Latent Hardeners for the Assembly of Epoxy Composites

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Introduction

Large-scale composite structures are commonly joined by secondary bonding of molded-and-cured thermoset components. Secondary bonding (Fig. 1), is the joining of two cured components with an adhesive. This approach, while highly effective in most cases, sometimes results in a weak bond at the adhesive/adherend interface. Due to the unpredictable nature of the interface, FAA certification of primary structures with secondary bonds requires that aircraft manufacturers incorporate redundant load paths accomplished mostly by adding mechanical fasteners.[1-4] In contrast, the co-cure process, shown in Fig. 1, is the joining of two uncured parts without adhesive. For thermosetting polymers (e.g. epoxies) the resin reflows upon heating and then undergoes a curing reaction (cross-linking) giving structural continuity through a joint. Assemblies made by co-curing, although limited in size and manufacturing complexity, result in predictable structures which are certifiable for commercial aviation without redundant load paths.[5] Removing redundant fasteners may reduce the part count in a largely composite commercial transport aircraft by 120,000 parts and the weight by 5000 lbs (2%). We propose a co-cure-ply technique that relies on a multifunctional epoxy resin that may enable sub-structures to be fully cured while leaving the joining surfaces uncured. Assembly in a subsequent, out-of-autoclave, co-cure process may meet federal regulations and help realize the potential of composites by reducing cost and increasing aircraft performance.

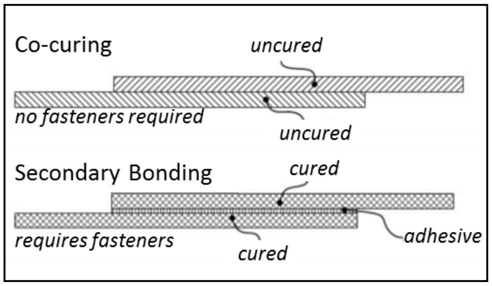

Figure 1: Co-curing is the joining of two uncured parts without adhesive and secondary bonding is the joining of two cured parts, which requires adhesive.

The multifunctional epoxy resins prepared do not completely polymerize until they are activated. Prepreg tape infused with one of these switchable resins, referred to here as the "co-cure-ply," will be placed on joining surfaces and cocured with the part. During the initial cure cycle, the part develops its full mechanical properties, but the inhibited resin in the co-cure-ply may remain tacky. After the co-cure-plies are activated, two parts can then be joined using a secondary bonding process to give an assembly with no interfaces.

Inhibited amines were prepared from aromatic mono- and di-amines by condensation with a ketone or aldehyde to form imines. Figure 2 shows the generalized reaction scheme. A parallel-plate rheometer was used to observe the vitrification of an aromatic epoxy mixed with inhibited hardeners using a standard epoxy cure cycle. The glass transition temperature obtained by calorimetry indicated the degree of cure. Imidazole and acidic alumina were studied individually for their catalytic effects on polymerization. Data from Layer suggested that ketimines were less stable than aldimines in the presence of water.[6] Optimum conditions to reverse the protecting chemistry and activate the epoxy hardeners with moisture and catalysts were investigated using time-resolved nuclear magnetic resonance (NMR) studies.

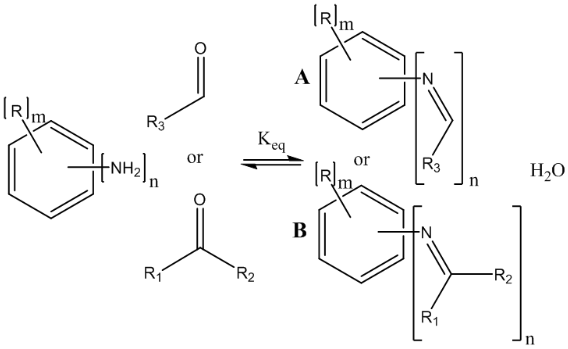

Figure 2: General reaction scheme for the protection of primary amines with ketones or aldehydes.

Experimental

The following materials were used as received: Ethacure 100 from the Albermarle Corporation, p-toluene sulfonic acid monohydrate, methylisobutylketone (MIBK), aniline, imidazole, diethyl ether, hexanes, and deuterated chloroform ($CDCl_3$) and dimethysulfoxide (d_6-DMSO) from Sigma Aldrich, *p*-tolualdehyde from Kodak, toluene from Acros Organics, and acidic alumina from Fisher Scientific. DER 331 epoxy resin from Dow Chemical Co. was dried under vacuum at 50 °C for at least 72 h before use. The *m*-phenylenediamine obtained from Sigma Aldrich was purified by vacuum distillation.

Ketimines were prepared using the generalized scheme adapted from Browning et al.[7] An example preparation of a ketimine is as follows. Ethacure 100 (10g) is placed in a 3-

neck, 300 mL round bottom flask fitted with a magnetic stirrer, reflux condenser, nitrogen inlet, oil bubbler, and moisture trap. A ketone (e.g. MIBK) was added in excess (2.5 mol equivalents based on amine groups) and enough toluene was added to achieve ~20% solids based on the theoretical yield. *P*-toluene sulfonic acid monohydrate (0.05 mol%) was added and the reaction was heated to reflux overnight. Progress was monitored by observing the volume of water collected in the moisture trap. The anhydrous workup involved removal of solvent by atmospheric distillation followed by vacuum distillation (130 °C, 0.7 mmHg) of the product which was recovered as a light yellow oil in moderate yield.

The generalized scheme for the preparation of the aldimine is as follows.[8] Five grams of amine and a stoichiometric amount (based on amine groups) of aldehyde were mixed in a 100 mL, 3-neck, round-bottom flask equipped with a nitrogen inlet, oil bubbler, and magnetic stirrer. The neat reaction mixture quickly crystallized and then formed water droplets on the flask walls at room temperature over 2 to 5 hours. Water was removed by heating to 80 °C at reduced pressure (100 mmHg). The products were purified by recrystallization from ether or hexane.

Reaction products were characterized with a Bruker (Avance 300) Multinuclear Spectrometer operating at 300.152 MHz and a Thermo Scientific attenuated total reflectance Fourier transform infrared spectrometer (ATR-FTIR). Thermal analysis was performed on a SETARAM DSC131 differential scanning calorimeter (DSC) and a TA Instruments Aries rheometer. The DSC was programmed to heat at 20 °C/min to 120 °C followed by cooling at 50 °C/min to 0 °C and a second heating cycle at 20 °C/min to 120 °C. The T_g was measured during the second heating step. The rheometer was programmed to follow the standard heating cycle recommended by Dow Chemical Co. to heat the DER 331 epoxy resin to 100 °C for 2 h followed by 175 °C for 4 h under flowing nitrogen gas.

Results and Discussion

The inactive form of Ethacure 100 is given as ketamine **B** in Fig. 2 where m=3, n=2, R is ethyl, ethyl, and methyl, R_1 is methyl, and R_2 is isobutyl. Traces from the rheometer in Fig. 3 show the trends for viscosity, storage- and loss-modulus for DER331 epoxy mixed with a stoichiometric amount of either active Ethacure 100 hardener (top trace) or inactive Ethacure 100 imine (bottom trace). The active Ethacure 100 shows a steady increase in all three parameters at 100 °C and a sharp increase upon heating to 175 °C. The test was ended abruptly at 140 min due to overloading of the torque sensor as the sample vitrified (viscosity > 40 kPa-s). The resin that contained inactive Ethacure 100 imine showed no signs of advancement during the 100 °C heating phase and showed a slow curing progression over approximately 3 h; the rheometer reached the torque limit after 330 min of total cure time. The rheometer tests show that the imine group hinders epoxy polymerization, but does not prevent it. No advancement was observed (graph not shown) for a sample of pure DER 331 (without hardener), which verifies that the rheology observed in Fig. 3 was due to the added hardener.

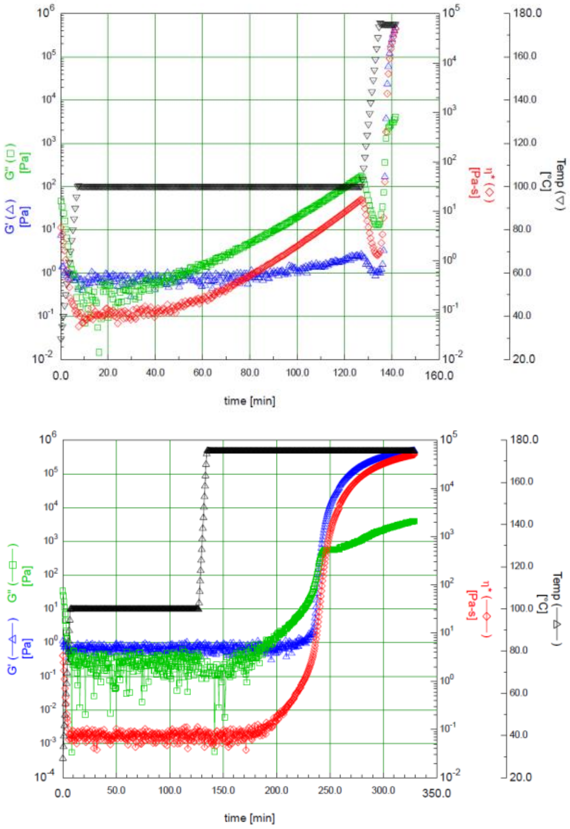

Figure 3: Rheometer results for DER 331 epoxy with Ethacure 100 (top) and Ethacure 100 imine (bottom).

After the full cure cycle, samples from the rheometer were immediately tested in the DSC. The measured T_g values are presented in Table 1. As expected from the rheometer results, the T_g with the inactive Ethacure imine was 128 °C lower than with the active form. Although the T_g advanced beyond room temperature, the partially cured material can easily be rendered tacky with heat for a subsequent bonding process.

Catalytic amounts of acidic alumina or imidazole were added to DER331 and Ethacure 100 imine mixtures to observe the effect on polymerization. With the acidic alumina, rheology appeared identical to that of the inactive Ethacure 100, but the T_g was suppressed to a lesser extent (93 °C). With imidazole, the inhibited resin vitrified, and the torque sensor overloaded 215 min into the cure cycle.

Phenylenediamine protected with p-tolualdehyde had the structure of compound **A** in Fig. 2 where m=0, n=2, and R_3 was 4-methylphenyl and is referred to here as phenylenedialdimine. The epoxy sample hardened with phenylenediamine overloaded the rheometer at 100 °C within 35 min, but the sample with phenylenedialdimine remained fluid (viscosity < 10 Pa-s) after 4 hours at 175 °C. Phenylenedialdimine suppressed the cured T_g by 118 °C relative to the T_g with phenylenediamine.

Table 1. Glass transition temperatures of DER 331 epoxy with various hardeners after the standard cure cycle.

Hardener/Catalyst mixed with DER 331	**T_g (°C)**
Ethacure 100 (control)	173
Ethacure 100 imine	45
Ethacure 100 imine, acidic alumina	80
Ethacure 100 imine, imidazole	108
m-phenylenediamine (control)	161
m-phenylenedialdimine	43

A series of time resolved NMR experiments observed the activation of a model aldimine (compound **A** in Fig. 2 where m=0, n=1, and R_3 is 4-methylphenyl) with water to form an amine in d_6-DMSO. Additional experiments were conducted with acidic alumina or imidazole as catalysts for the deprotection reaction. The chemical shift of the imine and aldehyde protons, at 8.54 and 9.94 ppm, respectively, were monitored to measure the consumption of imine and production of amine. The reaction was assumed to follow a second order reversible rate law. A linearized form of the rate law was adapted from Hassan et al.[9] Table 2 shows the forward rate constants, equilibrium constants and reaction conditions obtained at 20 °C.

Table 2. Kinetic and equilibrium constants from time-resolved NMR experiments for the reaction shown in Fig. 1 using the model aldimine (see above). K_{eq} is the equilibrium constant, k_f is the forward rate constant, and X^E is the equilibrium fractional conversion of amine.

Catalyst	**k_f** (L/mol h)	**K_{eq}**	**X^E**
None	0.87	52.2	0.86
Acidic alumina	2.63	57.7	0.84
Imidazole	1.96	59.7	0.85

Both K_{eq} and X^E are independent of the catalyst type, but acid alumina accelerates the reaction by a factor of 3 and imidazole accelerates the reaction by 2.25.

A simulated co-cure process will be used to demonstrate the activation of the hardener in the solid state and measure the recovery of the T_g after the final cure cycle. Based on these results, co-cure-ply prepreg will be prepared and used to make coupons for mechanical testing of co-cured joints.

Although imine protection shows some promise to control the activity of two-component epoxy resins, several issues still remain. A significant percentage of the hardener mass is released into the resin upon activation, which is a possible source of volatiles and porosity. One possible solution is the preparation of hardeners with intramolecular (covalently bound) protecting groups. Self immolative polymers could also be used to generate hardener in the solid state with very little release of non-reactive species.[10] Finally, if the hardener could be activated using radiation, it would be stable in the presence of environmental moisture.

Conclusions

A co-cure-ply resin based on protected amines was proposed to prepare co-cured joints using a secondary bonding process. Inactive hardeners prepared by protecting amines (imines) were shown to partially inhibit the polymerization of an aromatic epoxy during a standard cure cycle. The T_g of resins cured with inactive hardeners were as much as 128 °C lower than resins cured with active hardeners. Deprotection of imines was accelerated by both acid and alkaline catalysis.

Acknowledgements

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