA, Aldrich) and different imidazoles (Anchor). These initial substances whose chemical structures are given in Table I, were used without further purification.

TABLE I
Formulas of Materials Used in This Work

Name	Formula	Molecular Weight
Diglycidyl ether of bisphenol A (DGEBA)		350
Benzylidimethylamine (BDMA)	<p style="text-align: center;">$n = 0.03$</p>	134
1-Methylimidazole (MIA)		82
2-Ethyl 4-methylimidazole (EMI)		110

1-Propyl imidazole (PIA)		110
1-Cyanoethyl 2-ethyl 4-methyl imidazole (1C 2E 4MIA)		163
1-Benzyl 2-methyl imidazole (1B 2MIA)		172
Methyltetrahydro- phthalic anhydride (MTHPA)		166
5-Methylnorbornene 2,3- dicarboxylic anhydride (nadic anhydride) (MNA)		178

Different formulations with stoichiometric ratios $r = 2[\text{anhydride}]/[\text{DGEBA}]$ varying from 0.7 to 1.2 with 1% and 3% by weight of catalysts were analyzed.

The DSC Mettler TA 3000 was used for all calorimetric measurements. For each formulation, two types of scan were made: in the first one, the sample, in a sealed pan, was heated at a constant rate of $10 \text{ K} \times \text{min}^{-1}$ and the integration of the exothermic peak gave the enthalpy of polymerization in kJ/epoxy equivalent (kJ/ee). This measurement was followed by a rapid cooling and a second scan was made on the same sample immediately after at the same rate of heat. In this way, the glass transition temperature T_g of the network was obtained.

For the water-swelling procedure, rectangular specimens of $(7 \times 2 \times 0.1) \text{ cm}^3$ were cut from plates of epoxy network. Before swelling measurements, each specimen was stirred under vacuum at 40°C during 24 h to remove all traces of humidity, after that the initial weight was determined. Specimens were moisture conditioned by immersion in distilled water, with the desired water temperature controlled to be better than $+0.5^\circ\text{C}$ using a constant temperature bath. Swelling was determined by direct weighing of dry and swollen specimens as follows:

$$\% \text{ weight gain} = \frac{m_t - m_o}{m_o} \times 100$$

where m_t is the weight of swollen specimen at time t , m_o is the weight of dry specimen.

RESULTS AND DISCUSSION

The differential calorimetry scanning (DSC) results of DGEBA-MTHPA and DGEBA-MNA systems, catalyzed with various concentrations of different imidazoles are reported in Tables II and III, respectively. First, we can remark that the exothermic peak shifts to low temperatures with increasing imidazole concentration (value of T_i , T_p , T_f diminishes). Second, the reaction with 1-cyanoethyl 2-ethyl 4-methylimidazole takes place at higher temperature than that with other imidazoles; notably in the case of MNA, T_p is found at 171.9°C instead of 156°C in the case of MTHPA. Other imidazoles and BDMA give a T_p within the range of $145\text{--}150^\circ\text{C}$. This observation can be explained by the presence of $-\text{C}=\text{N}$ group in 1C2E4MIA molecule.

The thermograms of DGEBA-MTHPA catalyzed by 1% or 2% (by weight) of MIA and BDMA are presented in Figure 1. We have two peaks in the case of an excess of epoxy ($r = 0.85$) but only one for $r \geq 1$. The peak at low temperature could be attributed to the catalyzed anhydride-epoxy copolymerization. The peak at high temperature could be due to the epoxy homopolymerization because of the epoxy excess. This reaction has been observed elsewhere.¹²

In Figure 2, we notice that the DGEBA-MNA system catalyzed by MIA or 1C2E4MIA gives an exothermic peak in a narrow temperature range in comparison with that obtained with BDMA. This observation confirms the effectiveness of imidazoles as catalyst for epoxy-anhydride systems.

TABLE II
 DSC Results of DGEBA-MTHPA System

Catalyst * mol/10 g of reactive mixture	<i>r</i>	ΔH (kJ/ee)	T_i (°C)	T_p (°C)	T_f (°C)	T_g (°C)
1% MIA	0.7	50	80	141	178	126
1.2 × 10 ⁻³ *	0.85	58	90	145	190	131
	1	56	95	145	185	120
	1.2	62	75	146	185	111
3% MIA	0.85	55	61	129	173	105
3.6 × 10 ⁻³	1	59	75	133	170	120
1% EMI	0.7	50	95	145	187	130
0.9 × 10 ⁻³	0.85	54	95	149	193	133
	0.94	55	94	143	184	131
	1.2	62	95	151	185	107
3% EMI	0.85	58	90	141	175	119
2.7 × 10 ⁻³	1	60	87	168	168	103
1% PIA	0.7	51	83	143	190	125
0.9 × 10 ⁻³	0.85	54	103	155	198	130
	0.94	57	95	146	185	120
	1.2	62	84	147	183	104
3% PIA	0.85	59	74	135	175	104
2.7 × 10 ⁻³	1	60	67	136	169	99
1% 1C 2E4 MIA	0.72	48	92	148	191	123
0.6 × 10 ⁻³	0.85	54	103	155	198	128
	1	59	102	156	199	—
	1.2	62	106	158	196	110
3% 1C 2E4 MIA	0.8	52	91	139	183	109
1.84 × 10 ⁻³	1	56	86	142	181	108
1% 1B 2MIA	0.85	46	88	146	191	124
0.58 × 10 ⁻³	1	59	89	148	204	130
	1.2	62	88	150	199	111
3% 1B 2MIA	0.85	53	78	134	173	109
1.74 × 10 ⁻³	1	55	79	135	167	100
1% BDMA	1	55.3	75	146	210	103
1.2 × 10 ⁻³						

T_i : temperature of exothermic peak beginning; T_p : temperature of exothermic peak maximum; T_f : temperature of exothermic peak end; T_g : glass transition temperature; $r = 2$ [anhydride]/[DGEBA].

With 1% of catalyst, the glass transition temperature is the highest for $r = 0.85$ in the case of MIA, EMI, and PIA (Fig. 3). On the contrary, the maximum T_g is observed in the case of BDMA, 1B2MIA, and 1C2E4MIA when r is slightly less than 1 (Fig. 4). We can explain this result by the difference in molecular weight of these two classes of catalyst. At 1%, the former (MIA, EMI, PIA) corresponds to about 1×10^{-3} mol/10 g, while with the latter (BDMA, 1B2MIA, 1C2E4MIA) we have only about 0.6×10^{-3} mol/10 g (Table II); a quantity that is not sufficient to catalyze simultaneously both anhydride-epoxy copolymerization and epoxy homopolymerization at higher temperature. Moreover, in Figure 4, the network obtained with imidazoles possesses a T_g higher than that with BDMA, around 130°C compared with 105°C. In fact, Farkas and Strohm¹³ have found that EMI acts

TABLE III
DSC Results of DGEBA-MNA System

Catalyst * mol/10 g of reactive mixture	<i>r</i>	ΔH (J/g)	δH (KJ/ee)	T_i (°C)	T_p (°C)	T_f (°C)	T_g (°C)
2% 1C 2E 4MIA 1.2×10^{-3} *	1.2	262.11	50.3	112	166.6	200	113
	1	283.88	49.3	110.7	167	198.7	140
	0.85	309.92	49.8	109.3	166	198.7	150
	0.7	287.34	42.3	113.3	164.2	189.3	143
	0.6	271.92	37.64	113.3	163.8	192	126
1% 1C 2E 4MIA 0.6×10^{-3}	1	282.2	46.9	114.7	171.9	208	136
	0.85	299.19	48.1	118.7	171.5	212	160
	0.7	300		105	171.7	210	130
1% MIA 1.2×10^{-3}	1.2	259.85	49.8	93.3	157.7	190.7	131
	1	287.63	50	93.3	158.5	202.7	142
	0.85	311.08	50	94.7	156.7	201.3	158
	0.7	310.93	45.8	94.7	155.4	193.3	143
	0.6	296.75	41.1	97.3	161.6	202.7	128
0.5% MIA 0.6×10^{-3}	1.2	274.66	52.7	93.3	170.1	230	125
	1	285.94	49.7	95	168.3	233.3	145
	0.85	303.18	48.7	96.7	168.7	225	151
	0.7	274.52	40.44	102.7	162.9	190.7	133

Symbols the same as in Table II.

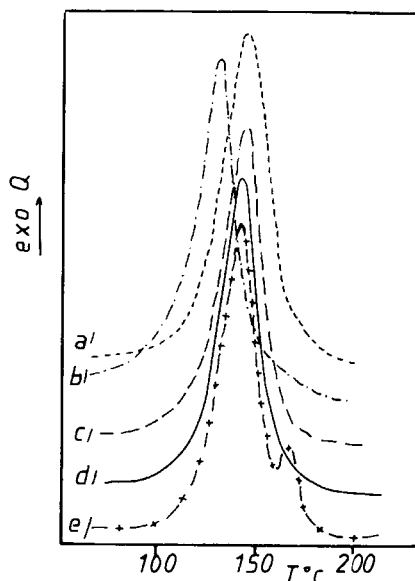


Fig. 1. Thermograms of DGEBA-MTHPA mixture. (a) $r = 1$, 1% of BDMA (ref. 6); (b) $r = 1$, 2% of MIA; (c) $r = 1.2$, 1% of MIA; (d) $r = 1$, 1% of MIA; (e) $r = 0.85$, 1% of MIDA.

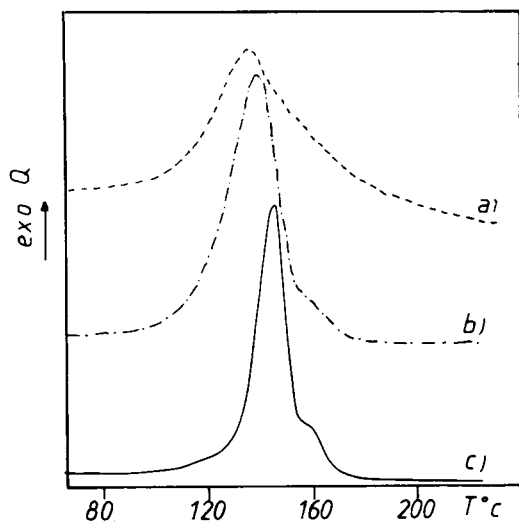


Fig. 2. Thermograms of DGEBA-MNA mixture with $r = 0.85$ and 1.2×10^{-3} mol/10 g of catalyst. (a) BDMA; (b) MIA; (c) 1C 2E 4MIA.

as a crosslinking agent, its incorporation in the network leads to superior physical and chemical properties, according to the following scheme:

In the case of most imidazoles, the glass transition temperature decreases with increasing concentration of catalyst (Table III). This is in good agreement with the results obtained by Heise and Martin.¹¹ According to these authors, at weak concentrations of imidazole there are two kinds of reactions: the first corresponds to the formation of an epoxy/imidazole adduct, the second to etherification or crosslinking reactions.

The plot of the reaction enthalpy versus the ratio r for all types of imidazoles gives a straight line (Fig. 5). Thus we can conclude that the chemical structure of imidazoles does not influence the reaction mechanism. The same result is obtained with nadic anhydride (Table III). For various imidazoles, nadic anhydride gives a network with a higher T_g than methyl tetrahydrophthalic anhydride (Fig. 6).

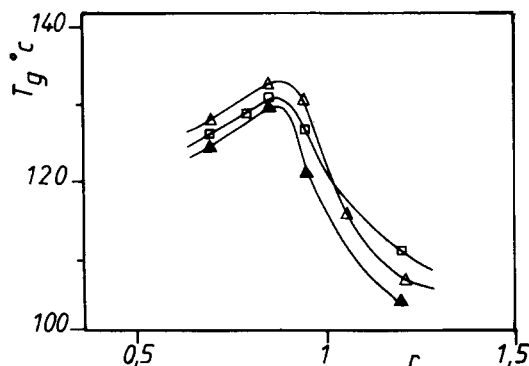


Fig. 3. Influence of the ratio r on the glass transition temperature of DGEBA-MTHPA matrix. (□) 1% MIA; (Δ) 1% EMI; (▲) 1% PIA.

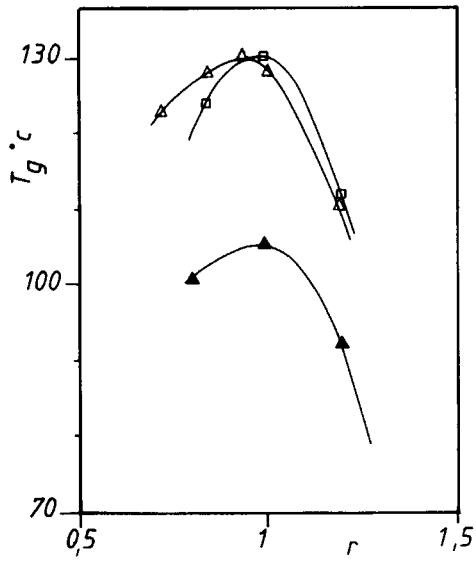


Fig. 4. Influence of the ratio r on the glass transition temperature of DGEBA-MTHPA matrix. (▲) 1% BDMA; (□) 1% 1B2 MIA; (△) 1% 1C 2E 4MIA.

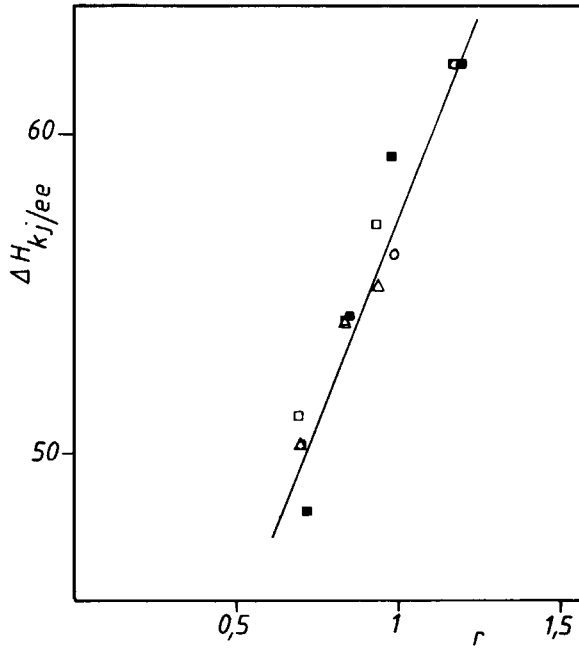


Fig. 5. Enthalpy variation of DGEBA-MTHPA system versus ratio r . (○) 1% MIA; (△) 1% EMI; (□) 1% PIA; (■) 1% 1C 2E 4MIA.

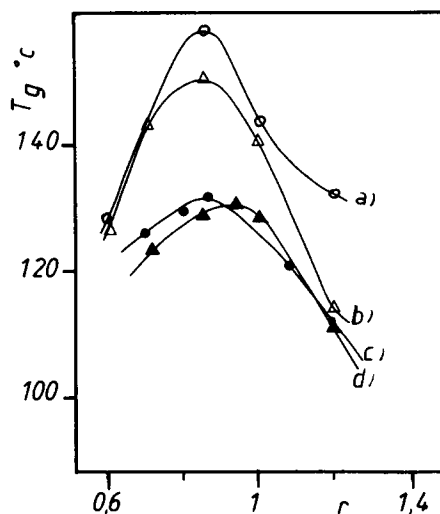


Fig. 6. T_g variation versus r of DGEBA-MNA and DGEBA-MTHPA. (a) 1% MIA-MNA; (b) 2% 1C 2E 4MIA-MNA; (c) 1% MIA-MTHPA; (d) 1% 1C 2E 4MIA-MTHPA.

TABLE IV
Glass Transition Temperature of Epoxy Networks $r = 0.85, 0.12 \times 10^{-3}$ mol of Catalyst for 10 g of Reaction Mixture

Epoxy network	Catalyst	
	BDMA	MIA
DGEBA-MTHPA	105	130
DGEBA-MNA	66	158

Table IV reports the glass transition temperatures of DGEBA-MTHPA and DGEBA-MNA. The network based on MNA has superior characteristics in the case of MIA, but deterioration results with BDMA, and with a rather low T_g . In both cases, we have the same comonomers and the same structures between crosslinks, therefore, the discrepancies can only be explained by different structures of the networks: dangling ends, number of crosslinks, etc... when imidazole on BDMA is used.

The water absorption curves of DGEBA-anhydride matrices are presented in Figure 7. The cure regime and T_g of network plates are described in Table V. Initially, the absorption curve is linear if plotted against square root of time up to slightly less than 2% weight gain. This linearity suggests that absorption is predominantly diffusion controlled in this region. Above 2% moisture, the absorption rate begins to decrease and equilibrium is reached. The same behavior is observed with DGEBA-MTHPA-1% BDMA at a lower temperature of 68°C. Thus at a same temperature, the DGEBA-MNA-imidazole network swells less than the DGEBA-MTHPA-BDMA matrix.

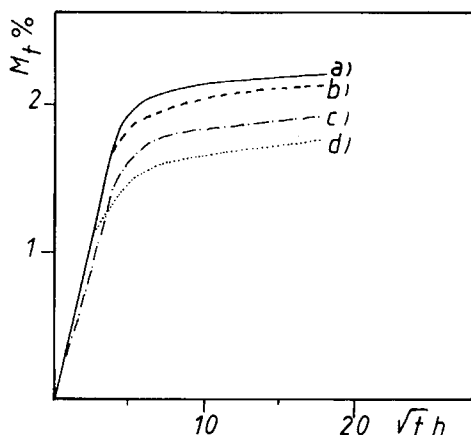


Fig. 7. Absorption of watercured, DGEBA-anhydride resins; $r = 0.85$ specimen fully immersed in water. (a) 2% CEMIA-MNA $T = 78^{\circ}\text{C}$; (b) 1% MIA-MNA $T = 78^{\circ}\text{C}$; (c) 1% BDMA-MNA $T = 68^{\circ}\text{C}$; (d) 1% 1C 2E 4MIA-MNA $T = 78^{\circ}\text{C}$.

TABLE V
Curing Conditions of Various Plates of Epoxy Networks ($r = 0.8$)
for Swelling Measurements

Anhydride	Catalyst		Curing cycle
	By weight	Mol/10 g of reaction mixture	
MNA	2% 1C 2E 4MIA	0.12×10^{-3}	1 h at 100°C 3 h at 160°C 1 h at 100°C
MNA	1% MIA	0.12×10^{-3}	3 h at 160°C $50^{\circ}\text{C} \rightarrow 145^{\circ}\text{C}$ during 30 min
MTHPA	1% BDMA	0.07×10^{-3}	2 h 30 at 145°C 1 h at 100°C
MNA	1% 1C 2E 4MIA	0.06×10^{-3}	3 h at 160°C

CONCLUSION

For the anhydride-epoxy cure, the use of imidazoles is of a great advantage compared with tertiary amine. They exhibit a higher glass transition temperature, which enables additional additives, such as reactive diluents, to reduce the viscosity which facilitates processing. Moreover, to obtain a high T_g preferable to use a ratio $r = 2(\text{anhydride})/(\text{DGEBA}) = 0.85$ (excess of epoxy) and a concentration of imidazole around 1% (by weight) to obtain simultaneously two kinds of reactions such as the catalyzed anhydride-epoxy copolymerization and epoxy homopolymerization. Moreover, with this family

catalysts, nadic anhydride provides the better thermal and hydrothermal properties than methyltetrahydrophthalic anhydride.

References

1. R. F. Fischer, *J. Polym. Sci.*, **44**, 155 (1960).
2. Y. Tanaka and H. Kakiuchi, *J. Appl. Polym. Sci.*, **7**, 1063 (1963).
3. Y. Tanaka and H. Kakiuchi, *J. Polym. Sci. Chem.*, **8**, 3405 (1964).
4. Y. Tanaka and H. Kakiuchi, *J. Macrom. Chem.*, **1**, 307 (1966).
5. L. Matejka, J. Lovy, S. Pokorny, K. Bouchal, and K. Dusek, *J. Polym. Sci. Chem.*, **21**, 2873-2885 (1983).
6. J. Galy, A. Sabra, and J. P. Pascault, *Polym. Eng. Sci.*, **26** (21), 1514-1522 (1986).
7. M. Ito, H. Hata, and K. Kamagata, *J. Appl. Polym. Sci.*, **33**, 1843-1848 (1987).
8. V. Jisova, *J. Appl. Polym. Sci.*, **34**, 2547-2558 (1987).
9. J. R. Jones, C. Poncipe, J. M. Barton, and W. W. Wright, *Polymer*, **28**, July, 1358 (1987).
10. J. A. Schroeder, P. A. Madsen, and R. T. Foister, *Polymer*, **28**, May, 929 (1987).
11. M. S. Heise and G. C. Martin, *J. Polym. Sci., Part C: Pol. Letters*, **26**, 153 (1988).
12. J. Peloux, L. Tighzert, J. P. Pascault, J. Malinge, and B. Sillion, *Polym. Bull.*, **20** (2), 207-213 (1988).
13. A. Farkas and P. F. Strohm, *J. Appl. Polym. Sci.*, **12**, 159-168 (1968).

Received October 3, 1988

Accepted October 7, 1988