Novel processing and cure of epoxy resin systems*

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Thermoset-resin-based prepregs are typically fabricated into advanced composite parts using autoclave cures of up to 12 h in duration. In general, these systems have acceptable handling characteristics but limited shelf-lives and out-times. Prepregs based on high-performance engineering thermoplastic resins, on the other hand, have better shelf-lives but are more difficult to handle and require very high (300°C) temperatures for fabrication. This paper describes the development of epoxy resin systems that offer the potential of extended shelf-life while curing at relatively low temperatures. These systems offer the user reductions in autoclave usage of 75% (or greater), the possibility of vacuum-bag fabrication and display some of the sought-after processing characteristics of a thermoplastic thermoset. In addition, neat resin characterization, rheology information and cure conditions are described.

(Keywords: processing; cure; epoxy resin; composite; characterization; rheology)

INTRODUCTION

During the late 1950s and early 1960s, numerous investigations were reported in the technical literature on the use of dynamic mechanical properties of polymers to develop an understanding of the relationships between chemical structure and mechanical performance. Although much of this effort concerned thermoplastic materials[1-3], the value of these measurements as applied to thermosetting resins was also recognized. Drumm and coworkers[4] correlated dynamic mechanical measurements with the degree of cure in phenolic resins. Kaelble[5] and Kline[6] studied the dynamic mechanical properties of epoxy resins. The β-transition in epoxy resins was discovered in our laboratories by May and Weir[7] using an early model torsion pendulum, which led to a better understanding of the 'toughness' of these relatively new materials. Concurrently, Professor Gillham at Princeton University was developing torsion braid analysis[8], which resulted in a greatly simplified method for understanding the curing of thermosets[9]. Today, numerous instruments are available for this purpose, such as the Rheometrics Dynamic Mechanical Spectrometer (RDS).

Our own experiences and the technical literature[10] indicate that thermoset resins, particularly epoxies, continue to react at cure temperatures (T_c) 20–30°C below the existing glass transition temperature (T_g) up to its ultimate value (100% reacted). Current, conventional composite fabrication procedures involve heating the prepreg lay-up under heat and pressure (autoclaving) until most of the organofunctional groups in the resin system have reacted chemically. The part is then subjected to a free-standing post-cure to achieve the ultimate T_g of the system and optimum elevated-temperature performance. Experience has shown that virtually no distortion of the composite part results from this procedure. The reasons for this are two-fold. First, during post-cure the matrix resin is, most probably, in the glassy state, affording a high bulk modulus, which does not yield readily to the stresses caused by the residual curing. Secondly, because of the small differences between T_g and T_c, the thermal stresses are small. Larger thermal stress occurs only at the completion of the curing process on cooling from the post-curing temperature to ambient conditions. Our development efforts have shown that, based on the above reasoning, once a laminated structure is consolidated (void-free), the rigours of consolidation can be abandoned. The remainder of the composite curing process can be carried out in a simple, preprogrammed, unattended oven. The only prerequisite is that the oven be programmed so that $T_g - T_c$ remains positive throughout the remainder of the cure.

Gillham's recognition that a time–temperature–transformation (TTT) relationship can be developed for thermosetting resin systems[11,12] permits an understanding of the physical transformations of the material as it cures. A schematic example is shown in *Figure 1*[13]. The axes of time and temperature are used to define the physical state, i.e. rubbery, glassy, etc., of a thermoset matrix at any point during its heat history (cure). This diagram dicates that the most efficient cures can be achieved by heating the thermoset rapidly to its glass transition (*T_g)

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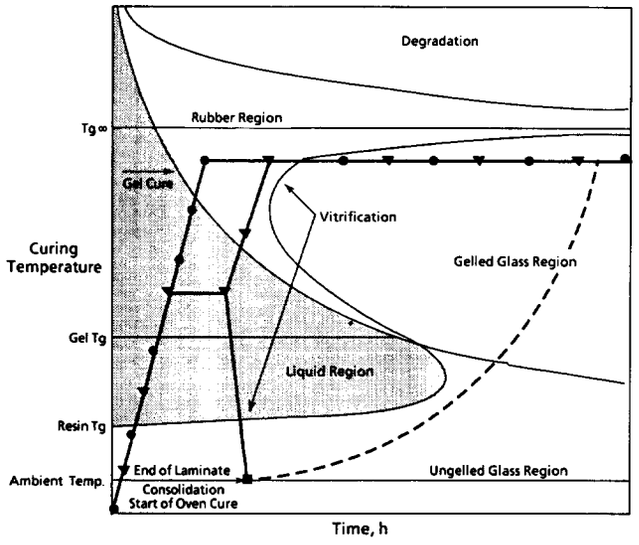
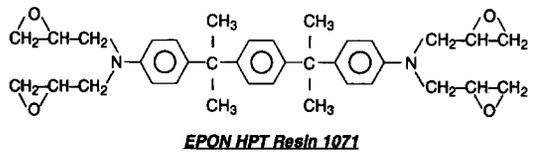
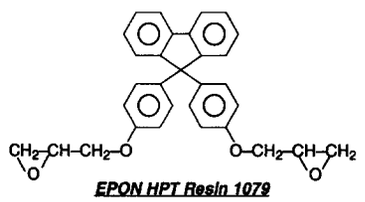


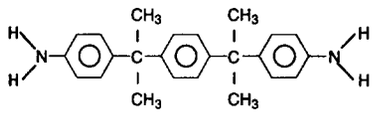
Figure 1 Time–temperature–transformation (*TTT*) diagram



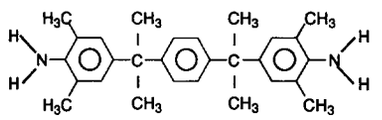
EPON HPT Resin 1071



EPON HPT Resin 1079



EPON HPT Curing Agent 1061



EPON HPT Curing Agent 1062

Figure 2 EPON HPT Resins and EPON HPT Curing Agents

temperature and holding this temperature until the cure is complete (the full circles in *Figure 1*). Unfortunately, the practicalities of most laminating processes require more time in the liquid state to consolidate the resin–fibre mass. Thus, cure cycles requiring longer times in the liquid region (as shown by the path of the full triangles) are more commonly followed.

The study reported herein discusses an alternative approach for processing of epoxy thermoset composites. Complete cure can be achieved by following the path of the broken curve in *Figure 1*. Once consolidation has been accomplished, cure can be completed in an unattended preprogrammed oven. The only prerequisite of this technique is that the matrix must be kept in the vitrified (high-modulus, glassy) state to avoid part distortion. In the example shown, autoclave or vacuum-bag processing time is reduced approximately 75%. This rapid thermoset processing (RTP) offers a number of attractive features:

1. Processing time requirements in expensive equipment such as autoclaves are minimized. Processing temperatures are also much lower. In the examples that follow, laminate consolidations were accomplished at temperatures in the range of 100–155°C (215–310°F) in 30 min under vacuum and 60–100 psi (~410–690 kPa).
2. Although this work was carried out using ambient-temperature, glassy-state resin matrices, properly formulated, tacky, drapable prepregs may be adaptable to the process. This allows for a broad range of thermoset formulations and a broad range of composite properties.
3. Employing glassy-state resin system permits the formulation of pre-orientated broad goods by techniques similar to those proposed for thermoplastic prepreg, but at much lower temperatures and pressures.
4. Following the autoclave or vacuum-bag consolidation, the formulations used herein remained thermoplastic-like. Thus, some of the processing advantages claimed for thermoplastics such as reworkability, thermoforming, large-structure filament winding, vacuum forming, heated tape laying, etc., can be accomplished at much lower temperatures.

MATERIALS SELECTION

The materials chosen for the initial studies on the RTP concept were the EPON HPT® Resins and the EPON HPT® Curing Agent systems. Their chemical structures are shown in *Figure 2*. The only other resin used in the investigation was EPON® Resin 828, the diglycidyl ether of bisphenol A, which served the purpose of lowering the melt viscosity of the uncured resin system.

Previous investigation had shown that many of these resin/curing agent combinations would yield prepregs with out-times of 60 days or more at room temperature. The seven resin systems evaluated in this investigation are shown in *Table 1*. As illustrated by the gel times, a broad range of chemical reactivities was observed. These findings provide the opportunity to select matrix systems with *TTT* charts covering a broad range of cure conditions. All of the materials shown were glassy solids at room temperature and became quite fluid on mild heating, as evidenced by rheological measurements.

Although the formulations shown in *Table 1* are relatively simple, it was a further goal of this investigation to demonstrate RTP using resins that could be 'toughened' and had improved hot–wet performance compared with the currently popular tetraglycidyl methylenedianiline/diaminodiphenylsulphone matrices. It has been shown that these materials offer substantial improvement in hot–wet performance[14], and can be toughened by the addition of either thermoplastics[15] or elastomers[16,17].

PRELIMINARY EXPERIMENTATION

Before conducting a detailed investigation of the three resin systems described above, preliminary experiments were conducted using the uncatalysed EPON HPT Resin 1079/EPON HPT Curing Agent 1061 (S3) system to test the viability of the RTP concept. Using the material ratios shown in *Table 1*, a satin weave glass cloth (Hexcel 7781-F69) prepreg was fabricated by hot melt processing.

Table 1 HPT resin systems

Sample number	S1	S2	S3	S4	S5	S6	S7
HPT 1071	100	–	–	–	85	–	85
HPT 1079	–	100	100	90	–	90	–
EPON 828	–	–	–	10	15	10	15
HPT CA 1061	–	–	32.28	33.0	–	33.0	–
HPT CA 1062	60.4	33.2	–	–	59.0	–	59.0
AMT-K2	–	–	–	1.0	1.5	–	–
Gel time at 350°F (min)	30.3	17.0	6.9	2.3	13.1	8.3	30.0
Gel time at 300°F (min)	–	–	16.0	3.7	31.0	18.0	60.5
Gel time at 250°F (min)	–	–	30.5	35.0	60	38.0	120

Two (4 inch × 6 inch) (10 cm × 15 cm) 15-ply laminates were prepared. The first was processed by heating the material to 177°C (350°F) at a rate of 1.4°C min^{-1} (2.5°F min^{-1}) and holding for a period of 2 h. Full vacuum and a pressure of 80 psi (~550 kPa) was used throughout this entire cure time. This was followed by a free-standing, oven post-cure of 4 h at 204°C (400°F). The resulting laminate appeared visually void-free and structurally sound. A second laminate was autoclave processed under similar conditions except that the temperature was increased from 25°C (77°F) to 121°C (250°F) in 1 h followed by a 0.5 h hold. This laminate also appeared to be of good quality. The resin content of both laminates was 38 wt%.

The dynamic mechanical properties of each of the above laminates were determined using the RDS. The shear or elastic modulus (G'), the storage modulus (G'') and the mechanical loss tangent (tan δ) of the fully cured laminate are shown in *Figure 3* as functions of temperature. The heating rate for this determination was 3°C min^{-1} up to 170°C (338°F) and 1.5°C min^{-1} up to 310°C (590°F). As shown by the peak in the tan δ curve, the T_g of this laminate was 243°C (470°F), consistent with data reported in the literature[14].

These measurements were compared with those of the partially cured laminated (*Figure 4*) as a test of the RTP concept. The latter laminate was heated using the same rate to approximately 140°C (284°F), at which a slight decline in the shear modulus was noted. The heating rate was then changed to one that approximated 0.75°C min^{-1}. Using this procedure, the shear modulus of the partially cured laminate remained equal to or slightly higher than that of the conventionally processed laminate well beyond the T_g for either sample. Thus, curing of a partially cured resin was continuing in the glassy (solid) state.

Figure 4 clearly shows that both laminates have almost identical dynamic mechanical responses. Based on the tan δ plot, there is little to choose between the products from the standpoint of the T_g. It could even be surmised that the partially cured laminate, after the final cure, had properties slightly better than those for the conventionally cured material. However, this is a somewhat tentative conclusion since differences of this magnitude could also reflect slight differences in the resin content.

Figure 5 shows the heating schedules used during the dynamic mechanical determinations. In the case of the partially cured (RTP) laminated, after an abbreviated autoclave cure requiring 1.5 h, as compared to the almost 4 h required for the conventional cure, the remainder of

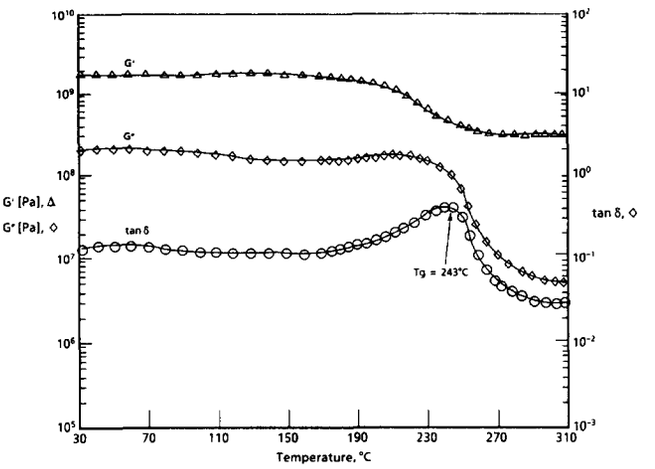


Figure 3 Dynamic mechanical properties of fully cured laminate

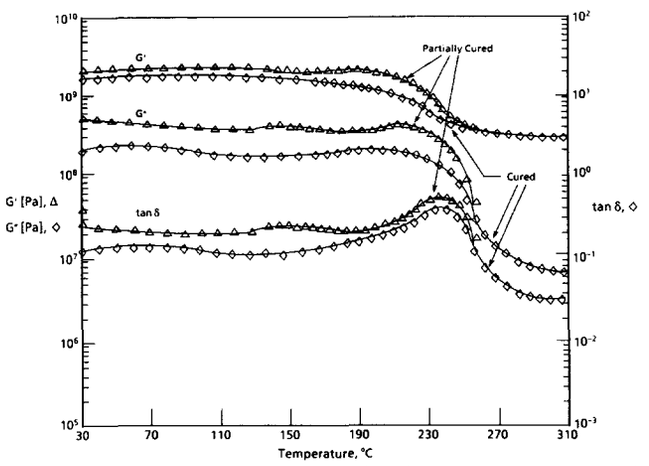


Figure 4 Dynamic mechanical properties of cured and partially cured laminate

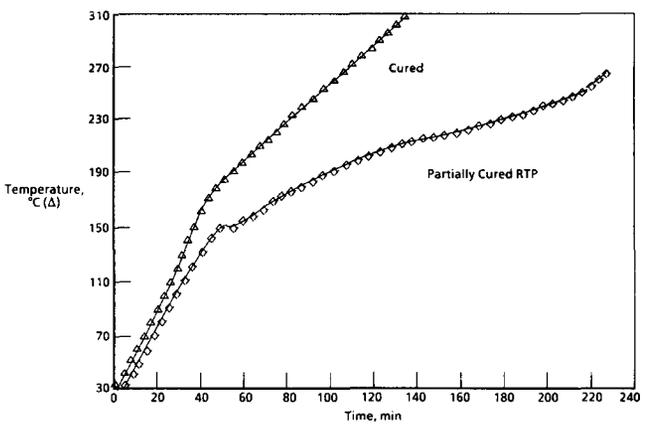


Figure 5 Heat schedules for dynamic mechanical determinations

the cure cycle could be completed in a simple, unattended, programmable oven. Based on information in *Figure 5* the final cure could be started around 140°C (284°F) and completed in about 3 h. Further, this was only the first, conservative, attempt to establish the final cure rate. Additional experimentation could allow for more rapid heating.

In terms of the *TTT* diagram, a cure cycle of the type shown by the broken curve in *Figure 1* was used following the consolidation period of a conventional cure cycle (full triangles). It is evident from these data that the RTP process is much simpler, requires far less autoclave time and involves lower cure temperatures than current laminating procedures.

During this investigation an even simpler method was devised for establishing the glassy-state cure cycles required for RTP fabrication. Following the consolidation step and subsequent cooling, the laminate was reheated to the consolidation temperature in an oven or on a press platen. The temperature was then increased at a rate whereby a positive Barcol hardness reading was obtained. This assured that the matrix was always in the glassy state until the known ultimate T_g of the fully cured matrix was attained. The cycle was verified by repeating the cure rate on a 1 inch × 12 inch (2.5 cm × 30.5 cm) strip of laminate supported on 10 inch (25.5 cm) centres. The absence of warping (sagging) indicated that the derived RTP cycle was proper and, once consolidation had been achieved, the final cure could be conducted in an oven in a free-standing condition.

TEST LAMINATE FABRICATION

To evaluate the RTP concept further, glass cloth (Hexcel 7781-F69) prepregs were prepared by the hot-melt process on a commercial hot-melt machine (Bryte Technologies) from the S1 and S6 (*Table 1*) resin systems. Four, eight-ply nested laminates were laid up for each resin system and the laminates were cured as follows (the imperial units reflect instrument settings, and are not converted to SI):

S1 (1): Standard autoclave cure cycle
Heat to 200°F under full vacuum at 3°F min^{-1}
Vent bag, apply 3 psi, heat to 240°F at 3°F min^{-1}
Apply 60 psi, heat to 350°F at 3°F min^{-1}
Hold at 350°F for 2 h and cool to 140°F before releasing pressure
Post-cure 2 h at 400°F

S1 (2): Vacuum-only cycle
Full vacuum, heat to 350°F at 3°F min^{-1}
Hold at 350°F for 2 h, cool to 140°F before releasing pressure
Post-cure 2 h at 400°F

S1 (3): Vacuum-only cycle, unrestrained post-cure
Full vacuum, heat to 310°F at 3°F min^{-1}
Hold at 310°F for 30 min, cool to 140°F before releasing vacuum
Heat on caul plate to 230°F at 3°F min^{-1}
Hold 25 min
Heat to 400°F at 1°F min^{-1}
Hold 2 h and cool to room temperature on caul plate

S1 (4): Autoclave cycle, unrestrained post-cure
Full vacuum, heat to 310°F at 3°F min^{-1}
Apply 60 psi, hold 30 min, cool to 140°F before releasing pressure
Post-cure according to directions for S1 (3)

S6 (1): Standard autoclave cycle
Heat to 200°F under full vacuum at 3°F min^{-1}
Apply 100 psi, heat to 310°F at 3°F min^{-1}
Hold 2 h and cool to 140°F before releasing pressure
Post-cure 2 h at 400°F

S6 (2): Vacuum-only cycle
Full vacuum, heat to 350°F at 3°F min^{-1}
Hold at 350°F for 2 h, cool to 140°F before releasing pressure
Post-cure 2 h at 400°F

S6 (3): Vacuum-only cycle, unrestrained post-cure
Full vacuum, heat to 215°F at 3°F min^{-1}
Hold 30 min, cool to 140°F before releasing pressure
Heat to 400°F at 1.5°F min^{-1}
Hold 2 h and cool to room temperature on caul plate

S6 (4): Autoclave cycle, unrestrained post-cure
Full vacuum, heat to 215°F at 3°F min^{-1}
Apply 100 psi, hold 30 min, cool to 140°F before releasing pressure
Post-cure according to directions for S6 (3)

It should be noted that, following the autoclave part of the RTP cycles, both laminates, S1 (2) and S6 (2), were still thermoplastic, as evidenced by their solubility in methyl ethyl ketone. Had an error been made during hardware fabrication, the lay-up could have been reworked. Both of these EPON HPT Resin

Table 2 Test result summary

	Average values[a]			Normalized values (30%)			
Resin (Process)	Flex. (ksi)	Mod. (Msi)	SBS (ksi)	Flex. (ksi)	Mod. (Msi)	SBS (ksi)	Resin (wt%)
S1 (1)	72.4	3.64	8.00	67.0	3.37	7.41	27.8
S1 (2)	64.6	3.03	5.94	73.4	3.44	6.75	34.1
S1 (3)	64.4	2.98	7.75	73.6	3.41	8.86	34.3
S1 (4)	74.8	3.47	8.98	73.3	3.40	8.79	29.4
S6 (1)	65.0	3.11	8.16	68.7	3.29	8.62	31.7
S6 (2)	56.9	3.21	7.03	67.5	3.81	8.34	35.6
S6 (3)	59.9	3.14	7.73	68.6	3.60	8.86	34.4
S4 (4)	62.9	2.78	7.92	80.7	3.56	10.16	38.5

[a] 1 ksi = 6.895 MPa; 1 Msi = 6.895 GPa

matrix systems appear to have thermoplastic/thermoset characteristics. This is another cost-saving potential long sought after by composites manufacturers.

RESULTS AND DISCUSSION

The mechanical properties of the S1 and S6 laminates prepared by the cure cycles shown above are given in *Table 2*. Comparisons have been made between the flexural strengths, moduli and short-beam shear strengths (SBS) at room temperature. Also shown are the resin contents of the laminates and the same mechanical properties after normalization to a resin content of 30 wt%. Although the RTP techniques appear to result in slightly higher resin contents, there is little question that the RTP technology can provide laminate properties similar to those obtained with the more lengthy, and more costly, conventional autoclave curing. On the basis of the normalized strengths, RTP could even be considered a slight advantage.

CONCLUSIONS

A new cost-effective approach to the curing of certain thermoset resin composites has been demonstrated. The duration of the processes, in either press or autoclave, is equivalent to or shorter than that required for thermoplastic processing, and the temperature requirements are much lower. A post-cure is required; however, this can be accomplished in relatively inexpensive equipment such as an unattended, programmable oven.

The EPON HPT Resin formulations used herein are of a preliminary nature and further modifications are anticipated to yield materials that better meet the overall needs of the aerospace industry. Through proper utilization of the principles discussed herein, it should be possible to fabricate room-temperature-stable, multi-layer broad goods, to use heated tape laying machines and to match many of the processing advantages claimed for thermoplastics but at lower processing temperatures. These findings offer considerable evidence that the much sought-after thermoplastic/thermoset matrix may be close to reality.

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