REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)*
4-04-2011

2. REPORT TYPE
Conference Paper

3. DATES COVERED *(From - To)*

4. TITLE AND SUBTITLE

The Role of Concurrent Chemical and Physical Processes in Determining the Maximum Use Temperature of Thermosetting Polymers for Aerospace Applications

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Andrew J. Guenthner, Kevin R. Lamison, Gregory R. Yandek, Kenneth C. Masurat, Josiah T. Reams, Lee R. Cambrea, and Joseph M. Mabry

5d. PROJECT NUMBER

5f. WORK UNIT NUMBER
23030521

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory (AFMC)
AFRL/RZSM
9 Antares Road
Edwards AFB CA 93524-7401

8. PERFORMING ORGANIZATION REPORT NUMBER

AFRL-RZ-ED-TP-2011-121

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

Air Force Research Laboratory (AFMC)
AFRL/RZS
5 Pollux Drive
Edwards AFB CA 93524-7048

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S NUMBER(S)
AFRL-RZ-ED-TP-2011-121

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution unlimited (PA #10991).

13. SUPPLEMENTARY NOTES
For presentation at the 241st American Chemical Society (ACS) National Conference, Denver, CO, 28 Aug-3 Sep 11).

14. ABSTRACT

Herein we report on our efforts to better determine the maximum use temperatures of thermosetting polymers through a combination of alternative thermo-mechanical analyses. We show that thermal cycling and attention to heating rates can often provide more reliable results with a minimum of additional effort.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Dr. Joseph M. Mabry
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			**19b. TELEPHONE NUMBER** *(include area code)*
Unclassified	**Unclassified**	**Unclassified**	SAR	3	N/A

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

The role of concurrent chemical and physical processes in determining the maximum use temperature of thermosetting polymers for aerospace applications

Andrew J. Guenthner[1], Kevin R. Lamison[2], Gregory R. Yandek[1], Kenneth C. Masurat[2], Josiah T. Reams[3], Lee R. Cambrea[4], and Joseph M. Mabry[1]

[1] Air Force Research Laboratory, Propulsion Directorate (Edwards AFB, CA)
[2] ERC Incorporated (Edwards AFB, CA)
[3] National Research Council / Air Force Research Laboratory (Edwards AFB, CA)
[4] Naval Air Warfare Center, Weapons Division (China Lake, CA)

Introduction

Thermosetting polymers such as epoxies, polyimides, bismaleimides, phthalonitriles, and cyanate esters have become widespread in aerospace applications due to their lower densities and ease of processing compared to metals. Although epoxy resins dominate, their maximum use temperatures are too low for some applications, particularly those involving propulsion, control surfaces, and electronic systems.[1] Thus, the defining characteristic that drives the use of most other types of thermosetting polymers in aerospace applications is the maximum use temperature. Traditionally, the maximum use temperature for a thermosetting polymer is determined by performing a dynamic mechanical thermal analysis (DMTA), using a pre-conditioned sample heated at no more than 5 °C / min. The maximum use temperature is based on the glass transition temperature (which in these experiments is actually the mechanical softening or weakening point no matter what the mechanism) observed under a variety of sample pre-conditions, minus a factor of safety designed to account for material and process variability as well as any unidentified causes of performance degradation.

For many thermosetting polymers (particularly those that exhibit excellent thermo-chemical stability and require thermal cure at temperatures greater than the maximum use temperature) the method works well. There is, however, a continuing drive to utilize materials with the combination of a high use temperature and a low cure temperature. In addition, for applications in which the exposure to high temperatures is short-term rather than long-term, there is a desire to utilize less expensive and easier to process materials with reduced thermo-chemical stability. For these materials, the determination of the maximum use temperature must take into account chemical effects that are often not considered in a purely mechanical analysis. These result from concurrent residual cure and thermo-chemical degradation in addition to mechanical softening. Herein we report on our efforts to better determine the maximum use temperatures of thermosetting polymers through a combination of alternative thermo-mechanical analyses. We show that thermal cycling and attention to heating rates can often provide more reliable results with a minimum of additional effort.

Experimental

Materials. Cyanate ester resins, and particularly the dicyanate ester of Bisphenol E, are notable for an unmatched combination of low cure temperature and high use temperature,[2] while possessing lower thermo-chemical stabilities than, for instance, thermosetting polyimides.[3] They are therefore outstanding candidates for the study of concurrent cure, softening, and chemical degradation and its effect on maximum use temperatures. Primaset® LECy, a commercial form of the dicyanate ester of Bisphenol E, was therefore purchased from Lonza, AG and used as-received. Copper(II) acetoacetonate from ROC/RIC and nonylphenol (Technical Grade) from Aldrich were combined to produce a liquid catalyst.

Sample Preparation. Catalyst batches were prepared by blending 30 weight parts nonylphenol with one weight part copper (II) acetylacetonate at 60 °C until dissolved. Batches were discarded after 30 days. Cyanate esters were melt blended (using 2 phr catalyst) and degassed at 95 °C for 30 minutes at 300 mm Hg. The samples were then poured into a 3.5" x 3" metal-framed vertical dual glass plate mold with a 1.5 mm gap. The cure cycle was 1 hour at 120 °C followed by 24 hours at 175 °C, with an optional post-cure for 2 hours at 240 °C. All curing and post-curing was done under nitrogen. Ramp rates between the long dwells were ~5 °C/min. Note that the as-blended level of Cu(II) was 160 ppm by weight.

Characterization. Oscillatory thermo-mechanical analysis was performed on a TA Instruments Q400 series using the standard cylindrical probe on pieces of the cured samples measuring approximately 10 mm x 10 mm x 1.5 mm thick. A preload force of 0.2 N was used to hold the samples in place. Force modulation of amplitude 0.1 N at a frequency of 0.05 Hz (maintaining an average force of 0.1 N) was used to investigate the samples. To determine thermal lag, the temperature was cycled at the desired ramp rate between limits of 50 °C and 150 °C twice. Generally, the observed thermal lag ranged from 1 - 5 °C, and all data shown have been corrected for this estimated thermal lag. After the thermal lag determination, each sample was heated to 350 °C then cooled to below 200 °C in multiple ramp cycles. The ramp rates used varied from 2 °C / min. to 10 °C / min. Further information on the TMA testing and analysis methods are provided elsewhere.[4] In addition to TMA testing, the results discussed below make indirect use of differential scanning calorimetry (DSC), density measurements, thermogravimetric analysis, FT-IR analysis, and moisture uptake measurements that have been performed previously on the material, with the results reported elsewhere.[5]

Results and Discussion

Normally, it is expected that, once corrected for thermal lag, the thermo-mechanical behavior and glass transition temperature (T_g) of a thermosetting polymer will be nearly independent of the heating (or cooling) rate. However, as shown in Figures 1, 2, and 3, markedly different oscillatory TMA traces were generated for Primaset® LECy cured to 185 °C simply by using heating rates of 2, 5, and 10 °C / min. (during the first heating ramp to 350 °C), respectively. The "as-cured" T_g of the sample (240 °C) was seen clearly only at 10 °C / min. At 5 °C / min., an artificially broad T_g with a peak well above the "as-cured" value was obtained. At 2 °C / min, the "as-cured" T_g generates only a small secondary peak. The strong dependence on T_g (as determined by the peak in the loss component of the stiffness) on heating rate is illustrated clearly in Figure 4. The T_g seen at low heating rates corresponds well to values determined by DSC after heating to 350 °C to obtain full cure. Thus, these samples clearly underwent residual cure *in-situ*, greatly complicating the task of measuring the "as-cured" T_g. At 5 °C / min., the rate at which the sample T_g rose due to *in-situ* cure was similar to the heating rate, creating the artificially broad transition.

These results demonstrate that for cyanate ester resins, and in fact for any thermosetting material in which the glass transition temperature can significantly exceed the cure temperature, care must be taken in the selection of heating rates to avoid incorrectly measuring T_g values. Based on the diBenedetto equation (which has been validated for Bisphenol E-based cyanate esters),[6] it can be shown that the *in-situ* cure rate for the LECy was around 0.5% per minute at around 240 °C. Since this type of *in-situ* cure typically takes place at high conversion under non-isothermal conditions, it would be difficult to estimate the rate *a priori*. Thus the best approach would seem to involve checking DMTA or TMA results in these cases by using multiple heating rates.

Further insight into concurrent *in-situ* cure, softening, and degradation processes can be obtained by incorporating multiple heating and cooling cycles into a thermo-mechanical experiment, as illustrated by Figure 5. The figure shows the T_g values as a function of the number of times the sample has been cycled past 300 °C (counting sequential heating and cooling separately). After only once, all of these samples were near complete cure. Interestingly, samples that were post-cured did not achieve a higher final T_g. These results are in accordance with the data of Goertzen and Kessler,[7] and could indicate either physical isolation of uncured cyanate ester groups due to overly rapid cure, or the effect of increased side reactions and thermal degradation during post-cure. In addition, the data do show a slightly declining trend for the T_g as the number of cycles increases, most likely indicating that a very small amount of thermal degradation did take place. It should be noted, however, that the ramp rates utilized provided roughly 1-5 hours of exposure to temperatures in excess of the post-cure temperature, and produced only roughly 10% of the decrease in T_g seen in the samples that were post-cured for two hours. Thus, if thermo-chemical degradation were the primary cause of the lower T_g values in the post-cured samples, it would need to be highly dependent on conversion and/or the relative value of T_g during post-cure, rather than just a simple matter of exposure to elevated temperatures.

Although the previous examples illustrate how the use of multiple heating rates and multiple thermal cycles can greatly aid in the interpretation of thermo-mechanical data for systems undergoing simultaneous *in-situ* cure, chemical degradation, and softening, other methods can also be very helpful. Comparative FT-IR, for instance, though not quantitatively accurate as a means of determining extent of cure for many systems in the solid state without special calibration procedures, can provide a quick indication of whether or not a sample has undergone substantial *in-situ* cure. Similarly, DSC studies carried out at the heating rates of interest may also detect the heat released by *in-situ* cure and thermal degradation. At high conversions, though, thermo-mechanical methods can be used in combination with the diBenedetto equation[8] to estimate the degree of cure to well within 0.5%, which is about an order of magnitude better than FT-IR or DSC. Thus, a careful and more extensive investigation using thermo-mechanical analysis is likely to provide the most useful data in the situations commonly encountered in aerospace applications where the maximum use temperature of a high-performance thermosetting resin at nearly full conversion is a key performance parameter.

Distribution A: Approved for public release; distribution is unlimited.

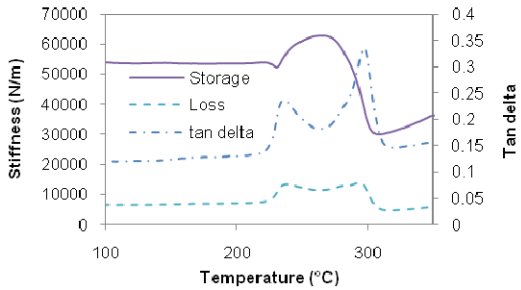

Figure 1. Oscillatory TMA of catalyzed Primaset® LECy using a ramp rate of 2 C / min.

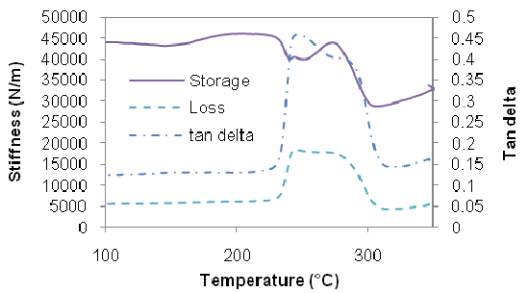

Figure 2. Oscillatory TMA of catalyzed Primaset® LECy using a ramp rate of 5 C / min.

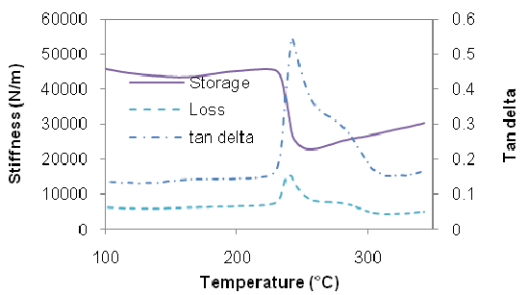

Figure 3. Oscillatory TMA of catalyzed Primaset® LECy using a ramp rate of 10 C / min.

Conclusions

For thermosetting polymers with glass transition temperatures that exceed their final cure temperatures, and for which short-term thermal stability considerations dominate, such as cyanate ester resins, traditional thermo-mechanical analysis can easily produce an inaccurate estimate of the maximum use temperature. In these situations, chemical rather than mechanical effects, such as *in-situ* cure and thermo-chemical degradation, can take place concurrently with mechanical softening and significantly affect thermo-mechanical measurements. In order to obtain accurate data on parameters such as T_g that are crucial for the determination of maximum use temperatures, a much higher heating rate than normal may be needed, and it is highly advisable to use multiple heating rates to check for *in-situ* cure. In addition, the use of multiple heating and cooling cycles can elucidate the effects of thermo-chemical degradation. For Primaset® LECy, a heating rate of 10 C / min was found to be sufficient to avoid significant *in-situ* cure for T_g values around 240 C. Although the effects of thermo-chemical degradation were detectable, the resultant changes in T_g were less than 1 C for the experimental parameters investigated.

Acknowledgements. The support of the Air Force Office of Scientific Research and the Office of Naval Research is gratefully acknowledged.

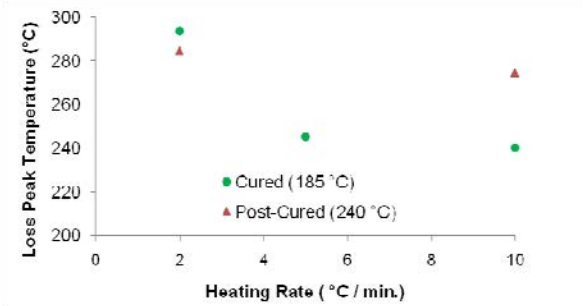

Figure 4. Glass transition temperature on first heating of catalyzed Primaset® LECy as a function of ramp rate.

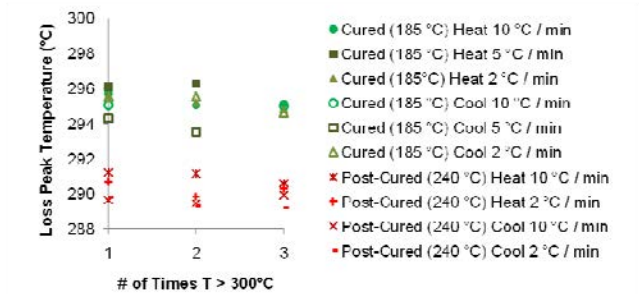

Figure 5. Glass transition temperature through multiple heating and cooling cycles of Primaset® LECy at multiple ramp rates.

References

(1) McConnell, V. P. *High Performance Composites* **2009**(5), 43.
(2) *Chemistry and Technology of Cyanate Ester Resins*. Hamerton, I. Ed.; Chapman & Hall: London, UK, 1994.
(3) Chuang, K. C.; Bowman, C. L.; Tsotsis, T. K.; Arendt, C. P. *High Performance Polymers* **2003**, 15, 459.
(4) Guenthner, A. J.; Yandek, G. R.; Mabry, J. M.; Lamison, K. R.; Vij, V.; Davis, M. C.; Cambrea, L. R. Proc. SAMPE '10, SAMPE Int'l: Covina, CA, 2010; Vol.. 55, 42ISTC-119.
(5) Cambrea, L. R.; Davis, M. C.; Groshens, T. J.; Guenthner, A. J.; Lamison, K. R.; Mabry, J. M. *J. Polym. Sci., Part A Polym. Chem.* **2010,** 48, 4547
(6) Sheng, X.; Akinc, M.; Kessler, M. R. *J. Thermal Analysis and Calorimetry* **2008**, 93, 77.
(7) Goertzen, W. K.; Kessler, M. R. *Composites, Part A Appl. Sci. Manuf.* **2007**, 38, 779.
(8) Pascault, J. P.; Williams, R. J. J. *J. Polym. Sci., Polym. Phys.* **1990**, 28, 85.

Distribution A: Approved for public release; distribution is unlimited.