INFLUENCE OF PROCESS PARAMETERS ON ELECTRON BEAM CURING OF A POLYMER COMPOSITE

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ABSTRACT

The influence of process parameters, viz. dose, dose rate, and temperature, on E-beam (electron beam) curing of an epoxy polymer matrix with a catioinc photo-initiator and its composite (with IM7 carbon fibers) was studied. While the extent of curing increased with dose, surprisingly incomplete curing (eg. 27% residual exotherm [measured using DSC] for the pure resin) was observed even at a dose of 500 KGy. A comparison of residual exotherms for 100% thermally cured material with that of samples irradiated with different levels of electron dose revealed that the interaction of the electron beam with the polymer and the photo-initiator led to secondary reactions that are weakly dependent on the electron dose. These reactions appear to be the cause for the incomplete curing. Significant exotherm (and temperature rise) was observed at a dose between 30 and 40 KGy for all dose rates (i.e. dose / pass). This suggests that a fine control of dose / pass during this crucial period of rapid cure under e-beam s needed to prevent temperature run-off. The fact that the chosen material cured thermally indicates that significant thermal curing can occur during E-beam processing of such catioinc formulations. The implications of the above results on E-beam processing of polymer composites are discussed in this paper.

KEYWORDS: E-beam Curing, Composite Processing, Radiation Processing

1.0 INTRODUCTION

A majority of on-going research and development efforts in the area of E-beam curing, in North America, are focussed on developing e-beam curable composites and adhesives as well as type-trials and application demonstrations. However available literature indicates that the current level of understanding of the e-beam curing process (for aerospace composites) and of the influence of process and material parameters on processing and process optimization is limited. Hence, this study is focussed on developing a fundamental understanding of the influence of process parameters on E-beam curing. (to be elaborated…)

2.0 MATERIAL AND EXPERIMENTAL PROCEDURE

A proprietary electron beam curable cationic epoxy resin (referred to as E-beam Resin 1 in Reference 1), developed under the Co-operative Research and Development Agreement (CRADA) sponsored by U.S. Department of Energy Defense Programs and 10 industrial partners, was used in this study. IM7 – GP plain weave fabric was used as reinforcement. 1 and 3 ml syringes were used for the e-beam curing of pure resin. The resin was heated to 75° C prior to mixing of the photo-initiator and about 1g or 3g of the mixed resin was transferred to the syringe. A thermocouple placed at the center of the syringe was used to monitor the temperature of the resin during e-beam curing. The composite was prepared by impregnating four plies of fiber fabric with the mixed resin using a brush. This was followed by consolidation in a hot-press under vacuum for about 1.5 hours at a pressure of 65 psi and at a temperature of 75° C. The temperature of the composite coupons was monitored during curing by a thermocouple placed at the bottom-center of the coupon. Both the resin and the composite were not under vacuum while curing under the e-beam. The fiber volume fraction in the cured composite was determined to be about 58% using density measurements.

E-beam curing was performed at Acsion Industries Inc. (previously Whiteshell Laboratories, AECL) using the I-10/1 Electron Accelerator (10 MeV; 1 KW). The instantaneous dose rate was 1.5 MGy s^{-1}. For the study on the influence of dose, both the resin and the composite samples were cured in steps of 25 kGy (i.e. 25 kGy / pass) to a total dose of 500 kGy. A time interval of 90 to 120 seconds between successive passes was inevitable to allow for the removal of a sample cured to a certain dose from the conveyor belt. While the composite was cured at room temperature (~ 22°C), the resin was cured both at room temperature and 0°C (syringes were placed on an ice pack) to study the effect of curing temperature. An ideal requirement to study the influence of dose rate would be to be able to vary the instantaneous dose rate. Since it was not possible with the accelerator used in this study, dose rate effect is currently studied using stationary samples (i.e. zero conveyor speed) and by varying the width of the beam and the distance of the accelerator horn from the specimens. Three average dose rates, viz. 46 kGy / min, 150 kGy / min, 250 kGy / min are used. In addition, the effect of dose / pass on e-beam curing process was studied since a knowledge on this is of practical importance during composite processing. The dose per pass was varied by varying the conveyor speed while maintaining the beam width and distance from the accelerator horn constant. Dosimeters were used to measure the dose.

TA Instruments 2910 DSC (Differential Scanning Calorimeter) and 2980 DMA (Dynamic Mechanical Analyzer) were used to measure the exothermic heat and glass transition temperature (T_g). A heating rate of 10°C / min was used. The e-beam cured material was subsequently tested in the DSC and the residual heat flow was taken to be a direct measure of the material not cured under the e-beam. The same e-beam curable formulation was also thermally cured. The total heat of reaction for 100 % thermally cured material was used along with the residual exothermic heat obtained for e-beam cured material to determine the % cured as a function of dose. It is to be pointed out that the above procedure is valid only if the heat of reaction for 100 % thermal curing is same as 100% e-beam curing. This equality requires that the extent of curing is same in both cases. The same service temperature (discussed in section 3.1) for both e-beam cured and thermally cured resin suggests that the extent of curing may be the same. However, further study is required to clarify this aspect. In all DSC exothermic plots used in this report, a two point rotation was used to correct for the baseline slope. Thermal curing of DMA samples was carried out in a hot press at 177°C and at a pressure of 65 psi for 3 hours. Single / Double cantilever loading mode was used in the DMA. A frequency of 1 Hz and an amplitude of 20 μm was used.

3. RESULTS AND DISCUSSION

3.1 Influence of Dose The exothermic heat flow during thermal curing of the resin (designated as "untreated") is compared, in Figure 1, with the residual exothermic heat flow for the resin samples (with 3 phr [parts per hundred of resin] of photo-initiator) irradiated to electron doses of 25, 50 and 500 kGy at room temperature. While the residual heat flow decreased with increase in dose, surprisingly a 27% residual heat flow (total heat of reaction of the thermally cured resin is 544 J/g) was measured even at a dose of 500 kGy. This data re-plotted in Figure 2 highlights the progress in curing with dose. The rate of curing increases rapidly until 50 kGy and decreases beyond that. A rapid increase in resin temperature was noticed during this rapid cure period between 30 and 40 kGy (discussed in section 3.3). Similar results were obtained for the composite as shown in Figures 2 and 3. Incomplete curing (18% of the total heat flow of 222 J/g) was observed even at a dose of 500 kGy. At any given dose composite exhibited higher extent of cure than resin except at doses below 50 kGy. The trend in cure progress during electron irradiation is also exhibited by the increase in T_g (measured using the tan δ peak) with dose as shown in Figure 4 for the composite. An attempt was made to measure the Tg of the e-beam cured composite, after the thermal post-cure that progressed during the first DMA run (temperature ramp to 350° C), during the second DMA run. However, the composite started to degrade significantly beyond 325° C and hence Tg could not be determined with certainty. Nevertheless, the T_g appears to be greater than 370°C. Therefore, the service temperature (temperature at which the storage modulus decreases to 50% of the room temperature value), tabulated in Table 1, was used to compare the efficiency of the thermal and e-beam curing processes. The service temperatures for both 100% thermally cured composite and e-beam cured composite (25 to 500 kGy) followed by thermal post curing were same. This is not surprising since the degradation is dependent on the polymer matrix, which is the same in both cases. From Figures 2 and 4, and Table 1, it can be inferred that though the amount of curing due to thermal post-cure for composite irradiated to doses beyond 100 kGy is less than 31%, the increase in T_g appears to be 3 fold. In Figure 5, the DMA curves for the e-beam cured and thermally post-cured composite are plotted to illustrate this. The reason for such a three-fold increase in T_g is not known at this time and further studies are currently underway to understand this.

The same resin was also mixed with 31 phr of commercially available DDS (4,4'-Diamino Diphenyl Sulfone) hardener (which is used for thermal curing of epoxies) instead of the photo-initiator and was thermally cured. A total heat flow of 254 J / g is 47% of the heat flow for the resin with the photo-initiator, thus highlighting the high reactivity of the photo-initiator and the possibility of similar extent of curing of the e-beam curable resin formulation under both thermal energy and e-beam.

A striking feature of the curves in Figure 1 and 3 is that the heat flow curve, for the 100% thermally cured material, with a narrow exothermic peak and a high temperature threshold (~140° C) for the onset of reaction has been broadened with a decrease in reaction threshold temperature to approximately 50°C due to the interaction of the e-beam with the polymer matrix and the photo-initiator. Residual exothermic heat flow curves for resin and composite irradiated to different doses of e-beam at room temperature are plotted in Figures 6 and 7 respectively. The curves exhibited multiple peaks whose intensity decreased with increase in dose indicating the progress in curing. Since the temperature of the resin and composite increased to a maximum of 150°C and 64° C during e-beam

curing, simultaneous thermal and e-beam curing cannot be ruled out and this made the interpretation of the curves in Figures 6 and 7 difficult. Hence new resin samples were e-beam cured at an ambient cure temperature of 0° C. The DSC results for these samples are shown in Figures 8, 9 and 10 for doses of 25, 50 and 250 kGy respectively. Three distinct peaks (designated as I, II and III in the plot) are observed whose intensity decreases with increase in dose indicating the progress in curing. However, the presence of one or more of these peaks and the rate of decrease of the peak intensity with increase in dose are dependent on the photo-initiator concentration.

While peak III is absent in 1 phr sample for all doses, the 5 phr sample exhibited the maximum intensity for peak III. In addition, during the initial rapid cure stage (until 50 kGy), the decrease in peak intensity was minimal with increase in dose. These results suggest that the reaction(s) corresponding to peak III needs a high e-beam dose for completion and that it is triggered by a photo-initiator concentration greater than 1 phr. A similar peak, whose intensity was dependent on the initiator concentration was also observed during thermal curing of resin as shown in Figure 11. Further studies are needed to confirm whether the reactions corresponding to the two peaks are same. The presence of peak I is independent of initiator concentration but was absent in the residual heat flow curve of pure resin with no photo-initiator and irradiated to an e-beam dose of 250 kGy. This suggests that the reaction(s) corresponding to peak I is caused by the interaction of e-beam with the photo-initiator. The peak II was present for all initiator concentrations and its intensity decreased relatively faster than the other two during the initial stage of rapid cure (dose level of 50 kGy) suggesting that the reaction(s) corresponding to peak II may be dominant during this initial stage of rapid curing. Finally, a residual exothermic heat corresponding to an incomplete curing by 40 to 55% was observed even at a dose level of 250 kGy as shown in Figure 12. Based on these results, it can be surmised that further studies are needed to understand the interaction between the e-beam, and the resin and photo-initiator for optimal selection of resin and photo-initiator and to optimize the dose.

3.2 Influence of Cure Temperature

The fact that the same epoxy formulation is curable by both thermal energy and e-beam suggests that simultaneous thermal and e-beam curing of resin and composite is inevitable during e-beam irradiation if the cure temperature is sufficiently high or if there is a increase in material temperature due to e-beam absorption. This is corroborated by the results in Figure 12. Higher percentage of curing observed in resin cured at room temperature, when compared to resin cured at 0° C, indicates that the cure temperature has a significant influence on e-beam curing of the resin formulation used in this study. Many free radical and cationic resin and composite formulations were reported ( ) to exhibit such thermal post-curing after irradiation indicating that these formulations are subject to substantial influence of the cure temperature. These results imply that (a) such e-beam curable formulations will not have unlimited shelf life and may impose restrictions on storage conditions. It should be mentioned here that variation in heat flow, for the composite pre-preg and irradiated composite used in this study, during a storage time of 6 months was well within the error range(± 5.7%) obtained for sample to sample variation; (b) additional step of thermal post-curing is required to achieve complete curing which may be time-consuming and costly, (c) freedom to cure the composite and resin at any service temperature may be curtailed (specifically sub-zero temperatures), and (d) reduced control over the curing and the temperature rise

3.3 Influence of Dose Rate The recorded resin temperature during irradiation at four different dose / pass trials is plotted in figure 13. At time intervals between successive passes the resin was away from the e-beam and this time interval was dependent on the speed of the forward and backward motion of the conveyor belt. A drop in temperature (beyond the peak temperature) observed in Figure 13 corresponds to this time interval between successive passes. It is interesting to note that a rapid increase in resin temperature occurs at dose levels in the range 30 to 40 kGy at all four dose / pass trials. Since the temperature rise due to e-beam absorption cannot be this rapid, the temperature increase has to be due to e-beam curing of the resin. Hence, fine tuning of the dose / pass (i.e. smaller dose / pass than used) is required, for the formulation used in this study, during the initial rapid cure period to prevent any temperature run-off. Outside this crucial dose range, a dose / pass that minimizes the e-beam absortion heating while maximizing the cure rate may be selected. In the above four trials, the average dose rate was same. Since the dose / pass can also be varied by altering the average dose rate, a study of the influence of average dose rate on the rate of curing under e-beam is pertinent. Hence, work is currently underway to delineate this process parameter and the results will be published soon.

4. CONCLUSIONS

Incomplete curing, even at a high dose of 500 kGy, observed in both the resin and the composite used in this study highlights the importance of further study needed to understand the interaction among the e-beam, resin and the photo-initiator. Such a study is needed to optimize the resin-initiator selection process as well as the cure dose. Higher cure temperature led to higher extent of cure due to simultaneous thermal and e-beam curing. Implications of such thermal curing combined with low e-beam cure efficiency of the e-beam formulation used in this study are (a) limited shelf life, (b) costly thermal post-curing, (c) restriction on cure temperature and (d) reduced control over the curing and the temperature rise. The dose / pass experiments suggest that temperature rise during to e-beam curing may be managed optimally by using a smaller dose / pass during a crucial dose interval (30 - 40 kGy in this study) when the rate of reaction is rapid. Outside this interval, a judicious choice of dose / pass can be chosen to minimize the absorption heating while maximizing the thoroughput.