Polymer Bulletin 20, 207–213 (1988)

Polymer Bulletin

Some aspects of reaction between epoxy and bisphenol

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SUMMARY.

This study deals with a new system based on the reaction between a , dihydroxy polyaryleneoxy-2,6 pyridylene (PAOP) and a Novolac epoxy prepolymer. The functionality of the later is higher than two which allows to reach a cross-linked network without curing agent. The reactivity of this mixture is compared to the reactivity of a system in which PAOP is replaced by a bisphenol without pyridine ring. It appears that the phenol functions - pyridine ring association catalyses the epoxide - phenol reaction.

Not only are the kinetics of reaction of some systems with different stoichiometric ratio studied, but the effect on these ones of an external catalyst like imidazole as well.

INTRODUCTION.

Epoxy networks are one of the most important classes of thermosetting polymers and find extensive use as coatings, matrix for composite materials, adhesives and encapsulating compounds. They have various desirable properties as high tensile strength and modulus, good thermal and chemical resistance. Liquid epoxy prepolymers are cross-linked and converted to a useful thermoset stage through their oxirane or/and hydroxyl functionality by using a suitable comonomer. This process has some drawbacks, for example the toxicity of aromatic amines, the low resistance to hydrolysis of diacid anhydride, or the low impact strength of the final product.

Numerous studies have been conducted on toughening of epoxy networks using reactive oligomers such as butadiene-acrylonitrile copolymers with carboxyl or amine end groups (CTBN or ATBN) [1-4]. In this case rubber particles precipitated during curing increase the fracture toughness of the network. Tough thermoplastics such as polyethersulfone have also been used to increase cured epoxy toughness [5]. Other workers [6] have focused on what makes many thermosets inherently brittle and what makes thermoplastics like polycarbonate inherently tough ; and they have developped a new class of epoxy systems which form stiffer, higher molecular weight chains between crosslinks than conventional resins do.

In order to improve the fracture toughness our study consists in the modification of a classical epoxy novolac prepolymer which shall react with a polyaryloxypyridine α-ω diphenol used as a chain extender.

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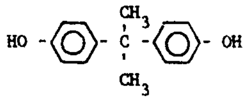
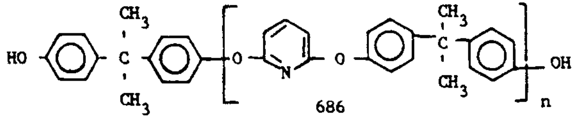
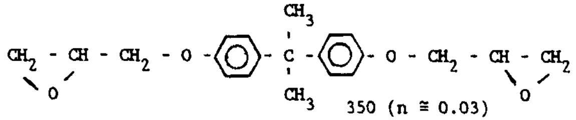
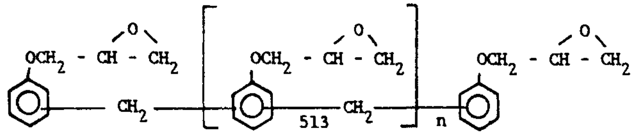
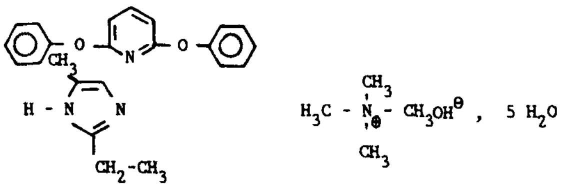
TABLE I. Formulas and characteristics of different materials

Name and origin	Formula and molecular weight	Fonctionality $\overline{Fn}$	Tg	Tf
Bisphenol A (Aldrich) BA	 128	2		
Polyaryloxypyridine α-ω diphenol (CEMOTA) PAOP-2	 686	2	63	>90
Diglycidyl ether of bisphenol A (DER 332 - DOW CHEMICALS) DGEBA	 350 (n ≅ 0.03)	2	-20	47
Glycidyl ether of novolac (DEN 431 DOW CHEMICALS) GEN 431	 513	2.96	-17	
Catalysts : . 2,6-diphenoxypyridine DDP (Cemota) . 2-ethyl 5-methyl imidazole (EMI) . Tetraméthyl Ammonium hydroxyde Pentahydrate (TMAH)	 $H_3C-\overset{CH_3}{\underset{CH_3}{N^{\oplus}}}-CH_3OH^{\ominus}$, $5\ H_2O$			

EXPERIMENTAL.

Materials.

All materials used and their characteristics are listed on the Table I. The polyaryloxypyridine α-ω diphenol prepolymers PAOP-2 were synthesized by reaction of an excess of bisphenol A with 2,6-dichloropyridine according to a patent [7].

Characterization techniques.

. The DSC Mettler TA 3000 was used for all calorimetric measurements. For each formulation two scans were made : In the first one, the sample, in a sealed pan, was heat at a constant rate of 10 K/min and the integration of the exothermic peak gave the enthalpy of polymerization in J/g or in kJ/epoxy equivalent. This measurement was followed by a rapid cooling and a second run was made on the same sample immediately after at a rate of 7.5 K/min. In this way we obtained the glass transition temperature T_g of the network prepared during the first scan.

. The molecular weight of epoxy novolac prepolymer was determined by vapor tension osmometry at 40°C using 2-butanone as solvent. Meanwhile, the molecular weight of PAOP prepolymer was measured in size eclusion chromatography which is calibrated with internal calibration using identified low molecular weight pyridylether.

. Epoxy and phenolic equivalent were calculated respectively from the titration of pyridine method [8] and potentiometric titration in DMF with tetrabutylammonium [9]. Thus the average functionality $\overline{F_n}$ can be inferred.

. Good correlation is observed for $\overline{M_n}$ determination of PAOP between SEC and potentiometric titration (686 and 678 respectivelyl).

Experimental procedure.

. As the PAOP-2 prepolymer is solid powder at ambient temperature, their incorporation in epoxy prepolymers is performed with the tetrahydrofuran which is then evaporated. This procedure is for the DSC measurements.

. The maximal quantity of PAOP-2 that can be dissolved in epoxy novolac is for the stoichiometric ratio $\dot{R} = (OH)/(epoxy) = 0.7$. Thus we cannot realize higher ratios.

RESULTS AND DISCUSSION.

Firstly we have examined the reactivity, by DSC, of DGEBA-BA catalysed by TMAH well-known as catalyst of epoxy-OH reaction, by DPP which is similar to the PAOP-2 except there is no phenolic group and without catalyst. In the absence of catalyst or with DPP the reaction occurs at temperature higher than 300°C, meanwhile with TMAH the exothermic peak takes place at 215°C (Table II). Thus DPP does not act as a catalyst of epoxy-phenolic reaction and a small effect appears only as a function of the concentration.

Imidazoles are known as active catalyst for epoxy homopolymerization [10,11]. The homopolymerization of GEN 431 without catalyst occurs at temperatures higher than 250°C. In presence of 1.5 % of imidazole, the epoxy homopolymerization is partially catalysed. Whereas with 3 % of imidazole the reaction is entirely catalysed (Table II), therefore the glass transition temperature of obtained network is 114°C instead of 105°C.

Table II. DSC Results

Reactive system	Catalyst$^{a)}$	$r^{b)}$	Exothermic peak			T_g (°C)
			T_i(°C)	T_p (°C)	T_f (°C)	
DGEBA + BA	none	1	240	380	430	76
	TMAH (0.15 %)	1	145	215	265	65
	DPP (7.5 %)	1	220	342	390	85
	DPP (150 %)	1	230	300	360	115
GEN 431 + BA	none	0.6	$150^{c)}$ $300^{d)}$	230 387	280	84
	imidazole (0.75 %)	0.6	$90^{c)}$ $195^{d)}$	147 252	180 320	100
	imidazole (1.5 %)	0.6	80	142	170	112
GEN 431 - PAOP-2	none	0.7	75	163	240	106
		0.56	80	157	230	109
		0.42	$80^{c)}$ $240^{d)}$	157 284	230 320	117
		0.28	$80^{c)}$ $225^{d)}$	158 305	215 365	103
	imidazole (0.75 %)	0.42	70	148	200	106
	imidazole (1.5 %)	0.42	70	137	190	113
GEN 431	none		300	373		?
	Imidazole (1.5 %)		$90^{c)}$ $190^{d)}$	140 249	195 320	105
	Imidazole (3 %)		80	133	200	114

a) g per 100 g of epoxy prepolymer ; b) $r = [OH] / [epoxy]$; c) first peak ; d) second peak

T_i : temperature of exothermic peak begining ; T_p : temperature of exothermic peak maximum ; t_f : temperature of exothermic peak end

Now, DGEBA prepolymer is replaced by GEN 431. The thermograms for BA copolymerization are presented in figure 1. Three hypothesis can be expressed as follow. The exothermic peak towards 145°C is attributed to epoxy-OH and epoxy homopolymerization catalysed reactions and certainly some degradation reactions. The peak at 230-250°C region could be imputed to epoxy-OH non catalysed reaction. The last peak at 387°C is due to the uncatalysed epoxy homopolymerization. All reactions are catalysed with 1.5 % of imidazole, the network has a glass transition temperature of 112°C against 106°C without catalyst (Table II).

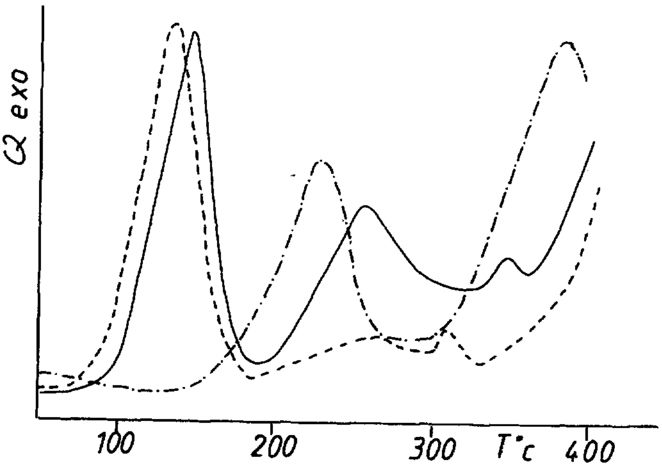


Fig.1. Thermograms of GEN 431-BA (r = 0.6)
(-.-.-) without catalyst ; (——) with 0.75 % of imidazole ;
(-----) with 1.5 % of imidazole

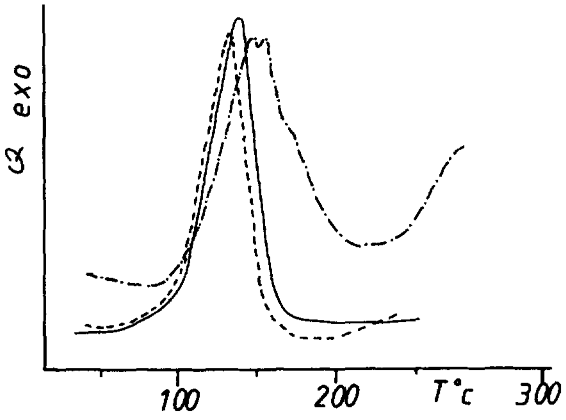


Fig.2. Thermograms of GEN 431-PAOP-2 (r = 0.42)
(-.-.-) without catalyst ; (——) with 0.75 % of imidazole ;
(-----) with 1.5 % of imidazole

Then the POAP-2 prepolymer is used instead of BA for a comparison. The GEN 431-POAP-2 system with r = 0.42 is studied with and without catalyst (Table II, figure 2). Without imidazole, the GEN 431 - BA reaction occurs at 230°C and at 388°C, meanwhile at 153°C and at 284°C for GEN 431 - PAOP-2 system. Whereas with imidazole the reactivity of both systems is almost the same. We suppose that the difference of reactivity in these two cases comes from the pyridine cycle in PAOP-2 prepolymer which can act as a catalyst for the phenolic reaction. Therefore this system is autocatalytic and the addition of an externe catalyst, such as a imidazole, is not absolutely necessary.

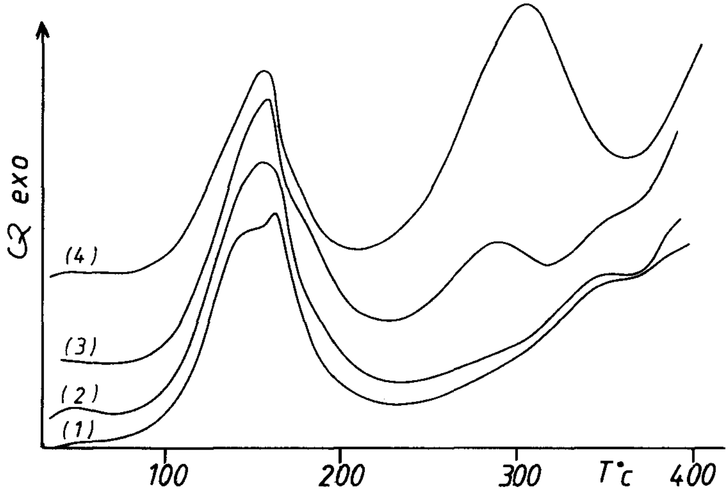


Fig.3. Thermograms of GEN 431-PAOP2
(1) r = 0.7 ; (2) r = 0.56 ; (3) r = 0.42 ; (4) r = 0.14

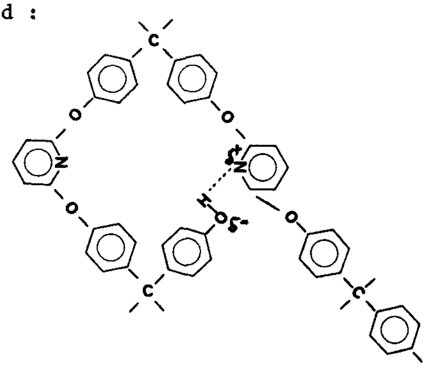
The thermograms of GEN 431 - PAOP-2 with different values of r are reported in figure 3. They have two superimposed peaks at 150°C and 163°C. In the novolac prepolymers, the methylene group can situate in ortho or in para of aromatic ring. These two positions possess different reactivity [12] . Therefore the peak at 163°C could be attributed to ortho position and the peak at 150°C could be attributed to ortho position and the peak at 150°C to para position because of its higher reactivity.

CONCLUSION.

A network can be obtained by reaction between an epoxy prepolymer, as Novolac, its functionality is higher than two and a new polymer bisphenol - pyridine.

All experiments performed in this work indicate that phenol functions associated with pyridine rings in PAOP-2 molecule catalyse the epoxy-OH reaction.

We could suggest a mechanism of this catalytic effect due to an intramolecular hydrogen bonded structure in which the second N atom forms a zwitterion with one phenol end :



The phenate anion, or delocalized phenol end, could open easily epoxy groups.

An intermolecular complex could not explain the specificity of PAOP-2 molecule compared to the bisphenol A plus 2-6-diphenoxypyridine reaction.

As for the imidazole, it can catalyse the epoxy-hydroxyl reaction and also initiate the epoxy homopolymerization.

At last, the PAOP prepolymers lead to impact properties improvement of final network. This is a great advantage compared with other classical epoxy networks. For example, DGEBA - 5 % PAOP-9 ($\overline{M_n}$ = 887) - DDS possesses a surfacic resilience of $2.6.10^4$ $J.m^{-2}$ against $1.7.10^4$ $J.m^{-2}$ for the DGEBA-DDS matrix.

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Accepted June 18, 1988 C