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The development of controllable metal-chelate curing agents with improved storage stability

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Summary

The novel latent epoxy curing agent and commercial epoxy system designated MY750/Cu(PGE-EMI)$_4$Cl$_2$ shows remarkable properties under both extended storage and cure conditions. For example, after a period of 2600 hours at ambient temperature the viscosity of an MY750/Cu(PGE-EMI)$_4$Cl$_2$ mixture is still low enough (*ca.* 3 x 10^6 cps) to be measured at ambient temperature, while the corresponding MY750/(PGE-EMI) adduct mixture is too viscous to be measured (*ca.* 8 x 10^6 cps) after only 430 hours. The slower increase in viscosity of the complex mixture indicates that it is much more stable than its parent imidazole when dispersed in an epoxy prepolymer over an extended period of time. FTIR and ^{1}H n.m.r. data suggest that after heating an MY750/Cu(PGE-EMI)$_4$Cl$_2$ mixture for 5 minutes at high temperatures (120-140°C) and a room temperature quench, almost no further cure occurs thereafter.

Introduction

Epoxy resins, by virtue of their extreme versatility, are extensively used in industrial applications (*e.g.*, as adhesives, as resin-impregnated fibres, or for resin transfer moulding, *etc.*). This could be enhanced if they fulfilled the following requirements: to cure quickly and be readily formulated as one-pot compositions (*i.e.*, the epoxide and curing agent are stored as a mixture rather than as two separate materials that have to be mixed prior to use). This formulation in turn means that the composition must have a stability of at least several months at ambient temperature. Imidazoles are used as epoxy curing agents due to their fast catalytic action and also the fine mechanical properties which they produce in the cured resin. Some imidazoles are highly effective epoxy curing agents (1) and recent studies (2,3) have demonstrated that epoxy resins cured with imidazoles can have superior physical properties (*e.g.*, better heat resistance, lower tensile elongation, a higher elongation, a higher modulus and a wider range of cure temperatures) than for example amine-cured systems (2,3) resulting in their wide useage in the electronics industry as moulding and sealing compounds. Imidazoles are added to epoxy systems to catalyze the homopolymerization of epoxide groups (polyetherification), but unmodified imidazoles have low stability when mixed with epoxies (cure occurs slowly at room temperature) making them unsuitable for use in one-pot compositions.

Much work has been carried out on stabilizing imidazoles for use as latent epoxy curing agents and one approach involves the preparation of metal-imidazole complexes (4,5). Transition metals have been used to prepare such complexes and these have exhibited good stability at room temperature and a rapid cure at elevated temperatures. Most metal-imidazole complexes are crystalline materials with very low solubility in common epoxides. Solubility of the curing agent in the epoxide is very desirable because heterogeneous dispersions are liable to settle out or agglomerate on storage. It is also useful to be able to form a solution containing both the epoxide and curing agent for the manufacture of pre-impregnated fibre composite materials (prepregs). Barton

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found (6) that adducts of phenylglycidylether (PGE) and 2-ethyl-4-methylimidazole (EMI) could be complexed with a variety of metal salts (the structure of one of these copper(II) complexes is shown in Figure 1 as (*1*)). Elsewhere we have shown (7) that these complexes are relatively unreactive at room temperature, but effective curing agents at higher temperatures. The kinetics of the metal-imidazole cure have also been investigated (8).

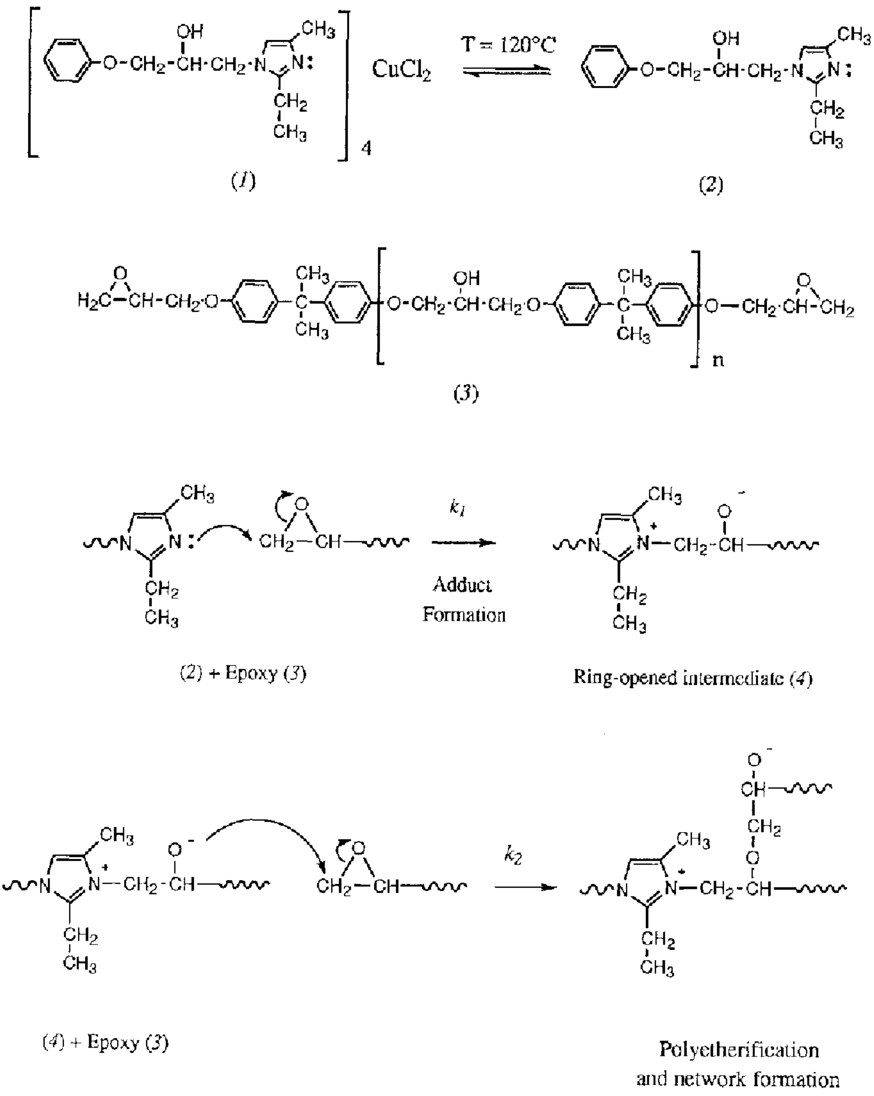

Figure 1. Structures of the compounds employed in this study and the proposed mechanism of cure

In this paper we show the potential of these systems as latent curing agents with significant ambient temperature storage stability. An important development is the action of complexation on retarding reaction effectively. This in turn allows partial cure of the epoxy resin and (after a quench) further storage at room temperature with no cure. These characteristics are useful in controlled cure schedules of resins or composites.

Experimental

Equipment

Viscometric measurements were made on a Brookfield RVTD113 viscometer (using a RV7 spindle) at ambient temperature and at a fixed shear rate of 64 Hz, and plotted against storage time. Infrared spectra were obtained on a Perkin-Elmer 1750 FT-IR spectrometer. A thin film (0.025 mm) sample was placed on a pair of KBr windows and scanned 24 times at a resolution of 2 cm^{-1}. ^1H n.m.r. spectra were obtained at 298K using a Bruker AC300 high field FT n.m.r. spectrometer. Samples were dissolved in DMSO-d_6 and a minimum of 64 scans were collected.

Materials

The commercial epoxy prepolymer MY750 (the structure of which is depicted in Figure 1 as (*3*)) was provided by Ciba-Geigy. PGE and EMI were obtained from Aldrich Chemical Company and purities were determined using ^1H n.m.r. Copper(II) chloride (*ex* Aldrich) gave satisfactory analytical results. The preparation of the 1:1 adduct of PGE and EMI (PGE-EMI) (*2*) and the corresponding copper complex, $Cu(PGE\text{-}EMI)_4Cl_2$ (*1*), have already been reported elsewhere (7). Compositions of 5% (by weight) of the 1:1 adduct of PGE-EMI and 5.6% (by weight) of the complex (in molar equivalence to the adduct) in MY750 were made respectively. The adducts were dispersed directly in the resin, while the complex was dissolved in dichloromethane prior to mixing (the solvent being removed under vacuum at 30°C for 4 hours).

Results and Discussion

Ambient Temperature Storage Stability

DSC data

In an earlier publication (7) we presented DSC data which demonstrated the increased storage life that could be realized for an epoxy formulation using the copper complex (*1*). Formulated samples were stored at ambient temperature underneath inverted Petri dishes and at intervals samples were withdrawn and scanned from -70 to 280°C at 10°K $minute^{-1}$ under nitrogen (40 cm^3 $minute^{-1}$). DSC was employed to determine the thermal properties of the mixture: the glass-transition temperature (T_g) of the mixture before cure was observed as the onset of a characteristic endothermic transition, while the onset of the thermal curing reactions was observed as the start of the exothermic peak due to cure. The change in T_g with time is a useful measure of storage stability as an increase in T_g indicates early reaction (which may eventually lead to solidification of the stored mixture, which occurs when the T_g reaches ambient temperature). We have included these data in this paper as a means of comparison with the results of the present viscometry study. Figure 2 shows the DSC data for uncured, formulated mixtures of MY750 and the adduct (*2*) and complex (*1*) after progressive ambient temperature storage. It is clear that the decrease in the temperature at which the cure exotherm commences is less marked for the epoxy/copper complex (*3*) mixture (and also falls less rapidly) than the mixture containing the corresponding adduct (*2*). The glass transition temperature of the uncured mixture (and hence advancement of network formation) also rises less rapidly in the $MY750/Cu(PGE\text{-}EMI)_4Cl_2$ mixture indicating its greater storage stability.

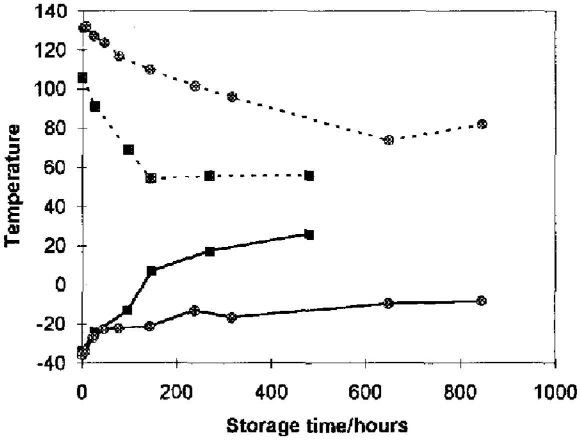

Figure 2 Glass-transition temperature (—) and cure onset temperature (---) *vs.* storage time for MY750/Cu(PGE-EMI)$_4$Cl$_2$ (●) and MY750/PGE-EMI (■)

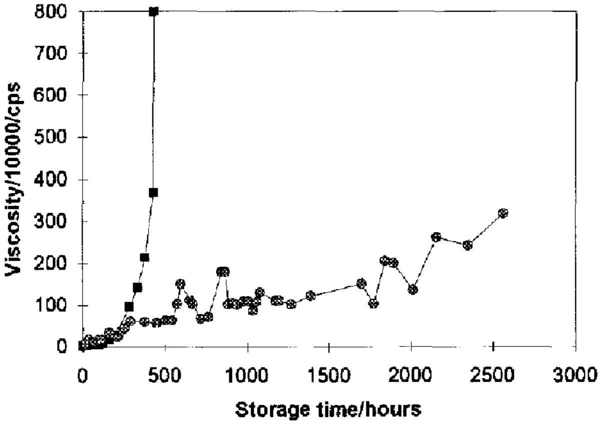

Figure 3 Viscosity of MY750/(PGE-EMI) (■) and MY750/Cu(PGE-EMI)$_4$Cl$_2$ (●) during ageing at room temperature

Viscometric data

The change in viscosity of a resin during storage is an important parameter from both a practical and a theoretical viewpoint. An increase in viscosity indicates early reaction leading to an increase in the molecular chain length of the polymer in the stored mixture. The observed change in viscosity due to the cure of the MY750/Cu(PGE-EMI)$_4$Cl$_2$ and MY750/(PGE-EMI) mixtures against storage time is illustrated in Figure 3. It is evident that after a period of 2600 hours at ambient temperature (which varied between *ca.* 16.5°C and 24°C during the timescale of the storage time - accounting for the anomalous data observed in Figure 3) the viscosity of the MY750/Cu(PGE-EMI)$_4$Cl$_2$ mixture is still low enough to be measured (*ca.* 3×10^6 cps), while the corresponding MY750/(PGE-EMI) mixture is too viscous to be measured at ambient temperature (*ca.* 8×10^6 cps) after only 430 hours. The slower increase in viscosity of the complex mixture indicates that it is much more stable than its parent imidazole adduct in epoxy over an extended period of time.

Controlled Cure of Epoxy/Complex Mixtures

FTIR data

MY750/Cu(PGE-EMI)$_4$Cl$_2$ (5.6 % by weight) samples were heated for 5 minutes in a thermostatted oil bath at both 120°C and 140°C. Soon after, the reaction was quickly quenched by cooling to room temperature and small amounts of sample were transferred to KBr plates and scanned at room temperature. The measurements were operated by a programmed routine ("SCANTIME") at 20 minute intervals. The absorbance of the oxirane ring breathing vibration at 916 cm^{-1} was monitored and the substituted aromatic ring skeletal stretch (1608 cm^{-1}) was taken as an internal standard. The ratios of $A_{(916/1608)}$ were obtained by a programmed routine ("AUTORATIO") and the change in the absorbance at 916 cm^{-1} was taken as an indication of the degree of cure. The results show (Figure 4) that $A_{(916/1608)}$ decreased after being heated for 5 minutes at the cure temperature, but that almost no further cure occurred for about three hours thereafter. This suggests that the reaction mixture was stable after the cure was arrested by quenching.

^{1}H n.m.r data

A further investigation into the stability of partially-quenched samples (containing 5.6 % by weight of MY750/Cu(PGE-EMI)$_4$Cl$_2$) at different fractional conversions was carried out using ^{1}H n.m.r. In each case, the reaction mixture was heated in a thermostatted oil bath at 140°C and samples taken at intervals of 5, 10, 15, 20, 40 and 80 minutes. The fractional conversion of the samples was determined by examining the integral of the epoxide -CH$_2$- protons at 2.82 and 2.87 ppm (and ratioing them against the aromatic protons shifts at 7.1 and 6.8 ppm as internal standards as reported elsewhere (9)). After quenching, no significant change in conversion was observed up to a period of 6 hours (any further cure is too small to be determined) and the data (Figure 5) are in agreement with the FT-IR measurements made under different conditions.

Conclusion

The possible re-association between copper(II) and terminal imidazole groups (already incorporated into the growing epoxy chain) has already been discussed elsewhere (7). Evidence for the existence of an equilibrium between the adduct and complex (in DMSO solution) was put forward from ^{1}H n.m.r. data (7), and was confirmed by the solution regaining a green coloration (after having become amber at a temperature of *ca.* 120°C). We believe that this ability of the complex to re-associate contributes a great deal to the stability of the quenched mixture to provide good processability. On the other hand, the interaction between imidazole and copper(II) in the epoxy resin system can reduce the rate of cure and can therefore provide an increased processing window.

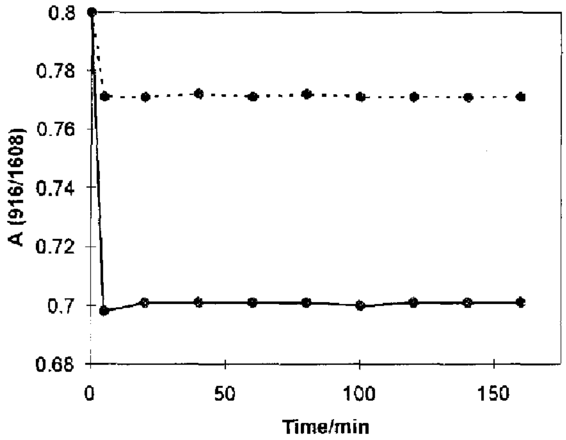

Figure 4 FTIR absorbance ratio of the MY750/Cu(PGE-EMI)$_4$Cl$_2$ samples after 5 minutes at initial cure temperature (---) 120°C and (—) 140°C (quenched and scanned thereafter at 20 minutes intervals at room temperature)

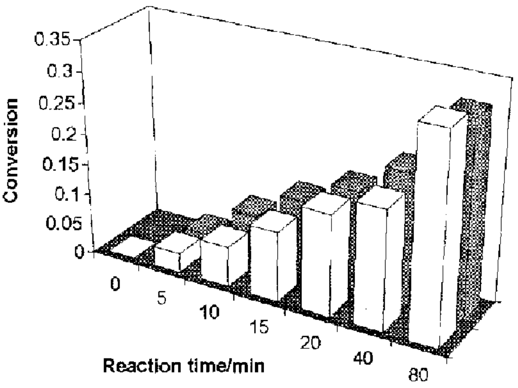

Figure 5 Fractional conversion of the MY750/Cu(PGE-EMI)$_4$Cl$_2$ directly after quench (☐) and again after 6 hours at room temperature (■)

In these investigations of the epoxy/complex mixtures the green coloration was also recovered to some degree depending on the cure temperature and the degree of cure. Of course this re-association is more difficult to achieve in the epoxy/complex system than in solution becuase the imidazole 'ligand' is incorporated into a chain after the cure commences. The higher the curing temperature and the degree of cure, the more difficult is the re-association. At present the exact mechanism by which the reaction is quenched is unclear. Re-association is a distinct possibility, but it must be borne in mind that the copper plays no further part in the reaction once the cure has been initiated. Hence, the possibility of association with the alkoxide (RO^-) groups formed during the reaction (Figure 1) can not be discounted at this stage.

In conclusion, the metal-imidazole curing agents presented here are excellent latent curing agents with fine ambient temperature storage stability and good solubility in commercial epoxy resins and common organic solvents. The complexation of a transition metal (in this case copper) effectively arrests the polyetherification reaction at ambient temperature until the temperature is elevated to effect cure. A further advantage over existing imidazole curing agents is the efficiency of complexation. After a period of time at the cure temperature (for example 120°C or 140°C) the epoxy/complex mixture may be quenched at room temperature with no further advancement of cure. This development makes the tailoring of a commercial epoxy possible thus facilitating more complex cure schedules in a more controllable manner.

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References

1. Ashcroft WR (1993) Curing agents for epoxy resins, Chapter 2 in *Chemistry and Technology of Epoxy Resins* Ellis B (Ed) Blackie Academic and Professional, Glasgow and London, p 58
2. Ito M, Hata H and Kamagata K (1987) *J Appl Polym Sci* 33: 1843
3. Jackson RJ, Pigneri AM and Gaigoci EC (1987) *SAMPE J* 23: 16
4. Dowbeno R, Chang WH and Anderson CC (1972) US Patent 3,677,978
5. Dowbenko R, Anderson CC and Chang WH (1971) *Ind. Eng. Chem.* 10: 344
6. Barton JM (1984) GB Patent 2,135,316 B
7. Barton JM, Buist GJ, Hamerton I, Howlin BJ, Jones, JR and Liu S (1994) *J Mater Chem* 4:379
8. Barton JM, Buist GJ, Hamerton I, Howlin BJ, Jones, JR and Liu S (1994) Development of Novel Epoxy Curing Agents. 2. Comparative kinetic analyses for epoxy resins cured with imidazole-metal complexes, in preparation
9. Barton JM, Buist GJ, Hamerton I, Howlin BJ, Jones, JR and Liu S (1994) High temperature ^{1}H NMR studies of epoxy cure: a neglected technique, submitted to *Polym. Bull.*

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