ARMY RESEARCH LABORATORY

Hybrid Helmet Cure Cycle Optimization

by David M. Spagnuolo and Eugene Napadensky

ARL-TR-4384 **February 2008**

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

DESTRUCTION NOTICE—Destroy this report when it is no longer needed. Do not return it to the originator.

Army Research Laboratory
Aberdeen Proving Ground, MD 21005-5069

ARL-TR-4384 **February 2008**

Hybrid Helmet Cure Cycle Optimization

David M. Spagnuolo and Eugene Napadensky
Weapons and Materials Research Directorate, ARL

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED (From - To)
February 2008	Final	

4. TITLE AND SUBTITLE
Hybrid Helmet Cure Cycle Optimization

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
778045

6. AUTHOR(S)
David M. Spagnuolo and Eugene Napadensky (both of ARL)

5d. PROJECT NUMBER
DE25

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
U.S. Army Research Laboratory
Weapons and Materials Research Directorate
Aberdeen Proving Ground, MD 21005-5069

8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-4384

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

Some of the recent work involving the use of thermoplastic materials for combat helmets has shown significant weight savings and improved protection. Unfortunately, the change to thermoplastic materials brings with it some important concerns. First, the stiffness is compromised with these materials so a hybrid type of helmet (a thermoplastic shell with thermoset inner or outer skins) is needed to reduce the deflection properties. This brings us to the second concern, processability. A typical combat helmet is made with a thermoset phenolic/polyvinylbutyral material, usually cured at 250°F with a 1-hour soaking time. Thermoplastics require higher temperatures for the fusion process to commence but require a much shorter soaking time. This work investigates potential cure cycles for a carbon fiber-epoxy prepreg[1], BT250-E, cured at higher temperatures, faster "ramp" rates, and shorter soaking times. A differential scanning calorimeter was used for measuring the degree of cure for the various cure cycles from which the most optimized cycle was selected, based on degree of cure and process time.

[1]pre-impregnated fibers; a reinforced plastics term for the reinforcing material that contains or is combined with the full complement of resin before the molding operation.

15. SUBJECT TERMS
BT250-E; cure cycle; degree of cure; DSC; epoxy

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			David M. Spagnuolo
Unclassified	Unclassified	Unclassified	SAR	15	19b. TELEPHONE NUMBER (*Include area code*) 410-306-0770

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Contents

List of Figures

List of Tables

1. Introduction

In an effort to develop a lighter weight helmet that provides the same or better ballistic qualities as compared to currently fielded helmets, a new system composed of thermoplastic fabrics, molded with thermoset prepregs was designed at ARL. Proposed manufacturing of the helmet involved pressure molding a number of plies of aramid fabric with a thermoplastic film, and two plies of carbon fiber-epoxy prepreg, BT250-E (Bryte Technologies, Inc.) that would add structural strength. The manufacturer's recommended cure cycle for BT250-E was to ramp (gradually increase) the part from 70 °F to 250 °F at rate of 2 to 5 °F per minute (while applying 25 inches mercury vacuum minimum) and to hold for 1 hour; the part was then cooled to below 160 °F, pressure was released, and the part removed (*1*).

It was assessed that because of the slow ramp times and long holding time, mass production of these helmets will be impractical. Following the manufacturer's recommended processing parameters for the carbon fiber-epoxy prepreg would result in a turn-over time of 78 to 96 minutes per helmet. In order to develop a shorter cure cycle, it was decided that a faster ramp time and a higher temperature should be investigated. Since the aramid-thermoplastic used in the helmet will have to be heated to 300 °F (149 °C) in order for the melting/solidification process to be complete, it was decided that a new cure cycle with a final temperature holding time at 300 °F should be designed for carbon fiber/epoxy prepreg.

2. Experimental

2.1 Theory

The degree of cure for polymeric resins can be monitored by a number of different methods such as thermomechanical analysis (TMA), differential scanning calorimetry (DSC), rheology, etc. (*2*). In this case, it was monitored by DSC. As the instrument increases sample temperature at a controlled rate, the amount of energy required to raise the sample's temperature changes when the material undergoes a physical (glass transition temperature [T_g], melting point, etc.) or chemical (any kind or reaction) changes.

Evaluating these changes in an energy flow provides quantitative insight to what is happening to the sample. In this case, the exothermic peak (approximately 150 ºC) related to the reaction of uncured resin was monitored (*3*). Since the peak area is proportional to the energy required for the reaction, it is related to the amount of uncured resin. Fully cured samples (with no unreacted resin) would have no peak at all, while "as received" prepreg would have the peak with the largest area (see figure 1).

Glass transition temperature could also be monitored. Since T_g is related to the degree of cure (which is the same as the degree of cross-linking), the T_g of the resin will gradually shift to higher temperatures as the material is approaching the fully cured state.

Attempting to monitor the degree of cure of prepregs is slightly more complicated as compared to a neat resin. Resin content in commercially available prepregs ranges from 30% to 45% by weight (*4*). T_g might be more difficult to observe since, for all intents and purposes, the sample size is dramatically decreased by the presence of fiber; thus, the signal intensity for the glass transition may be too low to monitor. On the other hand, the size of the exothermic peak (heat released during cure) is directly proportional to the amount of uncured resin, and since there is always some variation in prepreg resin-to-fiber ratios (resin-rich and resin-poor areas), it is expected that there will be some scatter in uncured and partially cured samples. These resin variations have minimal effect on the final properties of a manufactured part, but with DSC, this could be a major factor because of the small sample size (approximately 10 mg).

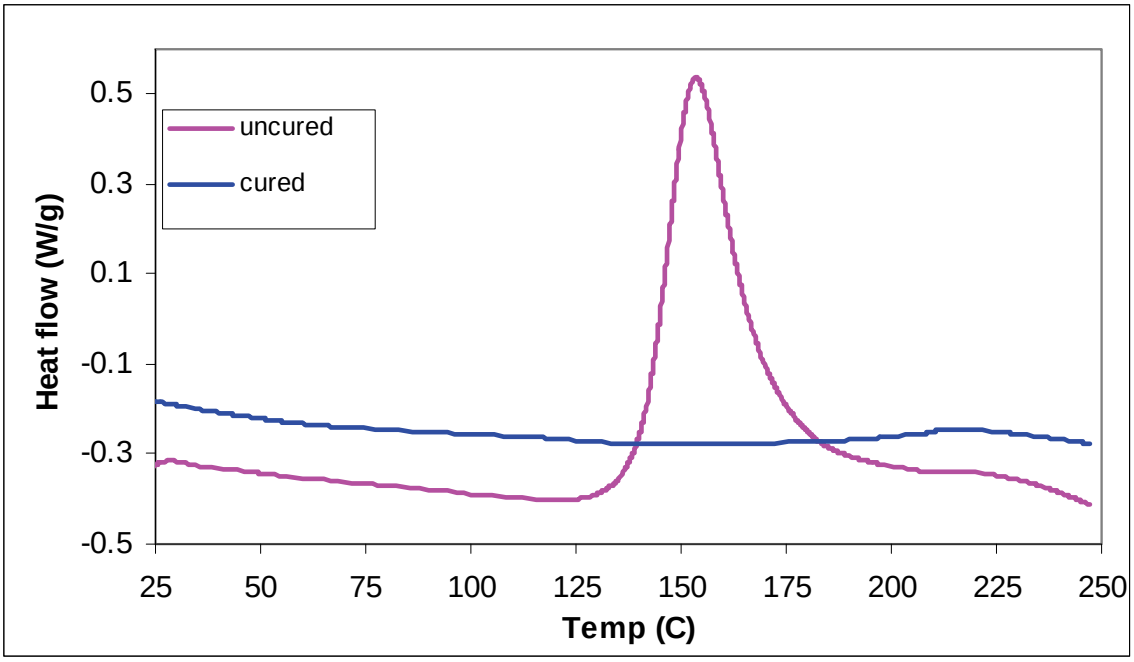


Figure 1. DSC scans of cured and uncured carbon fiber-epoxy prepreg.

2.2 Materials

Material chosen for this particular study was IM7-12K/BT250E-1, a Bryte Technology, Inc., prepreg. This prepreg, or unidirectional tape, was composed of IM7-12K graphite reinforcement with an epoxy resin, 37.8% resin content. The 12K represents the number of filaments per tow (untwisted bundle of filaments). The material was stored in a freezer at or below the manufacturer's recommended storage temperature of 0 ºF. The manufacturer-recommended cure cycle is 2º to 5 ºF temperature ramp to 250 ºF, and 1 hour holding time.

2.3 Equipment

Equipment used in these experiments consisted of a 2920 DSC (TA Instruments), and an HP5890 gas chromatograph (GC) oven (Hewlett Packard), chosen for its accurate temperature and rate controls to cure and partially cure prepreg samples. An analytical balance (precision- ±0.0001 g) was used to weigh the samples for the DSC.

2.4 Experimental Procedure

2.4.1 Cure Cycles

The carbon fiber-epoxy prepreg samples (approximately 2x5 cm) were clamped in a small metal holder and cured inside the HP5890 GC oven. Three cure cycles (A, B, and C) were chosen for this experiment (see table 1) in addition to the "standard" cure cycle recommended by the manufacturer. In addition to variations in the holding temperature, holding time was also varied in order to optimize minimal time required for a complete cure. Immediately upon cooling, cured and partially cured samples were analyzed with the DSC. Unused portions of samples were retained in a freezer for repeated analysis.

Table 1. List of evaluated cure cycles.

Cure Cycle	Initial Temperature (°C)	Ramp Rate (°C/min)	Final Temperature (°C)	Holding Time (min)	Cooling (min)	Run Time (min)
Standard[a]	25	3	121	60	3	95
A-5	25	5	121	5	3	27
A-15	25	5	121	15	3	37
A-30	25	5	121	30	3	52
B-0	25	5	149	0	3	28
B-2.5	25	5	149	2.5	3	30
B-5	25	5	149	5	3	33
B-10	25	5	149	10	3	38
C-5	25	10	149	5	3	20

[a]Cure cycle recommended by manufacturer and converted to degrees Celsius

2.4.2 Differential Scanning Calorimetry

DSC was performed on a 2920 DSC (TA Instruments). Samples were weighed (approximately 10 mg each), placed into hermetically sealed aluminum pans, and run under a nitrogen purge. The DSC run conditions were to stabilize the temperature at 20 ºC and then ramp at 10 ºC/min to 250 ºC. Reference for the analysis was an empty aluminum pan of the same type as the ones used for the actual samples.

3. Results and Discussion

3.1 Degree of Cure

The degree of cure was estimated from the area under the exothermic peak, normalized to the sample weight (5). An assumption had to be made that all samples have identical resin-to-fiber ratios. The degree of cure that resulted from various experimental cure cycles was estimated from the size of the exothermic peak relative to the "uncured" prepreg samples. Uncured samples were designated as 0% cured, and fully cured samples (showing no peak at all) as 100% cured. Technically, this is not correct, since prepreg by definition is already partially cured, but since prepreg is the starting point for these experiments, it is convenient to refer to that level of cure as 0%. The exothermic peaks in the DSC scans (at 150 ºC) are getting smaller and smaller (see figure 2) as more and more of the available functional groups in the resin react with each other during the cure cycle, indicating an approach to a fully cured material.

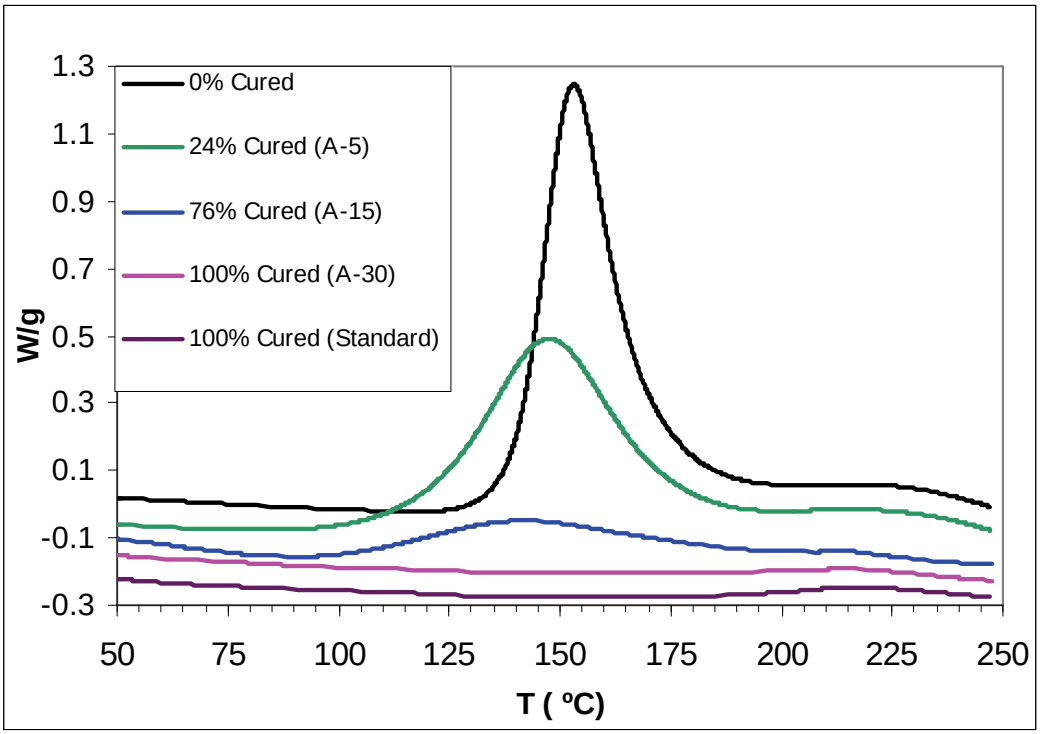


Figure 2. Determining the degree of curing from the exothermic peak.

3.2 Exotherm as an Indicator of Cure Level

The extent of cure/cross-linking reaction was estimated from the size of the exothermic peak, located in the vicinity of 150 ºC on the DSC scans, using the following relationship:

$$\%Cure = 100 * \frac{\Delta Hp - \Delta Hs}{\Delta Hp}$$

Where ΔHp is the partial heat of reaction for the original prepreg (128.25 joules per gram) and ΔHs is the partial heat of reaction for the specific partially cured sample being examined. In all cases, ΔH equals the area under the exothermic peak curve obtained by DSC and is measured in joules per gram.

Pure resin was not available for these experiments, and fiber-to-resin ratios can fluctuate, depending on location, when such small samples are used (resin-rich and resin-poor areas). It is believed that these variations in resin content are responsible for the significant scatter in the joules-per-gram values (peak area) in the partially cured samples and this is especially true in the "uncured" samples. DSC results from different cure cycles are shown in table 2. The table also shows the area of the exothermic peak, the cure percentage based on the exothermic peak area, and the glass transition temperatures.

Table 2. DSC results.

Cure Cycle	Weight (mg)	Cure Temperature (°C)	Ramp (°C/min))	Holding Time (min)	Peak Area (J/g)	Percent Cure	Cure Cycle Time (min)	T_g (°C)
Uncured	7.2	NA	NA	NA	106	17.3		
Uncured	8.1	NA	NA	NA	144	-12.3		
Uncured	7.3	NA	NA	NA	111	13.5		
Uncured	10.9	NA	NA	NA	152	-18.5		
AV Uncured					128.25	0.0		
Standard	10.2	121	3	60	0	100.0	92	123
A-5	13.6	121	5	5	97.5	24.0	24.2	35
A-15	9.3	121	5	15	30.8	76.0	34.2	33
A-30	9.9	121	5	30	0	100.0	49.2	121
B-0	9.8	149	5	0	18.2	85.8	24.8	62
B-0	11.5	149	5	0	19.2	85.0	24.8	65
B-2.5	11.1	149	5	2.5	5.3	95.9	27.3	
B-5	10.6	149	5	5	0	100.0	29.8	127
B-5	9.5	149	5	5	0.7	99.5	29.8	126
B-10	10.6	149	5	10	0	100.0	34.8	127
C-5	10.4	149	10	5	1.6	98.8	17.4	

The B series of cure cycles differs only in holding time at the final temperature. Figure 3 shows decreasing exothermic peaks as the holding time is increased from 0 to 10 minutes. The second peak (located at 220 ºC) is believed to be related to the thermal decomposition of the polymer and is not considered as an indicator of the curing process.

The data can also be represented to show the degree of cure as a function of holding time (see figure 4).

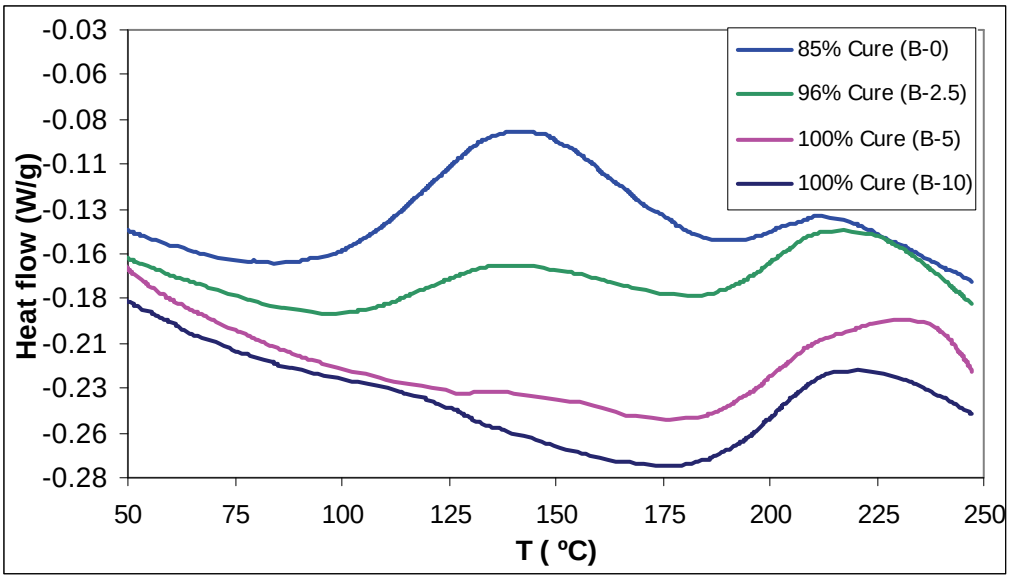


Figure 3. DSC scans for B-series of cure cycles (25 ºC to 149 ºC at 5 ºC/min).

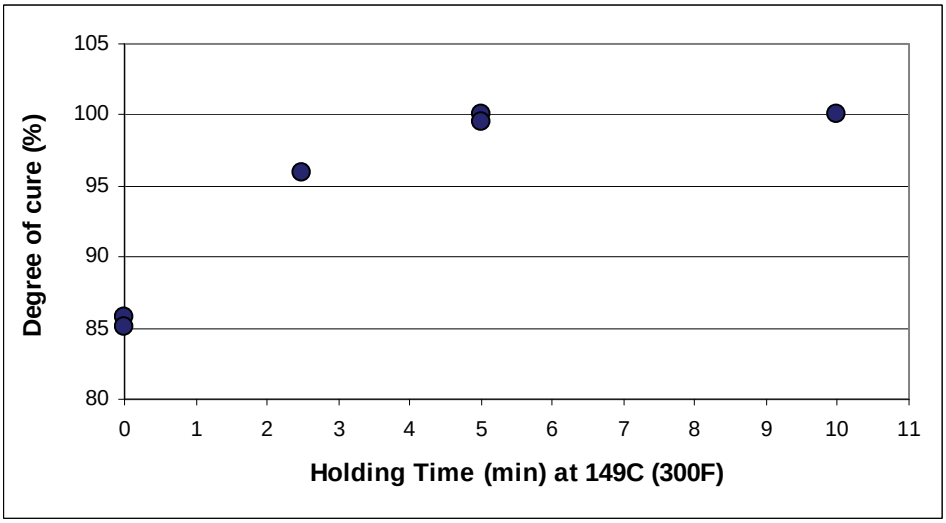


Figure 4. Degree of cure (for cycle B) as a function of holding time.

From this figure, it is clear that 99% of the curing process for cure cycle "B" is completed within the first 5 minutes. Of course, this pertains only to the experimental final temperature and heating rate (149 ºC and 5 ºC/min). Although it would be possible to make the claim that a 6- or 7-minute holding time would be sufficient, unforeseen considerations in the manufacturing process could require slightly longer holding times. For instance, a thicker sample will require a longer time to reach the desired temperature. Thus, it would be wise to add a few minutes as a built-in safety factor. As it is, a 10-minute holding time will result in only a 38-minute run: 15 minutes to ramp the temperature, a 10-minute holding time, and 3 minutes for cooling, unloading the finished part, and loading in a new pre-form (see table 1). That is a significant improvement from the original cure cycle of 95 minutes. Using this cure cycle will accelerate helmet

production capacity by 250%, resulting in significant financial savings and an increased supply of essential, protective equipment for the U.S. military.

These results can be further improved, provided that industrial manufacturing equipment can produce a controlled heating rate of 10 ºC per minute (50 ºF). The full scale of experiments using 10 ºC/min was not performed at this time, but with the use of the C-5 cure cycle (see table 2) as an initial indicator, required holding time can be estimated. A 5-minute holding time used for the C-5 cure cycle resulted in 98.8% cured resin. Assuming that the cure rate is similar to the B cycle shown in figure 4, it can be claimed that a cure cycle of 25 ºC to 149 ºC at 10 ºC/min, with a 10-minute holding time will result in a fully cured prepreg.

Final run time for this variation would be 25 minutes, as compared to 38 minutes at 5 ºC per minute ramp. With this cycle, the increase in production capacity would be 380%. However, industrial equipment of this type is more expensive and not readily available.

3.3 Glass Transition Temperature as an Indicator of Cure Level

Expected shift in the glass transition temperature (table 2) with increasing degree of cure to a higher temperature is well documented, even though different authors propose different equations describing the relationship between glass transition temperature and degree of cure (*6, 7, 8*). This technique sounded like a very promising path to verify a complete cure, but it did not give sufficiently reliable results in these experiments. Most likely, it is because of the combination of small amounts of actual resin in the sample and insufficient instrumental sensitivity. As a result, the T_g's performed in the DSC scans were difficult to positively identify from the baseline noise, and in some runs, it was not possible at all. Figure 5 shows two of the stronger T_g's, and one can see that even in these cases, exact value and or even the presence of a T_g can be argued for or against.

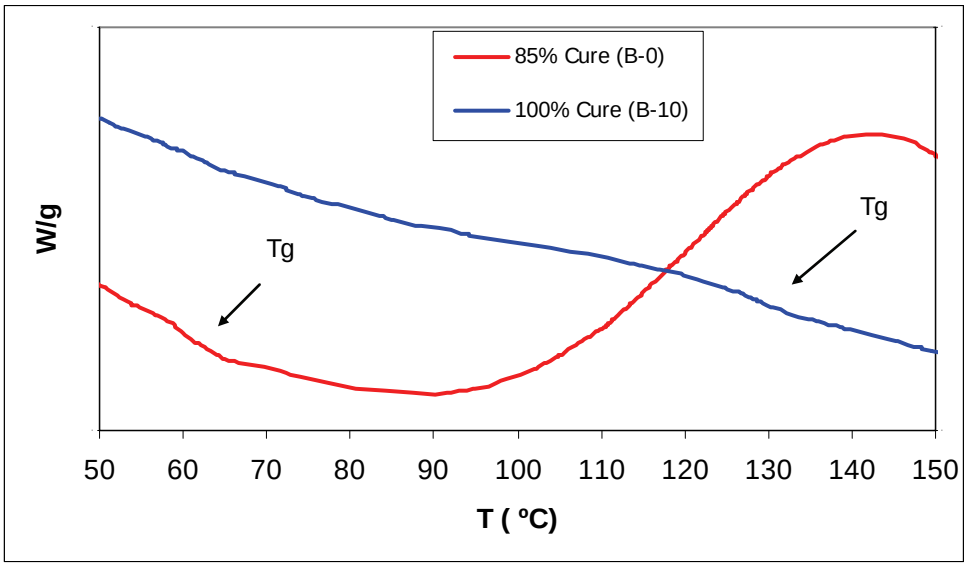


Figure 5. Examples of T_g shift related to cure levels.

Even though they were not strong enough to be useful, the pattern observed follows well-documented logarithmic relationships between the degree of cure (determined by area under the exothermic peak) and the glass transition temperature (see figure 6). The trend line shows a respectful (0.986) R^2 value[1], and that indicates that given better instrumental sensitivity, it would be possible to better monitor the degree of cure via this technique.

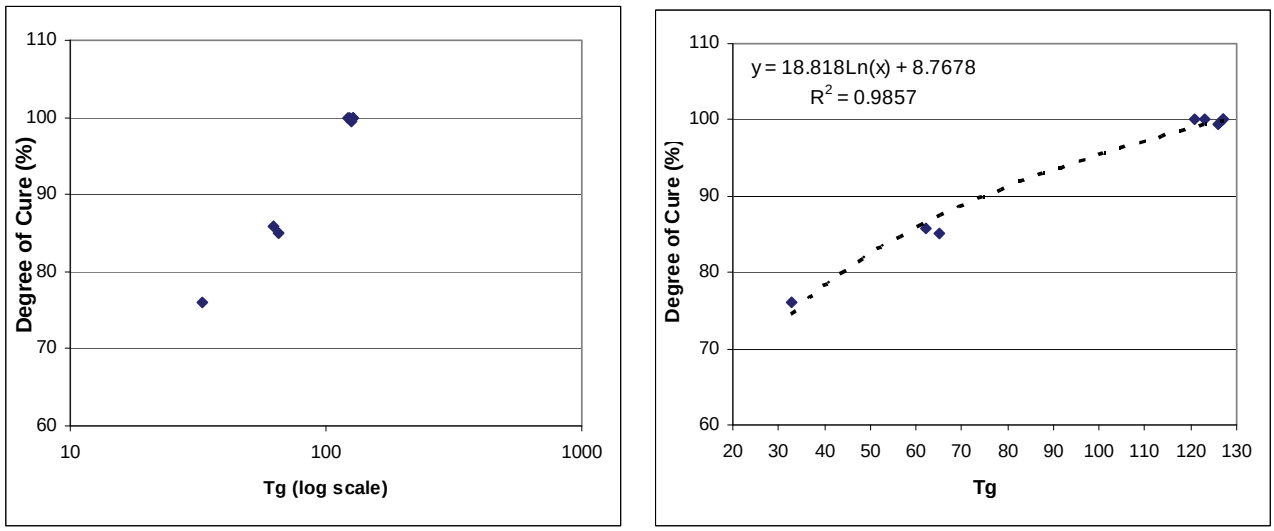
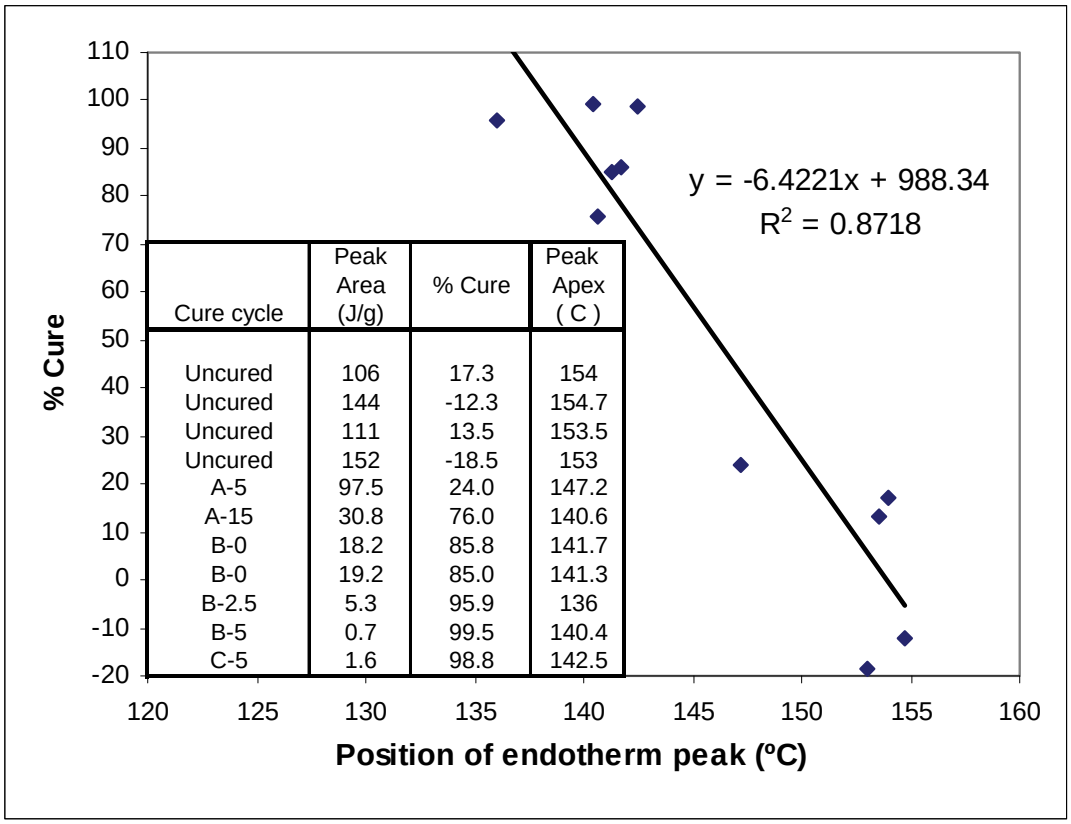


Figure 6. The relationship between T_g and cure level as estimated by exothermic peak area.

3.4 Apex Position as an Indicator of Cure Level

It was also noticed that the apex of the exothermic peak itself shifts positions, and this position may give some indication to the degree of cure (see figure 7). Here, the degree of cure is calculated from the area under the peak. Overall, the shift from 0% to 100% of cure is not very large (approximately 20 ºC), but it does look like a real trend. Scatter of the T_g data points for uncured samples is very low (153 to 154.7 ºC). This indicates that the position of the peak is independent of the quantity of unreacted resin—the issue that was the cause of large scatter in the data based on the peak area. However, as the cure rate progresses above 90%, scatter becomes a problem. This is mostly because of difficulties encountered with locating the apex on a peak that is rapidly disappearing as the degree of cure approaches 100%. Thus, this method favors accuracy in partially cured samples but becomes less useful as a tool to determine cure levels in highly cured samples. It still may be a very useful technique for determining the shelf life of prepreg or evaluating its condition after long periods of storage.

[1] R^2 value means the square of the correlation coefficient.



Cure cycle	Peak Area (J/g)	% Cure	Peak Apex (C)
Uncured	106	17.3	154
Uncured	144	-12.3	154.7
Uncured	111	13.5	153.5
Uncured	152	-18.5	153
A-5	97.5	24.0	147.2
A-15	30.8	76.0	140.6
B-0	18.2	85.8	141.7
B-0	19.2	85.0	141.3
B-2.5	5.3	95.9	136
B-5	0.7	99.5	140.4
C-5	1.6	98.8	142.5

Figure 7. Apex position as an indicator of cure level.

4. Conclusions

Performed experiments show that it is possible to significantly shorten the cure cycle of IM7 carbon fiber prepreg by increasing the cure temperature to 149 ºC (300 ºF) and boosting the heating rate. Depending on the capability of the heating press that will be used, manufacturing cycle times can be cut by 60% to 75%. This can be achieved if we increase the ramp rate to 5 to 10 ºC/min (9 to 18 ºF/min) and shorten the holding time at the final temperature to 10 minutes. These numbers have about a 5-minute safety factor built in, since experiments with only 5-minute holding times showed that the cure is 99% complete. Time required to produce each unit using this cure cycle would be 22 to 35 minutes as compared to 92 minutes with the manufacturer's recommended cure cycle (5 ºF/min temperature ramp to 250 ºF and 1 hour hold). It is estimated that an additional 3 minutes would be required to cool the press, remove the finished product, and load the new pre-form. This would increase the production times to 25, 38, and 95 minutes, respectively. The overall potential benefit of this cure cycle (temperature ramp to 149 ºC and 10 minutes holding time) would increase the production rate by 280% to 150%, depending on the maximum controlled temperature ramp capabilities of the press (5 ºC or 10 ºC), resulting in significant savings and flexibility of supply of essential military equipment.

5. References

1. Web site: http://www.brytetech.com/products_view.aspx?productid=7, May 2004.
2. ASM International. *Engineered Materials Handbook, Engineering Plastics*, Volume 2, Materials Park, OH, 1988.
3. Stevens, M.P. *Polymer Chemistry*, 3rd edition, Oxford University Press, 1999.
4. Mallick, P. K. *Fiber-Reinforced Composites Materials, Manufacturing, and Design*, Second Edition, Marcel Dekker, Inc.: New York, 1993.
5. Sun, L.; Pang, S.; Sterling, A.; Negulescu, I.; Stubblefield, M. *Journal of Applied Polymer Science.* **2002**, *83*, 1074-1083.
6. Riccardi, C. C.; Adabbo,H. E.; Williams, R. J. J. *Journal of Applied Scence.* **1984**, *29*, 2481.
7. Aronhime, M. T.; Gillham, J. K. *Journal of Coatings Technology* **1984**, *56*, 35.
8. Hale, A.; Macosko, C. W.; Bair, H. E. *Macromolecules* **1991**, *24*, 2610.

NO. OF
COPIES ORGANIZATION

1 (PDF ONLY) DEFENSE TECHNICAL INFORMATION CTR
DTIC OCA
8725 JOHN J KINGMAN RD
STE 0944
FORT BELVOIR VA 22060-6218

1 US ARMY RSRCH DEV & ENGRG CMD
SYSTEMS OF SYSTEMS INTEGRATION
AMSRD SS T
6000 6TH ST STE 100
FORT BELVOIR VA 22060-5608

1 DIRECTOR
US ARMY RESEARCH LAB
IMNE ALC IMS
2800 POWDER MILL RD
ADELPHI MD 20783-1197

1 DIRECTOR
US ARMY RESEARCH LAB
AMSRD ARL CI OK TL
2800 POWDER MILL RD
ADELPHI MD 20783-1197

2 DIRECTOR
US ARMY RESEARCH LAB
AMSRD ARL CI OK T
2800 POWDER MILL RD
ADELPHI MD 20783-1197

ABERDEEN PROVING GROUND

1 DIRECTOR
US ARMY RSCH LABORATORY
ATTN AMSRD ARL CI OK (TECH LIB)
BLDG 4600

1 DIRECTOR
US ARMY RSCH LABORATORY
ATTN AMSRD ARL WM M S MCKNIGHT
BLDG 4600

9 DIRECTOR
US ARMY RSCH LABORATORY
ATTN AMSRD ARL WM MA L GHIORSE
E NAPADENSKY (5 CYS + PDF)
R JENSEN C PERGANTIS
M VAN LANDINGHAM
BLDG 4600

NO. OF
COPIES ORGANIZATION

11 DIRECTOR
US ARMY RSCH LABORATORY
ATTN AMSRD ARL WM MD J ADAMS
E CHIN P DEHMER J SANDS
B SCOTT D SPAGNUOLO (5 CYS + PDF)
S WALSH
BLDG 4600