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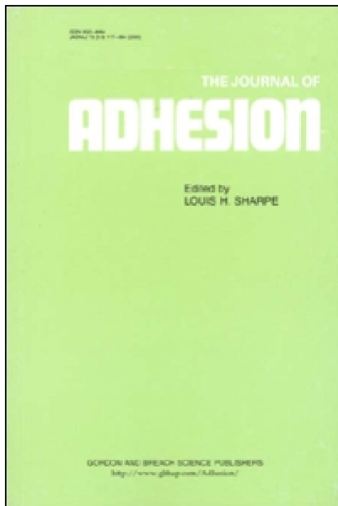

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Reply to Comment on "Linking Cure Process to Adhesive Bulk Strength by Differential Thermal Analysis"

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Reply to Comment on "Linking Cure Process to Adhesive Bulk Strength by Differential Thermal Analysis"

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KEY WORDS Kinetic reaction cure model; pre-reaction; differential thermal analysis; glass transition temperature; adhesive bulk strength; full cure; epoxy adhesive.

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A Comment published in this issue and authored by B. C. Ennis refers extensively to one of our earlier papers entitled[1] "Linking Cure Process to Adhesive Bulk Strength by Differential Thermal Analysis." We are delighted to see that our work can capture the attention of scientists working in this area and stimulate them to write lengthy reviews. At the same time, however, we feel that this particular note, in various discussions, misinterprets our paper, and does not seem to contribute any new or substantial scientific information to the literature.

Let us reiterate what was published in our paper. Quoting from the conclusions section:[1]

1) "A first-order kinetic reaction model was utilized to model the cure process of structural epoxy adhesive Metlbond 1113."

2) "Actual states of full cure corresponding to a spectrum of cure temperature-time schedules were identified using the DTA method."

3) "The theoretical degree of cure as predicted by the first-order kinetic reaction model was progressively lower for higher-temperature/shorter-time cure conditions which were judged to result in full cure on the basis of the DTA method. Obviously, the first-order kinetic reaction model is not adequate (at least not for the full course of the cure process) for high-temperature/short-time cure reactions."

4) "The adhesive bulk tensile strength resulting from such cure conditions was also found to be lower than that obtained at low-temperature/long-time conditions that fell close to the T_g for the adhesive."

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Careful reading of the above paragraphs along with the rest of the paper[1] reveals that we did not have any confusion between model prediction, experimental determination of full cure and optimum tensile strength. In fact, the above paragraphs describe exactly the results of our analytical calculations and experimental measurements and we stand behind them.

Ennis states that "the final properties of thermosets are developed in the last stages of cure during a relatively small extent of reaction". It is not known what type of thermosets, and what mechanical properties he is referring to, how were they measured and what data or references he has to support it. Our paper[1] refers to the bulk tensile strength of a solid film adhesive and the optimum strength curve presented was obtained as an envelope curve over numerous cure *time*-temperature curves.[2] In other words, we already have ample data on the variation of the bulk tensile strength with cure time[2] and the optimum strength curve presented in our current paper[1] was obtained from such data. In fact we published several papers[2–7] on the effects of cure *time,* temperature and cool-down rate on the mechanical behavior of the same adhesive. Data on the cure time and temperature dependent variation of mechanical properties: ultimate stress, Young's modulus, fracture energy, fracture toughness, plastic zone radius, stress whitening stress, stress relaxation and void area are available in our papers.

A judicious reader realizes that the important message being conveyed by our paper[1] is not magnitudes of certain material parametes but the overall trend in the behavior of the bulk tensile strength depending on the cure time/temperature and the applicability of the first order kinetic reaction cure model.

Ennis states that "the correction for voids in the test specimen did not consider stress concentration effects." In fact as a standard stress-strain formula book[8] reveals, the stress concentration is dependent on the radius (r) of the voids and the distance (L) between their centers. The stress concentration is reduced when r/L gets larger, as long as r is smaller than L. In our experiments our observations were consistent with reduction in stress concentration at high temperature-short time conditions. Therefore, the relative flattening of the optimum tensile strength curve at high temperature-short time conditions, as presented, represents a conservative calculation and is not expected to flatten any further if stress concentration was considered. In fact, it is expected to curve down further to a shape similar to the uncorrected curve.

We find Ennis's reference to our experimentally determined extents of cure as "ill-defined" completely arbitrary. In fact, our procedure is a well-accepted industrial procedure[9–11] and we stand behind our data.

We fail to understand why Ennis is troubled over the application of routine TA methodology. The first order kinetic reaction model utilized by us is marketed by DuPont in their DSC Thermal Stability Kinetics-ASTM E698 software program.[12] Their Application Brief on this program states that the first order kinetic reaction model is "applicable to" "curing of thermosets" as well as "polymerization of thermoplastics."

For our model adhesive, use of second order cure kinetics rather than the first

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order significantly reduces the ability of the model to predict full cure determined experimentally.

Using poetic language, Ennis refers to the identity of reactive commercial materials seven years (in reality he does not know when the experiments were performed) and an ocean apart. Particularly, he objects to us using the pre-reaction (α_0) determined by Schiraldi *et al.*[13] and his objection is well taken. However, in his own words, this criticism is "trivial" and irrelevant to the main objective of our paper. As we stated earlier, our purpose was not to determine specific material parameters but to convey general trends and analysis. For our model adhesive he shows that assuming $\alpha_0 = 0$ does not significantly change the α *versus* cure condition behavior and we agree. This does not justify, however, leaving α_0 out of a complete theoretical cure analysis as he suggests. In fact, those who are familiar with current literature[14] know that α_0 is included in software packages designed to predict cure of epoxy matrix composites.

After rederiving our cure Eq. (8)[1] Ennis goes into lengthy discussion of how it can be made simpler. Aside from helping those who are not mathematically inclined or do not have simple desk calculators or personal computers we do not see any advantage in simplifying this expression.

As far as the issue of T_g for the adhesive in the uncured form is concerned, a careful reader realizes that the T_g's measured and compared for the resin in the partially-cured states are well defined in our paper.[1] They represent an endothermic shift in the DTA baseline (a glass transition) during non-isothermal scanning of the material heated up from room temperature.

We believe that the research in structure property relationships of structural adhesives should be interdisciplinary. It is through these interactions that significant improvements in new approaches and theories can take place to solve engineering and commercial problems.

It is understandable that our work is more prone to comments than usual as a new, bold and approximate approach has been made to close the gap practically and economically between adhesives chemistry and macroscopic ultimate properties such as strength and performance.

The interpreted high complexity of our model is subjective. The assumption of first order reaction being the only governing cure reaction is merely for simplicity and the absolute value of the extent of pre-reaction is irrelevant. This is all due to the fact that the main objectives of our work were to utilize a simple thermal analysis technique to understand the dependence of the adhesive bulk strength to cure temperature and time semi-quantitatively. As our effort was mainly targeted at revealing causes for relative trends; the absolute values for such quantities as degrees of reaction, pre-reaction, etc., are not to be taken as the main points of criticism.

Repetition of our derivation of the kinetic equation does not reveal anything new. However, we do agree that accurate determination of degree of reaction or the type of reaction require a more quantitative approach.

We also agree that a complete characterization of the cure process for adhesives requires more rigorous and costly and analytical methods. However,

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reiteration of the degree of complexity of the problem does not offer any solutions.

We know that industrial adhesives are complex mixtures and full structural and chemical characterization of these materials require costly and time-consuming techniques. However, a wise judgement of our work should really consider it an economical engineering method to determine the optimum performance conditions of these materials.

We do agree with Ennis that the DSC method would reveal more quantitative information regarding extent of cure, residual heat of cure, etc.

In conclusion, we believe that we have offered a simple and inexpensive engineering approach to assess the optimum performance conditions for the Metlbond 1113 adhesive in the bulk form. Due to the fact that during thermal cure process a number of complex reactions and phenomena may take place, we resorted to DTA as a means of evaluation of states of cure with varying time-temperature histories. We know that there is place for further refinement of this approach.

Some comments of B. C. Ennis which are constructive are appreciated. We hope that we have also conveyed our message regarding efforts in arriving at economical engineering solutions to today's problems in structual adhesives based on constructive interdisciplinary interactions and communications.

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