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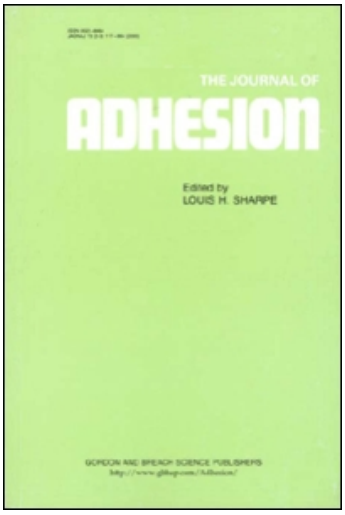

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
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Loss of Curing Agent During Thin Film (Droplet) Curing of Thermoset Material

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To cite this Article Rao, V. and Drzal, L. T.(1991) 'Loss of Curing Agent During Thin Film (Droplet) Curing of Thermoset Material', The Journal of Adhesion, 35: 4, 245 — 249
To link to this Article: DOI: 10.1080/00218469108041011
URL: http://dx.doi.org/10.1080/00218469108041011

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J. Adhesion, 1991, Vol. 35, pp. 245–249
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NOTE
Loss of Curing Agent During Thin Film (Droplet) Curing of Thermoset Material

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(Received February 22, 1991; in final form May 31, 1991)

KEY WORDS Fiber-matrix adhesion; loss of curing agent; interfacial shear strength; variable stoichiometry effect on epoxy properties; T_g as a measure of degree of crosslinking.

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Recently, it has been reported by our group and others[1,2] that loss of curing agent is encountered during the curing of small droplets or thin films of amine cured epoxies. In our earlier study,[3] results were reported on loss of curing agent in small droplets used in conducting the microbond, single fiber test for determination of interfacial shear strength (ISS). It was reported that use of a volatile curing agent (meta-phenylene diamine (m-PDA) with DGEBA resin) resulted in increasing amounts of curing agent being lost (as measured by T_g of the cured droplets) with decreasing droplet size during the processing procedure. Droplets smaller than 150 micrometers were seen to lose up to 40% of the curing agent leading to alteration of the mechanical properties of the droplet and, therefore, causing measured values of ISS to be exceedingly low. Use of a less volatile curing agent (Jeffamine 700, a polyether diamine, Texaco Specialty Chemicals) in combination with DGEBA resin produced results which indicated that loss of curing agent was not occuring. This study was undertaken to show the relationships between film (or droplet) size and the amount of curing agent lost (during the processing) for three different amine-cured epoxy systems.

The three different systems chosen for this study are all based on DGEBA resin cured with stoichiometric amounts of amine curing agents meta-phenylene diamine (m-PDA), Jeffamine 403 (J403) and Jeffamine 700 (J700). Relevant properties for these systems can be found elsewhere.[3,4] Glass transition temperatures of the "fully" cured samples were used as the measure of how much curing agent was lost during the curing process. As reported earlier,[3] glass transition temperatures were measured both with a Thermal Mechanical Analyzer (TMA) as well as with a Differential Scanning Calorimeter (DSC). The fully cured glass transition temperatures for the three different systems studied are shown in Table I.

TABLE I
Fully cured T_g's of the matrices

SYSTEM	T_g (c)
m-PDA/DGEBA	137 ± 7
J403/DGEBA	75 ± 3
J700/DGEBA	20 ± 3

The variation of T_g with size for the m-PDA/DGEBA system has been reported previously[3] and is shown in Figure 1. It can be seen that at small droplet sizes the difference between the measured (droplet) T_g and the bulk T_g of the matrix can be as large as 70°C. Even for the largest droplets tested (about 800 micrometers (0.8 mm)), the difference between the bulk T_g and the measured T_g is still about 20°C. Since the properties of the matrix themselves play a significant role in fiber-matrix adhesion,[4,5] and since most single fiber interfacial tests are done in the range below 200 micrometers, it is very important, since the properties of the droplet may be different from those of the bulk matrix due to loss of curing agent, to ensure that the mechanical properties are known before testing in this size regime.

Figures 2 and 3 show the variation of T_g with size for the J403/DGEBA and the J700/DGEBA systems, respectively. Though both Figure 2 and Figure 3 show that the J403 and J700 systems have a slightly lower T_g at small droplet sizes when compared with the bulk T_g, once the droplets are larger than 200 micrometers there

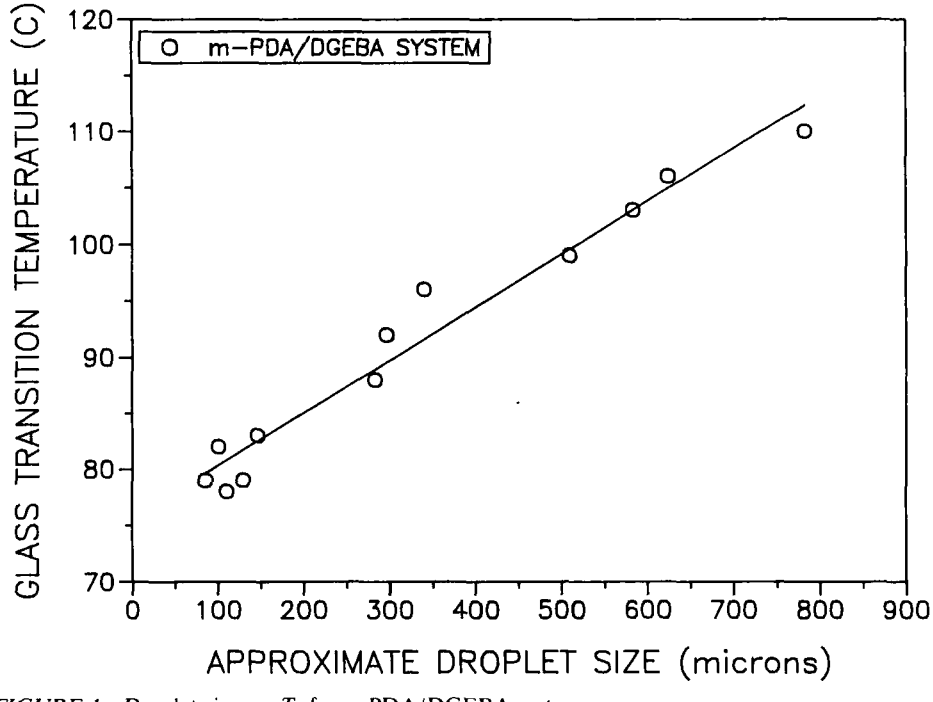

FIGURE 1 Droplet size *vs.* T_g for m-PDA/DGEBA system

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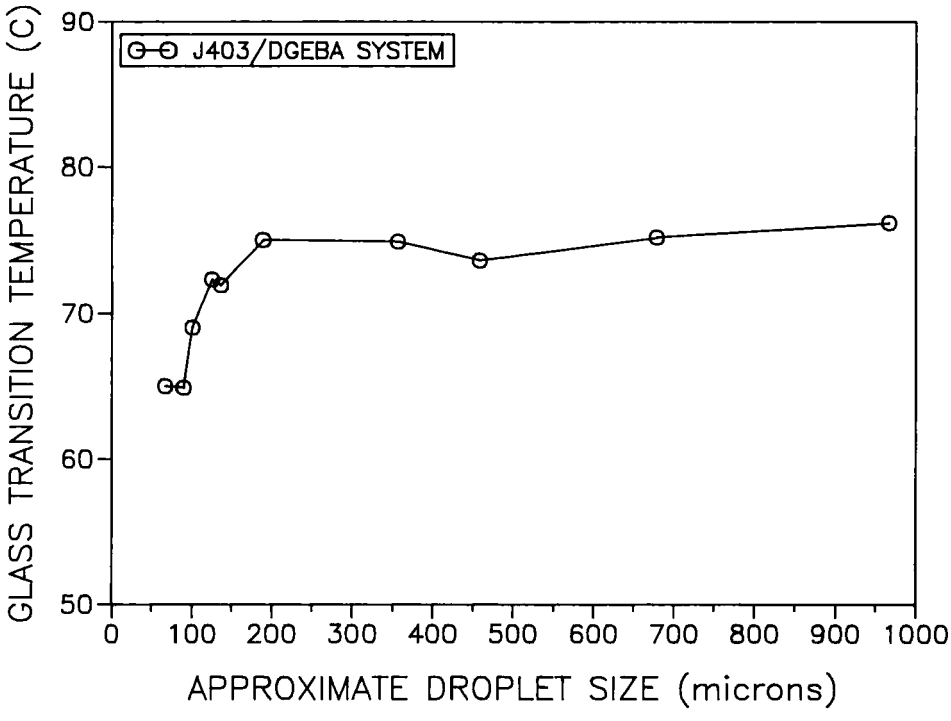

FIGURE 2 Droplet size *vs.* T_g for J403/DGEBA system

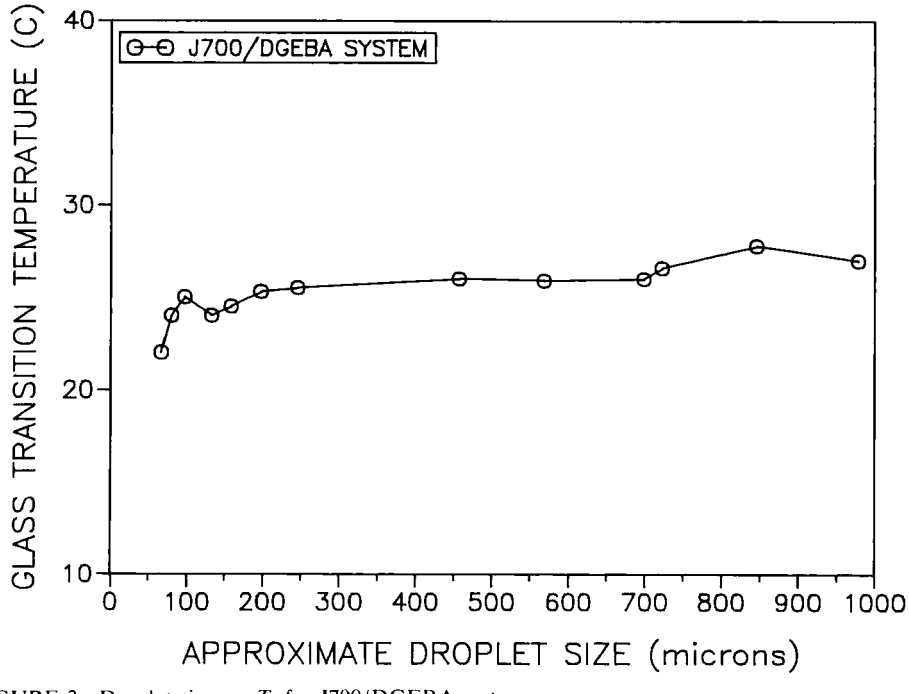

FIGURE 3 Droplet size *vs.* T_g for J700/DGEBA system

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is essentially no variation in T_g as a function of droplet size for either of the two systems. This indicates that the droplets should essentially have the same mechanical properties as those of the bulk matrix. This fact is supported by our earlier results[3] which showed that the microbond (droplet test) ISS of the J700/DGEBA system matched well with fragmentation (based on bulk matrix measurements) ISS results. The T_g of the bulk matrix for the J700 system is noted to be about 20°C while for the cured droplets, T_g values seem to range from 23–25°C. The reason for this slight discrepancy (though the values are within the error limits) is unknown, and the experimental results have been found to be reproducible. However, the point to be made is still valid; namely, that the T_g remains essentially unchanged over the entire size regime of testing.

In Figures 1–3, the effect of droplet sizes up to about 850 micrometers (0.85 mm) on T_g is shown. As mentioned above, even at the largest droplet sizes, the m-PDA system is seen to lose curing agent in the curing process. To determine whether there is a size at which the m-PDA/DGEBA system stops losing curing agent during processing, thicker films were prepared. Small aluminum hooks were dipped into pre-mixed solutions of the three thermosetting systems studied. These hooks were then held vertically in place in a chamber before being cured. Continous and repeated dipping showed that the practical maximum size of the film that could be made with this process was about 4000 micrometers (4 mm). The resulting specimens were prepared for DSC testing by snipping the uneven ends leaving behind a

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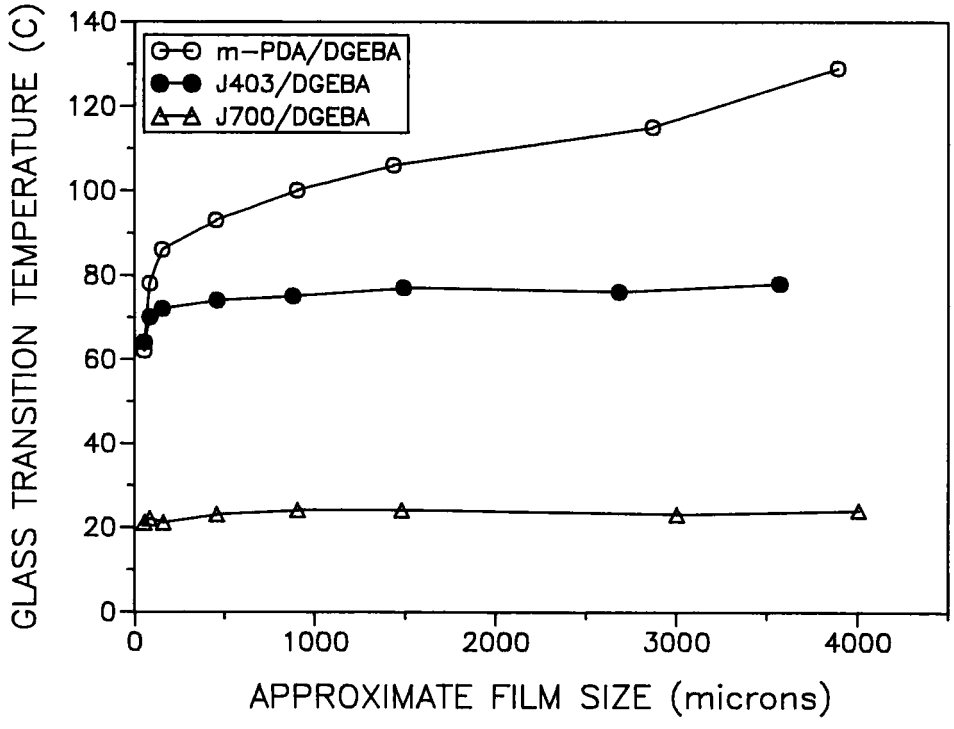

FIGURE 4 Film size *vs.* T_g for m-PDA/DGEBA, J403/DGEBA and J700/DGEBA systems

thin film with constant dimensions. Dimensions were measured with the aid of an optical microscope.

The data shown in Figure 4 are a combination of the data shown in Figures 1–3 and the data obtained from the film experiments described above. As expected, the two Jeffamine-based systems (which have a higher viscosity and lower volatility when compared with the m-PDA system) show nearly constant glass transition temperature throughout the testing regime. On the other hand, the m-PDA system, even at sizes of about 3000 micrometers (3 mm), shows that the measured T_g deviates from the bulk T_g (about 135–140°C) by about 10°C. This indicates that even at such large film sizes, the mechanical properties are different from those of the bulk matrix. Thus, extreme care must be taken to ensure careful measurement of mechanical properties of small dimension samples for the m-PDA/DGEBA system or any system where a volatile curing agent is used.

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