JOURNAL OF MATERIALS SCIENCE **36** (2001) 5301 – 5308

Accelerated cure of thermoset fiber composites utilizing latent cure agents

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Cure agents including micro-pulverized dicyandiamide, aliphatic amine, imidazole, dyhydrazide, and ureas have been formulated with DGEBA (diglycidyl ether of bisphenol-A) epoxides to provide preimpregnated fiberglass prepregs suitable for the rapid production of structural composites under an aggressive elevated temperature cure schedule (10 min at 110°C). Formulations have been developed utilizing in part Taguchi orthogonal experimental arrays and compared to existing chemistries. Chemical formulation properties including heat of reaction, viscosity, glass transition, process parameter determination, and impact of environmental exposure have been investigated. Formulations developed within this body of work appear to outperform current commercial systems for the production of structural composites rapidly processed at a relatively low temperature.

1. Introduction

Cost sensitive industries require inexpensive, rapidly cured polymer fiber composites that are processable in existing tooling. These industries consistently search for materials that process at higher throughputs and lower temperatures to reduce capital expenditures associated with tooling conversion. Current B-stage thermoset composite systems process between 121°C and 177°C in 120 minutes. While companies have investigated rapid processing techniques such as RTM [1–3], pultrusion [4–5] and resin infusion, there is a need for a B-staged preimpregnated fiber composite that is curable in 10 minutes at temperatures as low as 110°C. At this time, major preimpregnated fiber suppliers offer few material systems that meet these process parameters because the market size is small and developmental costs associated with prepreg development can be quite high. Consequently, economies of scale are rarely achieved and the price of rapid cure commercial systems remain cost prohibitive for certain industries.

The goal of this research is to present several systems processable using a resin bath prepreg manufacture machine and commercially available cure agents that meet the process window described above. The formulation and operational variables that determine the process window of B-staged materials include the structure of the prepolymer, functionality of the cure agent, stoichiometry of the reactive groups, the process parameters of the prepolymer and hardeners with special attention to the thermal history of the materials upon mixing [6].

The technology and chemical specifics of epoxies and their modifications are well understood [7–9] and accelerated prepreg materials have been developed utilizing two parallel strategies: encapsulated cure agents and highly reactive curatives. Encapsulated cure agents have been investigated, initially with polyacetone encapsulated DDS (Diaminophenyl sulfone) [10] and more recently phenyldimethyl urea [11] and imidazoles [12]. While this appears to be an effective means of inhibiting reactants from interacting with epoxies, at this time it is cost prohibitive for low cost consumer applications. Initial methods to accelerate Bisphenol-A epoxy-MDA (methylene dianiline) reactions using BF_3 (boron trifluoride) met with success, although far below the cure schedule expectations in this study [13]. Commercial prepreg manufacturers have utilized MDA in other schemes to produce accelerated prepregs [14]. However, MDA has been determined to be carcinogenic in laboratory animals and its use has been curtailed [15]. Accelerated prepregs produced from tetrafunctional epoxides (Tetraglycidyl-4, 4′ (4-aminophenyl)-p-diisopropyl benzene) combined with ungelled glassy amine cure agents achieve T_g's comparable to aerospace grades, although sacrificing tack and drape [16].

Thermoset materials continue to react with time at temperatures 20–30°C below the existing T_g until completely reacted [17]. A study of the affect of the epoxy-amine ratio on T_g (Shell Epon 828 plus Air Products PACM-20) identified a maximum T_g of 170°C at stoichiometric levels [18]. The factors that affect T_g of a DGEBA epoxy network cured with a catalyst that promotes the homopolymerization of epoxy groups to

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form ether linkages suggests the highest T_g is 190°C [19]. It further indicates that the degree of cure, catalyst concentration, and network structure/cure history have the greatest affect on epoxy polymer network T_g. The approximate orders of magnitude affect of the different factors on the T_g is listed below [19]:

Degree of cure	200
Catalyst concentration	>50
Network structure/cure history	>50
Purity of monomer	10
Physical aging (reversible)	10

The aim of our work is to formulate and characterize DGEBA backbone epoxy networks with selective cure agents suitable for incorporating both glass and carbon fibers into prepreg materials. These prepregs must be processable under aggressive time-temperature cure schedules (10 minutes at 110°C) at very high heating rates (25°C/min). Particular emphasis is given to the processability of each in the context of the final B-stage prepreg form. Several formulation factors were considered as input to a three factor, four level Taguchi orthogonal experimental array conducted to examine existing chemistries. Properties including heat of reaction, viscosity, T_g, and effect of environmental exposure have been analyzed. Formulation chemistries are presented with the process–property relationships of these new materials in the context of competing material forms.

2. Material selection

2.1. Material selection—epoxy

Materials considered in this project were determined by considering several factors. Some of the important factors are processability, properties, and cost. Epoxies examined include di-functional, tetra-functional, and novalac resins. Preliminary tests on highly functional backbone resins, costly in comparison to commodity DGEBA resins, led to highly exothermic reactions with the cure agents that we examined. It was thought that the use of a liquid DGEBA resin alone would result in a prepreg material with poor room temperature tack and a room temperature viscosity difficult to control. Combinations of DER 330 (room temperature viscosity of 850 Pa-s, Epoxy Equivalent Weight [EEW] 180, Dow Chemical Co., Midland, MI) and DER 661 (Dow Chemical Co., solid at room temperature, EEW of 525) led to systems with suitable viscosities. However, the repeatability of prepreg manufacture with these systems was poor and hence these combinations were not studied further.

Two liquid epoxy systems were evaluated, Dow DER 330 and Dow DER 383 (EEW of 180 each, room temperature viscosities of 850 Pa-s and 975 Pa-s, respectively). These were used in combination with two liquid hardener systems, Dow DEH 29 (aliphatic polyamine blend, added at 22 parts per hundred by weight, cured 10 min at 110°C) and Dow DEH 78 (tetraethylenepentamine/triethylenetetramine, added at 24 parts per hundred by weight, cured 6 min at 102°C). Composite laminates were constructed using E-glass unidirectional fiber (PPG Industries, Pittsburgh, PA, product code 2016). The mechanical properties of these two systems (flexural modulus and short beam shear strength) were almost identical for the two epoxy systems. Although the DER 330 was slightly more reactive with the cure agents tested, we chose to use the DER 383 based on cost and availability.

2.2. Material selection—cure agents

Cure agents were obtained from six different suppliers, although the overall number of cure agents to be used was deliberately minimized to ease in manufacture. Consideration was given to the material handling, latency, material properties, and application to prepreg manufacture. Differential scanning calorimetry (DSC) was used to characterize the phase transitions of the candidate cure agents and their reactions with DGEBA epoxy. Reaction exotherm (ΔH) of each system was measured using a Perkin-Elmer System 7 DSC and analyzed by integrating the area under the resultant reaction curve. Samples weighing approximately 10 ± 0.5 mg were scanned at 10°C/min. from 30°C to 200°C; the exotherm generated at transition was monitored and recorded by the DSC.

The class of cure agents selected for these formulations that exhibit the greatest latency are Dicyandiamide cure agents. Dicyandiamide cure agents come in several material forms and are supplied in combination with other amine curatives. Phase transitions of the following dicyandiamide cure agent systems have been analyzed: SKW 100SF (SKW Trostberg, Trostberg, Germany, 6 μm particle size), SKW 100S (10 micron particle size), and Air Product CG 1200 (Air Products, Allentown, PA, 10 μm particle size). As is evident in Fig. 1, the 100SF exhibits a peak endotherm at 206.4°C, the 100S a peak at 219.5°C, and CG 1200 peaking at 221.7°C. The latency of each one of these Dicyandiamides is adequate for the prepreg formulation parameters of this program.

The lower transition temperature combined with enthalpy magnitude led directly to the selection of the SKW 100SF material, when combined with other accelerators, for final formulation consideration. It is noted that the particle size may have greater impact on the phase transition due to the increased diffusion rate and the homogeneity achieved by the finer particle size.

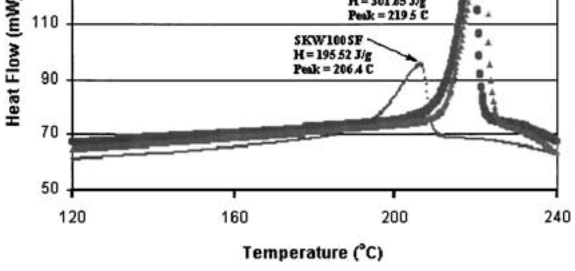

Figure 1 Comparison of commercial dicyandiamide phase transitions using DSC.

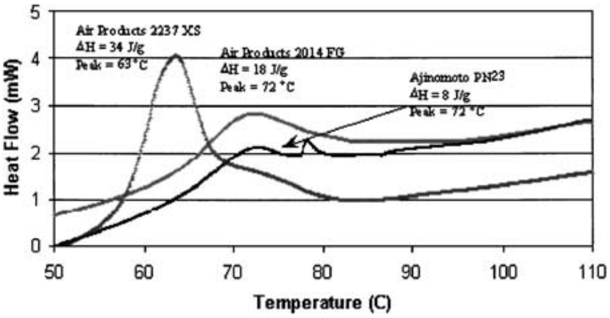

Figure 2 A comparison of the DSC signatures of Air Product 2014 AS, Air Product 2237 XS, and Ajinomoto PN23 dihydrazide amine cure agents.

Encapsulated amines evaluated for this study include a dihydrazide and an encapsulated modified amine. The DSC results for the amines are presented in Fig. 2. Reaction initiation for encapsulated amine 2237 XS (Air Products, Allentown, PA) is 63°C with a heat capacity of approximately 34 J/g. The dihydrazide (PN 23, Ajinomoto Chemical, Teaneck, NJ) exhibits a much lower heat capacity of 8 J/g at 72°C, with an additional uncharacteristic peak at 78°C which may be due to impurities. This is similar to the characteristics of the amine complex 2214 FG (Air Products, Allentown, PA). Despite the experimental nature of the 2237 AS, clearly it maintains favorable properties for formulators given the relatively low transition temperature.

Urea (UR, Air Products) and Imidazole (C17Z, Air Products) phase transitions occur at higher temperatures than encapsulated amines as exhibited in Fig. 3. It is noted that the urea exhibits an uncharacteristic transition at 124°C that is likely due to an impurity. By combining these two constituents with the lower transition amines, the formulator is able to control the system exothermic reaction in a step-wise manner to initiate the epoxide ring opening step and begin network cross linking.

A summary of the cure agent families considered follows in Table I. Listed are the transition temperatures and enthalpies of phase transition as measured by the differential scanning calorimeter.

The characteristics of the materials listed above vary significantly. Aliphatic amines were selected due to their ability to be adducted to modify their properties. Dicyandiamide (functionality $f = 4$) materials are selected due to their combination of addition polymerization and homopolymerization of epoxies. Additionally, dicyanidamide exhibits excellent room temperature latency due to phase transitions normally between 206°C and 225°C, providing several amine-like species, all of which react with epoxy. This transition increases the cure agent diffusion rate accelerating the cross-linking of the backbone epoxy molecule. Urea and imidazoles are selected based on their ability to accelerate dicyandiamide reactions upon phase change.

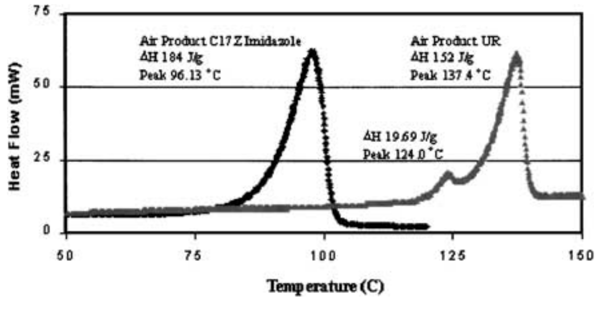

Figure 3 DSC signatures of imidazole and urea cure agents.

TABLE I Cure agents selected for consideration with the phase transition characteristics listed. Note that DEH 40 is a combination cure agent with three transition temperatures

Cure Agent Family	Designation	Description	Transition Temp. (°C)	ΔH (J/g)
Dicyandiamide	SKW 100SF	6 μm particle	206	195
	SKW 100 S		219	302
	Air Products CG-1200	10 μm particle	222	342
		10 μm particle	95/134/205	3/29/213
	Dow DEH 40	Combined cure agent		
Amine	Air Products 2014 FG	6 μm particle	72	18
			76	21
	Air Products 2014 AS	10 μm particle	63	34
		Latent catalyst	72	8
	Air Products 2237 AS	dihydrazide		
	Ajinomoto PN23			
Urea	Air Products UR	MW = 165	137	152
Imidazole	Air Products C17Z	Latency: 6 days	96	184

2.3. Taguchi orthogonal array

In order to limit the materials tested and better focus the experimental process, Taguchi experimental test arrays were performed using DSC scans and resin to hardener ratios as a guide. Experimental arrays serve as a simple method to determine material interactions in a multivariable problem and have been used successfully in industry for decades [20]. Typically, controls are set forth to provide a baseline for which data is to be compared. In the context of these experiments, baselines were assumed to be stoichiometric cure agent levels. In addition, controls in the process are as dictated by the project objectives in process time (10 minutes) and process temperature (110°C).

Cure agents supplied by Air Products were chosen for these test matrices. Two four-level, three-factor Taguchi orthogonal experimental design arrays were performed to determine hardener combinations using a combination epoxide formulation (Epon 826/862/1001 resin formulation of 60%/30%/10% quantities, Shell Chemical, Houston, TX). The epoxide equivalent weight (EEW) of the mix is 191, similar to the DER 383 epoxy resin chosen for final formulations. Since epoxies are frequently blended, filled, or modified with reactive and non-reactive components, it is necessary to adjust the concentration of the curing agent to cure only the portion of the mix that is reactive. EEW is computed in the following manner:

$$\text{EEW of mix} = \frac{\text{Total weight}}{\frac{\text{Wt. a}}{\text{EEW a}} + \frac{\text{Wt. b}}{\text{EEW b}} + \frac{\text{Wt. c}}{\text{EEW c}}}$$

TABLE II Cure agent levels

Cure agent designation	Material	Loading designation	Actual load level (phr)
A	Dicyandiaxnide	1	4
	CG 1200	2	8
		3	15
B	Aliphatic Amine	1	0
	201 4AS	2	1
		3	12
C	Imidazole C17Z	1	1
		2	3
		3	6
D	Urea 2T	1	1
		2	2
		3	4

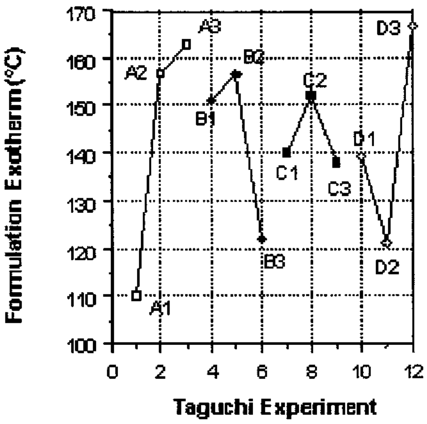

Figure 4 Taguchi variable interaction plot of exotherm results of Air Products cure agent testing. Labels indicate cure agent and distinct level of cure agent tested.

where EEW of commercial resins are determined statistically using a rule of mixtures calculation.

In the first Taguchi experimental array, the impact of combining four cure agents at three loading levels has been evaluated. Cure agents are described in Table II. The test variables in this array, labeled A–D, along with the quantities tested, corresponding to Levels 1–3, are listed below at different phr. The term "phr" is defined as parts per hundred by weight.

Samples of approximately 10 g each were cured at 110°C ± 2°C. The peak exotherm was measured using a temperature control monitor and transcribed from the digital display. A simple surface probe was used to determine the point at which the mixture hardened with the corresponding temperature recorded as the gel temperature. The matrix in Table III outlines the experimental results. To analyze the results, the average exotherm temperatures were computed for tests grouped by corresponding variable. For instance, all sample results that contained dicyandiamide at 4 phr are grouped and averaged. This set is labeled A1. This process is continued for each cure agent at each distinct phr load level (A1 through A3 for dicyandiamide, B1 through B3 for aliphatic amines, C1 through C3 for imidizole and D1 through D3 for urea). The aim is to identify a system with the lowest exotherm temperature. The average exotherm temperatures for all cure agents at different levels are plotted in Fig. 4.

The results from this set of experiments indicate the following:

- Exotherm is greatest at the highest levels of dicyandiamide and urea (A3 and D3).
- Exotherm is greatest at 3 phr imidazole (C2).
- Lower quantities of aliphatic amines produce higher exotherm (B2).

TABLE III Taguchi orthogonal array. Letters A–D represent cure agents listed in Table II

Test Number	A	B	C	D	Exotherm (°C)	Gel temp. (°C)
1	1	1	1	1	110	108
2	1	2	2	2	110	110
3	1	3	3	3	110	110
						186
4	2	1	3	3	200	
5	2	2	3	1	162	150
6	2	3	1	2	110	
7	3	1	3	2	143	143
8	3	2	1	3	200	174
9	3	3	2	1	146	132

Extent of cure of each combination was also determined using a similar method. These values were measured using a combination of a hardness and visual observation and each reaction was assigned a relative numerical value. It is recognized this method is not as accurate as possible (i.e. DSC measurements would provide a more accurate determination of the extent of cure of such a system), however, for the purposes of these early experiments these were deemed to be sufficient. From these experiments, the following observations have been made

- Higher levels of imidazole (C17Z) and urea produce greater extent of cure.
- Large quantities of dicyandiamide reduce the extent of cure.

The information extracted from the Taguchi Orthogonal Array experimental sequence was instrumental in determining the cure agent levels to concentrate on for further investigations. In particular, it was found that the dicyandiamide level most effective for quick cure and moderate exotherm was approximately 6 phr (between A1 and A2 in Fig. 4). Similarly, imidazole at 3 phr produced the greatest exotherm (C2 in Fig. 4), which proved valuable in determining the level of loading for prepreg formulations.

3. Prepreg development

3.1. Formulation for prepregs

Four resin/cure agent formulations were selected for the prepreg manufacture phase. Final formulation chemistry for each are based on the Dow 383 Epoxy resin and selected cure agents are combinations of those described previously. Cure agents and levels selected are reported in Table IV. Formulations 1 and 2 are variations on the same crosslink mechanism (dicyandiamide

TABLE IV Final formulations with each composition provided in parts per hundred by weight (phr)

Formulation	Cure agent	Phr
1	5KW 100SF	4
	PN23	4
	C17Z	4
	2014FG	4
2	SKWIOOSF	4
	PN23	4
	Urea	4
3	2237AS	3
	2014FG	3.5
	CI7Z	9
4	DEH4O	1
	PN23	1.75

(SKW 100SF) and dihydrazide (PN23)), each with a different initiator. Formulation 1, developed first, uses a two-part initiator consisting of an imidazole (C17Z) and aliphatic amine (2014FG). Upon working with this formulation, it was found that a variation using urea as the initiator provided a similar pot life at considerably lower cost. This resulted in Formulation 2. Formulation 3 was developed around the Air Product 2237 AS chemistry due to the unique phase transition exhibited by the encapsulated amine. Essentially, it was found that combining the 2237 As with a modified amine and imidazole produced a prepreg that exhibited excellent properties and was relatively easy to process. Formulation 4 was developed due to the ease of production in using a pre-packaged cure agent system such as the DEH 40 from Dow Chemical. This made the cure agent-resin system much easier to produce and reduced production time. PN23 was used in this formulation to accelerate the cure reaction.

In an attempt to better understand the reaction mechanism, individual constituent cure agents were added to resin and the reactions monitored using a DSC. An example of this using Formulation 1 is depicted in Fig. 5. The cross-link reaction is exothermic and a negative slope in the plot of heat input versus temperature is an indication of cross-linking reactions. As each additional constituent is added the reaction becomes more exothermic and indicating that the extent of cure increases. Signature Line 1 marked indicates DER 383 with dicyandiamide SKW 100SF. Lines marked 2 and 3 reflect the addition of dyhydrazide PN 23 and Imidazole C17Z to the resin and dicyandiamide, respectfully, while Line 4 indicates an increased kinetic reaction with the addition of the 2014 aliphatic amine. Note the complexity of the DSC output with the addition of the 2014 FG indicating the endothermic reaction beginning at 60°C and continuing until an exothermic reaction begins at 95°C. Similar DSC traces were developed for each formulation.

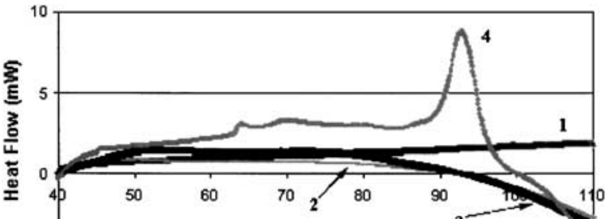

Figure 5 DSC plot of Formulation 1 cure agent addition to DER 383 resin. Line 1 indicates addition of dicyandiamide (8 phr), Line 2 addition of dyhydrazide (6 phr), Line 3 addition of imidazole (7 phr), and Line 4 the final formulation with the addition of an aliphatic amine (4 phr).

To compute the stoichiometric levels for each formulation, the amine hydrogen Equivalent Weight (AHEW) of the curing agents is necessary. It depends on the active number of hydrogen sites on the amine molecule and is computed as follows:

$$\text{AHEW} = \frac{\text{Mol. Wt. of Amine}}{\text{No. of Active Hydrogens}}$$

The calculation of the amine parts by weight per 100 parts resin is used to determine the stoichiometric amount of curing agent and is computed as follows:

$$\text{phr. of amine} = \frac{\text{Amine H eq. wt.} \cdot 100}{\text{Epoxide Eq. Wt. of resin}}$$

The introduction of accelerators are not included in these calculations and thus the formulator is forced to rely on alternative measures such as experimental techniques and experience to arrive at the optimum levels for them.

Stoichiometric levels were calculated for individual amines based on the constituent structures. The approximate stoichiometric level of each individual cure agent listed, based on a equivalent weight per epoxide of 180, are as follows:

SKW 100 SF	12.0
DEH 40	11.7
2014 FG	28.9
PN 23	8.7
2237 AS	14.0

Accelerator levels have been calculated although all references do not suggest the incorporation of these levels into a stoichiometric calculation. In order to calculate the stochimetric levels for the formulations which have multiple cure agents, the rule of mixtures is used $(\Sigma = (\text{phr})_i/(\text{stochimetric phr})_i$. Using this, Formulations 1 and 2 are above the stoichiometric level at 1.6 and 1.3, respectively, while Formulations 3 and 4 are well below stoichiometric at 0.6 and 0.84, respectively. Imidazol and urea accelerators are not normally contributing factors to stoichiometric calculations as they are seen as crosslink promoters and mainly contribute to the kinetics of the network formation and not to the decrease of epoxide end groups. However, higher than recommended accelerator levels may effect long term mechanical and physical properties due to the interstitial non-crosslinked component within the three-dimensional matrix.

TABLE V Formulation viscosity profiles of the "As-Formulated" and staged conditions (65°C/45 min)

	Virgin material			B-staged material		
Formulation	Minimum v (Pa-s)	Time to minimum v (min.)	Gel time (min.)	Minimum v v (Pa-s)	Time to minimum v (min.)	Gel time (min.)
1	45	4.67	8.5	85	6.0	8.0
2	30	4.75	9.0	35	5.75	8.5
3	10	5.1	8.5	15	6.0	8.67
4	12.5	5.1	8.5	12.5	5.75	8.25

3.2. Viscosity and cure characteristics of the prepregs

Viscosity tests were performed per ASTM D 2393, "Viscosity of Epoxy Resins and Related Components". A Brookfield Digital RVT viscometer in combination with a Brookfield Thermocell attachment for temperature control was utilized to perform the tests. The spindle number used was Number 28. While the initial spindle speed for room temperature viscosity was set at 10 rpm, the setting was adjusted to 100 rpm as the temperature increased. This adjustment was made between minute two and minute three of the tests. The temperature ramp rate achieved on each sample weighing 15 grams was approximately 25°C per minute. The start temperature for each test was approximately 30°C. The test was discontinued upon the gelation of the mix.

Results of these experiments provide insight into the viscosity decrease expected as the material is heated and are the basis for the fiber wet out anticipated upon cure in the preimpregnated form. In addition to measuring the viscosity of the virgin formulations, the viscosity profiles for formulations staged at 65°C for 45 minutes were also obtained. A temperature of 65°C for 45 minutes simulates the residence conditions for the resin in the resin pot during the prepreg manufacturing operation. The objective is to determine if the system undergoes significant cure characteristic change upon the prolonged exposure to the prepreg resin pot temperature. Commercial systems that cure at 121°C in two hours typically achieve viscosity drops to between 1 and 10 Pa-s [21]. As an example, in Fig. 6 the viscosity profile of Formulation 1 indicates a uniform viscosity decrease with a minimum viscosity of 45 Pa-s is achieved at 4 minutes, 40 seconds with gelation at 8.5 minutes. Similarly, staged Formulation 1 material achieves a minimum viscosity of 85 Pa-s at 6 minutes, achieving gelation at 8 minutes.

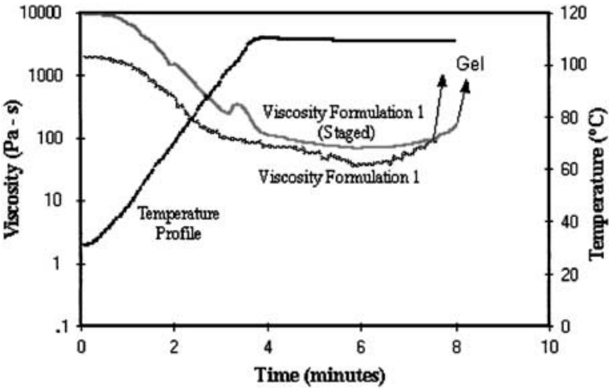

Figure 6 Viscosity profile of Formulation 1 "As Manufactured" and the same formulated system after upon exposure to 65°C for 45 min which simulates the time and temperature exposure during manufacture (referred to as "staged" in the figure).

In Table V, the viscosity results for all the formulations are summarized. It is particularly useful to consider Formulations 3 and 4 that show very low viscosity minimums in both the virgin and staged material forms. It is expected that these materials will achieve better consolidation when combined with fiber due to their propensity to flow and transport volatiles.

The cure processes for these four formulations have been characterized using a Perkin-Elmer System 7 Differential Scanning Calorimeter. The isothermal cure conditions were at $T < T_{\mathrm{g,max}}$, where $T_{\mathrm{g,max}}$ is the maximum possible glass transition temperature for a given composite as limited by system vitrification (loss of segmental mobility). The value of T_{g} for a cured epoxide resin, in turn, is a measure of the degree of cure. Tests conducted to determine the glass transition temperature of each cured formulation in the composite form were performed using DSC scan from 30°C to 200°C. After numerous trial runs and literature review, a 10°C per minute scan rate was selected [22]. The glass transition onset temperature was calculated from the inflection point to the baseline and recording the temperature at the intersection of these two lines. The final extent of cure (%) of each composite was calculated using DSC data by measuring the residual heat of reaction as follows:

$$\text{Extent of cure (\%)} = \frac{\Delta H_{\mathrm{o}} - \Delta H_{\mathrm{p}}}{\Delta H_{\mathrm{o}}}$$

where ΔH_{o} is the heat of reaction of a composite fully cured at 200°C and ΔH_{p} is the heat of reaction of the material after subjected to 110°C for 10 minutes. Table VI lists the glass transition temperatures and % cure of each material system.

Due to the chemical differences in the cure agents used in each of the four formulations, when each matrix system is combined with unidirectional glass fibers, the resulting composites exhibit a unique behavior. For example, Composite 4 has near the lowest total cure but maintains a high T_{g}. While the glass transition temperatures for all composites are deemed acceptable for the final application, it has been reported that a % cure of at least 90% is desired to insure long term stability for amine-epoxy reactions [23].

TABLE VI Determination of the T_g and % cure of the formulated composites using DSC

System	T_g (°C)	ΔH_o (J/g)	ΔH_p (J/g)	% cure
Formulated composite 1	126	138	16	88.4
Formulated composite 2	99	121	7	94.1
Formulated composite 3	127	84	6	92.7
Formulated composite 4	136	146	16.7	88.5

Storage of epoxy prepreg at room temperature will exhibit crosslinking in the resin matrix giving rise to an aging phenomenon. Aging is somewhat different from the cure process as aging may be retarded by vitrification before gelation [24]. In practice, several problems may be encountered in relation to prepreg aging including moisture absorption and chemical reaction of the resin matrix. Moisture absorption by the epoxy matrix usually accelerates the cure reaction, but may also result in void formation in the cured laminate [25]. The fabricated prepregs were thermally analyzed after storage at ambient temperature for 5 and 10 days.

Using formulated Composite 1 as an example and referring to the plots depicted in Fig. 7, heat of reaction of fresh prepreg (top plot) is 138.5 J/g. The ambient aged prepreg after 5 days (middle plot) exhibited a heat of reaction of 125.2 J/g and at 10 days (bottom plot) 111.6 J/g, corresponding to an $\alpha = 9.6\%$ and 19.4%, respectively, where α is a measure of the cure reaction during ageing and is defined as:

$$\alpha(\%) = \frac{\Delta H_{\text{As manufactured}} - \Delta H_{\text{Aged}}}{\Delta H_{\text{As manufactured}}}$$

A lower value of α indicates lower sensitivity to ageing and is desirable. A summary of the room temperature ageing effect on cure is listed in Table VII. Note that for Composite 4, only two data points were taken, fresh and at 10 days. Clearly, Composite 3 exhibits the least effect due to room temperature aging while the others react in a very similar manner when aged at room temperature.

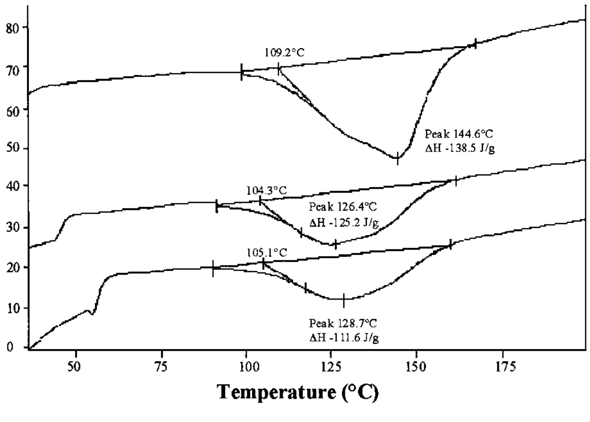

Figure 7 Effect of room temperature aging on heat of reaction—Composite 1.

TABLE VII Summary of aging (RT) on cure characteristics. The designation of O.T. indicates Out Time in days

System	Out Time (days)	ΔH (J/g)	α (%)	Peak (°C)	Onset (°C)
Formulated	0	138.5		144.6	109.2
composite	5	125.2	9.6	126.4	104.3
1	10	111.6	19.4	128.7	105.1
Formulated	0	120.8		136.6	108.5
composite	5	118.9	1.5	130.0	110.8
2	10	99.7	17.5	139.9	113.3
Formulated	0	83.7		134.1	123.0
composite	5	84.9	0	132.6	119.2
3	10	82.7	1.1	127.0	115.4
Formulated	0	136.4		127.0	107.4
composite 4	10	110.2	19.2	142.3	104.1

4. Conclusions

We have presented a methodology to design and tailor multi-constituent thermoset polymer formulations for prepreg composite applications. The candidate cure agents' thermal properties have been determined using differential scanning calorimetry and formulations have been optimized using a modified Taguchi orthogonal array in combination with thermal analysis data and stoichiometric calculations. The viscosity profile of each system has been used as a design tool for prepreg manufacture. Using this process, we conclude the following:

1. Four unique formulated DGEBA epoxy backbone matrices that cure at 110°C in 10 min. have been produced with E-glass to form composites adequate for many industrial and recreational structural composite applications.
2. We have determined that a DGEBA epoxy cured with DEH 40 cure agent at 7 phr combined with dihydrazide PN 23 at 1.75 phr produces a system that maintains a consistent viscosity profile even after exposure to 65°C for 45 min.
3. It has been shown that E-glass fiber prepreged with each of the four systems provides a cure of 88.4% or higher upon a cure of 110°C in 10 min. with formulated composite 2 (5 phr SKW 100SF, 7 phr dhydrazide PN 23, and 4 phr Urea) curing to a level of 94.1%.
4. Differential scanning calorimetry has been used to show that the degradation of the preimpregnated composite may be accurately determined. It is shown that formulated composite 3 (6 phr 2237 AS encapsulated amine, 3.5 phr complex amine, and 9 phr C17Z imidazole) will degrade only 1.1% in heat of reaction ΔH as a result of 10 days exposure at room temperature conditions.

Acknowledgments

The authors gratefully acknowledge financial support for this research from K2 Corporation, the Washington Technology Center and the National Science Foundation of the United States (Grant No. DMR-NYI

9257027). We also thank Dr. Brian Flinn for his assistance with the viscosity measurements.

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Received 22 November 1999
and accepted 1 May 2001