

Citric Acid–Diethylenetriamine Salts as Latent Curing Agents for Epoxy Resins

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SYNOPSIS

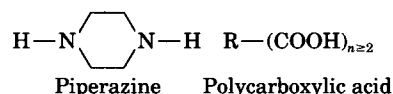
Citric acid (CA)–diethylenetriamine (DETA) salts (CADETA) were prepared by using a 4.5 : 1 molar ratio of DETA–CA and removing the DETA excess. The structure of CADETA was analyzed by ^{13}C -NMR, IR, and DSC associated with weight loss. One-step formulations consisted on dispersions of CADETA (variable amounts) in an epoxy resin based on diglycidylether of bisphenol A (DGEBA, EEW = 185.5 g/eq). The cure was followed in the pressure cell of a DSC (N_2 at 2.5 MPa), to avoid volatilization of DETA in the temperature range where decomposition of CADETA and beginning of reaction took place ($T > 175^\circ\text{C}$). A very small heat of reaction was observed, $(-\Delta H) \sim 10$ kJ/eq, resulting from the simultaneous endothermic salt decomposition and exothermic network formation. A stoichiometric formulation showed a $T_g = 180^\circ\text{C}$, i.e., some 60°C higher than the one observed for the usual DGEBA/DETA system.

INTRODUCTION

One-part epoxy formulations exhibiting long-time latent characteristics are desirable from a cost and handling viewpoint. Latent properties are usually derived from the room temperature stability of a complex hardener that is thermally decomposed to give a reactive species that initiates cure.

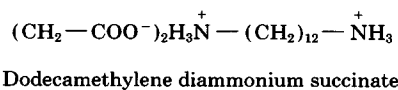
Our aim was to analyze how to give latency to a formulation based on the diglycidylether of bisphenol A (DGEBA)–diethylenetriamine (DETA), but the approach to be discussed here may be used for different epoxy–amine systems. The idea consisted of making a salt of the triamine and a polycarboxylic acid that would liberate the free amine by high-temperature decomposition.

Only a few systems have been reported in the literature that use latent curing agents based on salts of polyamines and polycarboxylic acids. Piperazine salts of polycarboxylic acids have been shown to function as curing agents for epoxy resins.¹



The shelf-life was increased from 2 h when using piperazine alone to 35–70 days when using one of the following diacids: succinic, adipic, sebacic, maleic, hexahydrophthalic, tetrahydrophthalic, phthalic, and isophthalic. The piperazine salts cured epoxy resins more rapidly than does dicyandiamide.

It was also reported that the salt of succinic acid and dodecamethylenediamine mixed with DGEBA has a shelf-life higher than 1 week at room temperature.¹



Moreover, the shear strength of steel–steel adhesive joints increased from 16.2 MPa when using the diamine alone to 23 MPa when using the salt (cure at 130°C during 2 h).¹

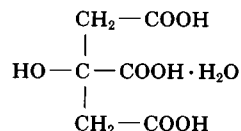
Here, results obtained for a citric acid–DETA salt will be reported.

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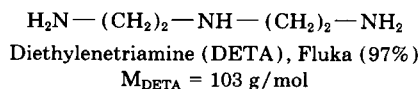
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SYNTHESIS AND CHARACTERIZATION OF THE SALT (CADETA)

Citric acid (CA) and diethylenetriamine (DETA) have the following structures:



Citric acid (CA), Chemapol
 $M_{\text{CA} \cdot \text{H}_2\text{O}} = 210 \text{ g/mol}$



When preparing a salt from a triacid and a triamine, it is convenient to use an excess of one of the reagents to avoid gelation of the polyelectrolyte. It was experimentally determined that, for formulations containing a DETA excess, a molar ratio $\text{DETA-CA} \leq 2$ led to gelation. (The value arising for the ideal polymerization of a trifunctional acid with a trifunctional base is $\text{DETA-CA} \leq 4$; the departure from the predicted value may be ascribed to a large fraction of intramolecular cyclisation.) The selected value for the synthesis was $\text{DETA-CA} = 4.5$. As both DETA and CA are trifunctional in the acid-base reaction, the molar ratio is equal to the ratio of amine to acid equivalents.

Citric acid (21 g) was dissolved in DETA (46.35 g) at 80°C to give a solution with the selected molar ratio ($\text{DETA-CA} = 4.5$). The DETA excess was removed after 30 min, by washing with ethanol-methanol. Following a drying step, the salt was obtained as a white powder.

^{13}C -NMR enabled us to establish the presence of the following structures in CADETA:

$\begin{array}{c} + & & + & & + \\ \text{N} - \text{C} - \text{C} - \text{N} - \text{C} - \text{C} - \text{N} \\ (1) \quad (2) & & (2) \quad (1) \end{array}$			C	δ (ppm)
		OH	(1)	36.9
			(2)	44.8
$^- \text{OOC}$	(3)	$^- \text{C}^{(4)}$	(3)	45.9
	(5)		(4)	75.0
		COO^-	(5)	178.4
	(6)		(6)	181.5

Figure 1 shows IR spectra of CADETA (KBr pellets). The salt is characterized by bands assigned to COO^- , NH_2^+ and NH_3^+ groups, as well as by the absence of bands due to free carboxylic acid. However, a fraction of free amino groups is still present because the use of a DETA excess leads to partially protonated molecules.

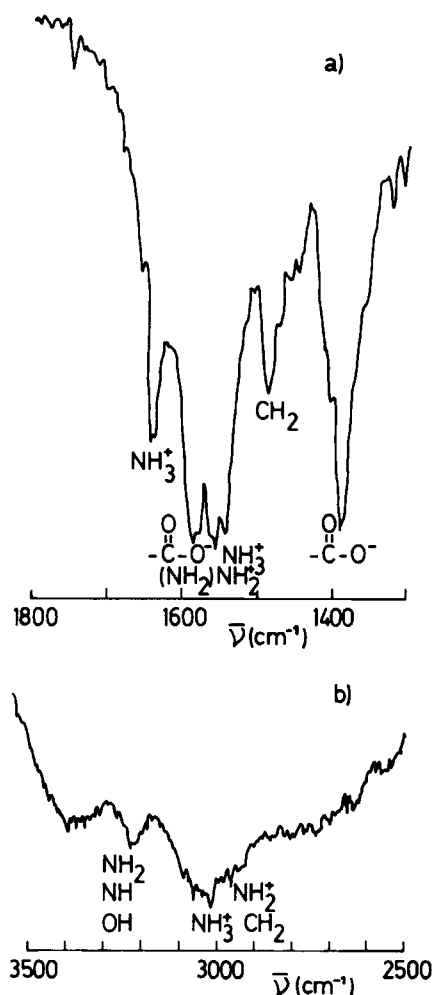


Figure 1 IR spectra of the citric acid-diethylenetriamine salt (CADETA): (a) $1300\text{--}1800 \text{ cm}^{-1}$ range, (b) $2500\text{--}3500 \text{ cm}^{-1}$ range.

The actual ratio of DETA-CA in the salt, after removing the unreacted DETA, may be calculated as follows. The initial ratio of acid to amine equivalents is equal to equivalent COOH /equivalent amine = $1/4.5 = 0.222$. By assuming that the basicity of primary and secondary amino groups is approximately the same, the factor 0.222 also represents the probability of finding a protonated amine group when the base-acid reaction is complete. Then, the fraction of DETA remaining free at the end of the reaction is given by the simultaneous probability that the three amino groups have not reacted, i.e., $(1 - 0.222)^3 = 0.47$. Therefore, 53% of the initial amount of DETA is effectively incorporated in CADETA, giving a molar ratio $\text{DETA-CA} = 0.53 \times 4.5 = 2.385$. This corresponds to a mass fraction of DETA in the salt equal to 56.1%. A salt synthesized with a very large excess of DETA would

contain 61.7% DETA (molar ratio DETA-CA = 3 in the final product).

Figure 2 shows a differential scanning calorimetry (DSC) thermogram of CADETA in N_2 (DuPont 990 provided with a pressure cell, at $10^\circ\text{C}/\text{min}$ and atmospheric pressure). The first endothermic peak at 144°C represents the salt melting (no weight loss was observed after this peak). The second endothermic peak, at 200°C , is associated to the volatilization of DETA (bp of DETA = 207°C), arising from the salt decomposition. The mass loss measured after 30 min heating at 200°C was $57.5 \pm 3\%$, in excellent agreement with the estimated mass fraction of DETA in the salt (56.1%).

Therefore, it is concluded that the salt contains a molar ratio of DETA-CA = 2.385, with no free carboxyls and 58% (1.385/2.385) free amino groups. It melts at 144°C and undergoes decomposition with DETA evolution in the $175\text{--}225^\circ\text{C}$ temperature range, at 0.1 MPa (atmospheric pressure).

CURE OF THE EPOXY RESIN WITH CADETA

The epoxy resin was a commercial product based on diglycidylether of bisphenol A (DGEBA, Ciba-Geigy GY250). It had an epoxy equivalent weight (EEW) = 185.5 g/eq and was carefully dehydrated under vacuum before use.

From the estimated mass fraction of DETA in the salt (56.1%), the equivalent weight in amine hydrogens may be calculated as 36.7 g/eq (DETA has a functionality 5 in its reaction with epoxides). Then, a stoichiometric mixture requires 19.8 g CADETA per 100 g of DGEBA (19.8 phr). Mixtures of CADETA and DGEBA were handled as disper-

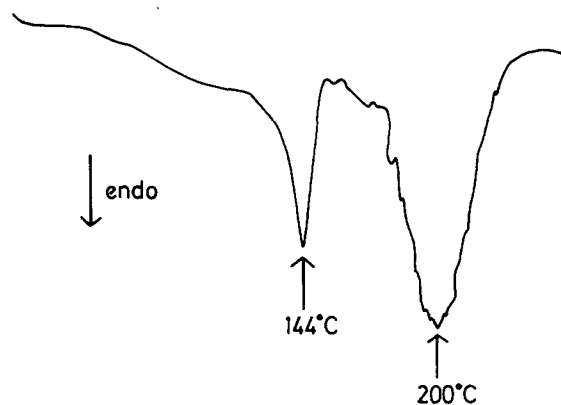


Figure 2 DSC thermogram of CADETA at $10^\circ\text{C}/\text{min}$, in N_2 at 0.1 MPa.

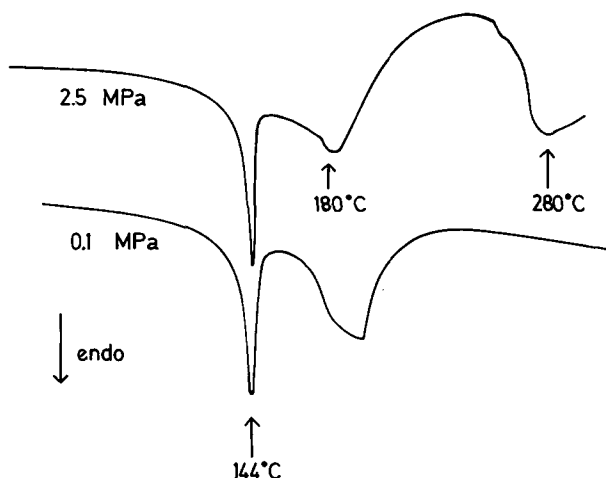


Figure 3 DSC thermogram of CADETA-DGEBA formulation with $r = 0.244$. Scanning rate = $10^\circ\text{C}/\text{min}$; N_2 pressure = 0.1 and 2.5 MPa.

sions as no dissolution of the salt was evident. In this sense the system is similar to commercial formulations based on DGEBA-dicyandiamide.

Formulations containing different ratios r = equivalent amine hydrogens/equivalent epoxy, were cured in the DSC at $10^\circ\text{C}/\text{min}$, up to 300°C , in a N_2 atmosphere. Figure 3 shows two thermograms carried out at 0.1 and 2.5 MPa, for a formulation with $r = 0.244$. No change is evident up to the salt melting. A high shelf-life at room temperature is thus expected. At T close to 175°C the salt begins to decompose giving free DETA. A competition between DETA evolution (endothermic process) and reaction with DGEBA (exothermic process) is established. By increasing pressure to 2.5 MPa the vaporization of DETA is prevented, and only a broad exothermic peak of reaction is registered.

As DETA is a low-temperature hardener, the specific rate constant with epoxy groups at $T > 175^\circ\text{C}$ must be extremely high. Therefore, it may be presumed that DETA-DGEBA reaction rate is controlled by the salt decomposition process. Besides, carbonyl groups of CA may lead to esterification reactions either with epoxy groups or with secondary hydroxyls of DGEBA. Cured products had the appearance of homogeneous dark-yellowish films.

The heat involved in the broad exothermic peak is the resultant of the endothermic process of salt decomposition and the exothermic network formation. (The epoxy-amine reaction is characterized by^{2,3} $(-\Delta H)_{E-A} = 102 \text{ kJ/eq}$). In our case the reaction heat for formulations with r values ranging

from 0.3 to 2 was $(-\Delta H) = 10 \text{ kJ/eq} \pm 4 \text{ kJ/eq}$, i.e., 10% of the epoxy-amine value. This is a very interesting fact for processing purposes involving thick parts. Precisely, as reported by Scola,¹ a disadvantage of some commercial one-part dispersions with a high shelf-life is that they exhibit a highly exothermic curing reaction, limiting their use to adhesives and coating applications. This disadvantage is not present in our systems. The resultant value of the reaction heat is also very much less than the one reported for the cure of epoxy resins with substituted ureas as latent initiators,⁴ i.e., $(-\Delta H) = 61 \text{ kJ/eq}$.

Glass transition temperatures (T_g) for formulations prepared with different stoichiometric ratios were determined as follows. Cure was performed in the DSC at $10^\circ\text{C}/\text{min}$, up to 250°C , in N_2 (2.5 MPa). Samples were cooled and rescanned in the same conditions. As a small residual reaction heat was occasionally observed, T_g was determined in a third scan using always the same conditions (T_g was defined as the onset value of the transition). Figure 4 shows T_g as a function of the stoichiometric ratio. Also shown is the T_g for the stoichiometric DGEBA-DETA system.

The maximum T_g for DGEBA-CADETA formulations is obtained for the stoichiometric system, as is always the case when there are no secondary

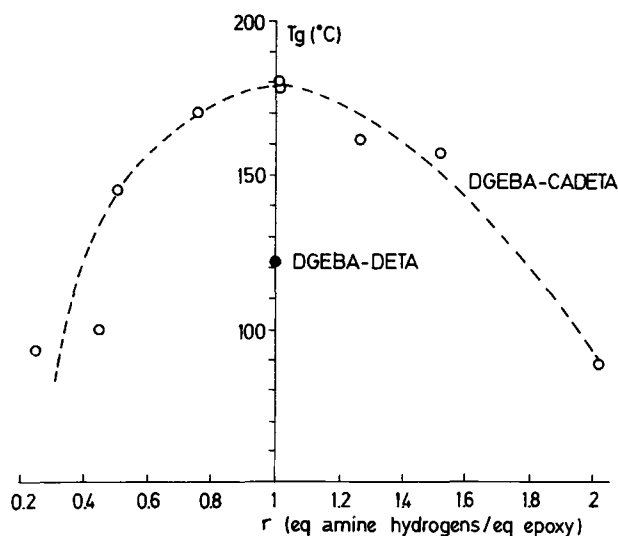


Figure 4 Glass transition temperature of DGEBA-CADETA formulations prepared with different stoichiometric ratios. The T_g of the stoichiometric DGEBA-DETA system is also shown for comparison purposes.

reactions.^{5,6} However, the most significant finding is that the T_g of the stoichiometric formulation is higher than the T_g of DGEBA-DETA by some 60°C . Then, CADETA does not only act as a latent agent for the cure but also leads to a high T_g product. To explain the increase in T_g would require an identification of the various possible chemical reactions and the associated network structures.

CONCLUSIONS

Citric acid-diethylenetriamine salts constitute a promising family of latent curing agents for epoxides using one-step dispersions. Although the shelf-life was not directly measured, the fact that no reaction was observed in the DSC before the salt melted ($T_m = 144^\circ\text{C}$), is a clear indication of a good stability at room temperature. The cure must be carried out at moderate pressures, i.e., 2.5 MPa, to avoid the volatilization of DETA in the temperature range where decomposition of the salt takes place and reaction begins ($T > 175^\circ\text{C}$). The overall heat of reaction is very small, i.e., $(-\Delta H) = 10 \text{ kJ/eq} \pm 4 \text{ kJ/eq}$, because it is the resultant of the endothermic salt decomposition and the exothermic polymerization. This is an important advantage for cure of thick parts. Another significant finding is the high T_g of cured products ($T_g = 180^\circ\text{C}$ for a stoichiometric formulation). This represents a T_g increase of some 60°C when compared with the pure epoxy-diethylenetriamine system.

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