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Thermal characterization and comparison of structural prepregs with different cure temperatures

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Abstract

Two different epoxy based prepreg systems were characterized and compared using thermal analysis. A prepreg system presently used in the commercial airplane industry was compared with a prepreg system that is a prospective candidate for the same applications. The commercial system in use is a controlled flow resin prepreg system which is a 177°C cure system, while the prospective prepreg system is marketed as a dual prepreg system that can be cured at either 121°C or 177°C. Thermal characterization techniques including differential scanning calorimetry (DSC), dielectric analysis (DEA), and dynamic mechanical analysis (DMA) were used to investigate these systems. The difference in the curing mechanisms of both prepreg systems were identified through these thermal analysis techniques. Although, the kinetics of these systems were found to be vastly different their heats of reactions were very similar. The activation energies for the prepreg systems were determined by DSC using Kissinger's method and were found to be quite different. DMA measurements on autoclave cured composites demonstrated that the prepregs obtained a different degree of cure as well as different glass transition temperatures (T_g). Furthermore, the use of DEA and DMA demonstrated a difference in gelation of the two prepreg systems examined.

Keywords: Composite; Controlled flow; Epoxy; Prepreg

1. Introduction

Many advanced composites are constructed from thin laminating sheets known as prepregs. Prepregs are formed by combining a polymeric matrix resin with reinforcing fibres. The excellent handle-ability of thermosetting prepregs makes them very desirable to the commercial airplane industry, where light weight parts can be manufactured with high temperature capabilities [1].

In spite of their wide-spread usage, composite materials are often not well understood. Within each class of matrix, (epoxies, bismaleimides and dicyanates) many different resin formulations and material systems are available. This great variation, with the capability of tailoring the material to specific applications, prevents generalizations about material properties and processing. Because of this limitation, it is necessary to characterize each individual material.

Thermal analysis techniques can be used to evaluate the effect of temperature on material properties. Thermal events such as gelation, cure, glass transition, and degradation are all properties of interest in the application of thermoset prepregs and composites [2]. This knowledge is required to develop appropriate cure cycles and optimized final properties. The thermoa-

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nalytical techniques used in this study include differential scanning calorimetry (DSC), dielectric analysis (DEA) and dynamic mechanical analysis (DMA). In DSC, the heat flow required to maintain a sample at a set temperature is measured, providing information about cure and degradation reactions. In DEA, the molecular mobility is measured as a function of an alternating electric field. Changes in molecular mobility are indicative of viscosity changes during cure. In DMA, mechanical property information is determined by flexing the specimen and measuring the material response. Taken together, these thermoanalytical techniques provide an in-depth characterization of the materials thermal properties.

In this study, two commercially available epoxy prepreg systems were characterized through thermal analysis. On system, a rubber modified controlled flow epoxy based resin prepreg system, Boeing Material Specification BMS 8-256, is widely used in commercial aircraft structures [3]. This material is a traditional 177°C curing system. The prospective material, a thermoplastic modified epoxy based resin prepreg system produced by Hexcel under the name M20, is a newly developed prepreg system which is being explored for the same applications. This prepreg is a dual temperature cure material that can be cured at either 121°C or 177°C. When cured at the lower temperature of 121°C, it has the potential of achieving mechanical and thermal properties similar to traditional 177°C curing epoxies. This dual cure property allows the possibility of replacing multiple materials for a wide variety of parts. In this study, the commercial prepreg system will be termed prepreg 'A', while the prospective prepreg system will be termed prepreg 'B'.

2. Experimental

Thermal analysis was used to investigate the thermal properties of both prepregs A and B. A TA Instrument, DSC model 912, was used to investigate the cure kinetics of both prepreg systems. Experiments were performed dynamically on both prepreg systems at heating rates of 2, 5, 7, 10 and 20°C min^{-1} in nitrogen. The heats of reaction reported for the prepreg systems were obtained from an average of the heats of reaction determined from the dynamic experiments. The DSC was also programmed to simulate a cure cycle. These experiments consisted of 2.5°C min^{-1} ramp to 121°C or 177°C with a 2 h isothermal hold.

A TA instrument, DEA model 2970, was utilized with a parallel plate geometry to observe the capacitive and conductive nature of the materials during dynamic temperature scans. Permittivity (e') and loss factor (e'') were recorded during scan rates ranging from 1.5 to 5.0°C min^{-1} as well as simulated cure cycles. The range of frequencies spanned for each experiment was 0.5–100 Hz. Because the different prepregs contained carbon fiber fabric, a layer of glass fabric was used to separate the sample from the upper and lower electrodes and prevent fiber dominated results. The thickness of the DEA specimens were approximately 0.50 mm. Samples were consolidated under 100 N to ensure adequate contact between the electrodes.

A TA instrument, DMA model 983, was used to mechanically analyze both the prepreg and the cured composites. A single strip of prepreg was used in the prepreg analysis. The heating rate was 2.5°C min^{-1}. A large amplitude of oscillation (1 mm) was used to get a strong signal from the relatively thin pliable samples. Wide samples ($\sim$ 10 mm) were used along with short distances between clamps ($\leq$ 10 mm) for the same purpose. Laminates were constructed from each prepreg using an autoclave process. For prepreg B, both 121°C and 177°C cure cycles were used while prepreg A was cured at 177°C. All cure cycles used 2.5°C min^{-1} heating and cooling rates and had an isothermal 2 h hold at the cure temperature. Samples were cut from the seven-ply laminates and analyzed in the DMA. These samples were all 5–6 mm wide, 1.2–1.4 mm thick and 14–16 mm long. All the composite samples were tested at 5°C min^{-1} with 0.15 mm amplitude deflection. The DMA was operated at a fixed frequency (1 Hz) in an air environment for all the tests.

3. Results and discussion

3.1. *Differential scanning calorimetry (DSC)*

The first experiments performed were DSC to determine the kinetics of both of the systems. An example of a 10°C min^{-1} dynamic DSC thermal curve

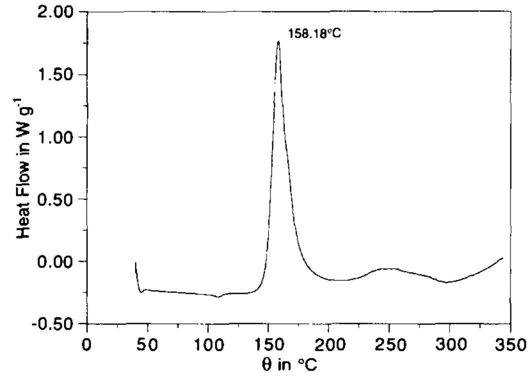

Fig. 1. DSC thermal curve of prepreg B, performed at a heating rate of 2.5°C min^{-1}.

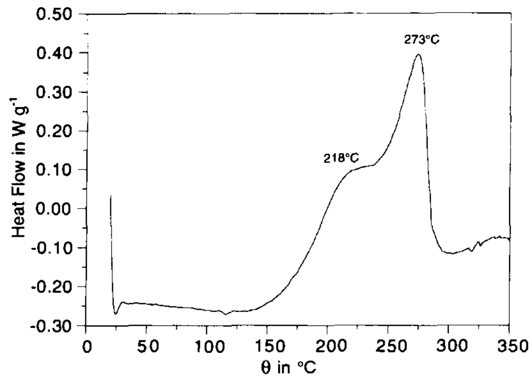

Fig. 2. DSC thermal curve of prepreg A, performed at a heating rate of 2.5°C min^{-1}.

Table 1
Summary of prepreg characteristics

Thermal analysis results	Prepreg A	Prepreg B
Resin content (%wt)	44	40.9
Heat of reaction (J g^{-1}) (Prepreg)	193.2	192.0
Activation energy (KJ mol^{-1})	63.1 (1st peak) 100.2 (2nd peak)	75.6
Cure temperature (°C)	177	121/177
Degree of conversion (2 h cure)	0.84	0.91(121°C) 1.0 (177°C)

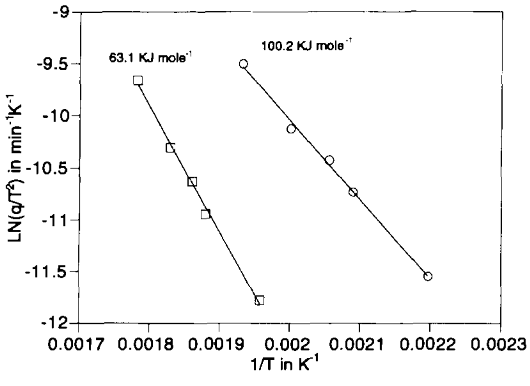

Fig. 3. Kissinger's method applied to prepreg A.

of prepreg B is shown in Fig. 1. This figure shows a single exotherm which begins at ~ 130°C and ends at ~ 200°C. For comparison, a 10°C min^{-1} dynamic DSC thermal curve performed on prepreg A is shown in Fig. 2. This figure shows a broader exotherm beginning at 130°C and ending at ~ 275°C which is well into the degradation region of epoxy. By comparing the exotherms of both of these prepreg systems, it is evident that the cure mechanisms are different. A distinguishing feature of prepreg A is that a shoulder is observed at an intermediate point in the cure exotherm. This demonstrated the possibility that a co-curing agent is used in addition to the main curing agent in the commercial resin formulation. On the other hand, the sharp single exotherm of the prepreg B reaction, exotherm suggests that this system is probably an accelerated cure system. The heat of reaction of prepreg B was found to be similar to prepreg A (Table 1). However, as can be seen by comparing Figs. 1 and 2, the overall time for the prepreg B reaction is much shorter.

The activation energies for both prepreg systems were calculated using Kissinger's method [4]. Figs. 3 and 4 show Kissinger's method applied to prepreg A and B, respectively. The activation energy was found to be 75.6 kJ mol^{-1} for prepreg B. Since there are two peaks in the dynamic DSC exotherms for prepreg A, two activation energies were calculated. The activation energies determined were 63.1 kJ mol^{-1} for the first peak and 100.2 kJ mol^{-1} for the second peak.

Prepreg B is available as a dual cure prepreg system which can be cured with either 121°C or 177°C cure cycles. Therefore, this prepreg was investigated using both 121°C and 177°C cure cycle using DSC. Fig. 5 shows a DSC thermal curve for the 177°C cure cycle

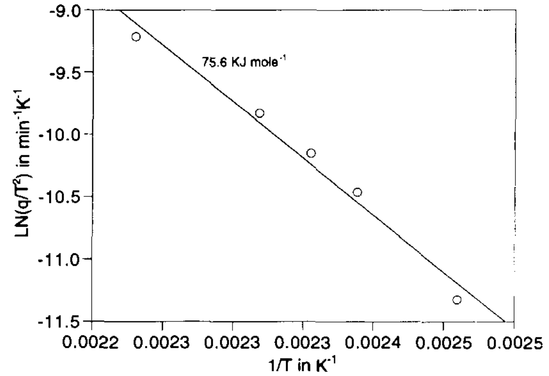

Fig. 4. Kissinger's method applied to prepreg B.

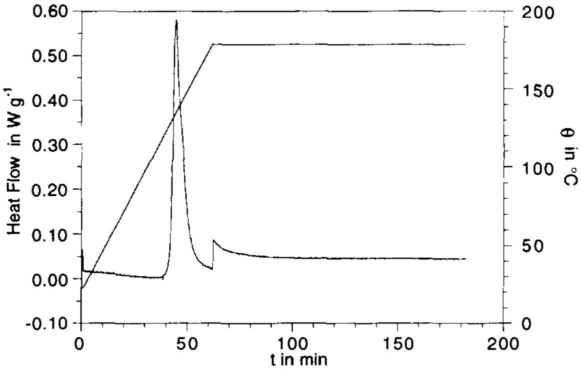

Fig. 5. DSC thermal curve of prepreg B, performed at a cure cycle consisting of 2.5°C min^{-1} to 177°C with a 2 h isothermal hold.

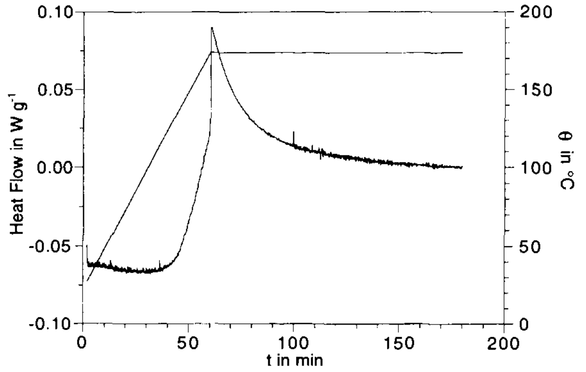

Fig. 6. DSC thermal curve of prepreg A, performed at a cure cycle consisting of 2.5°C min^{-1} to 177°C with a 2 h isothermal hold.

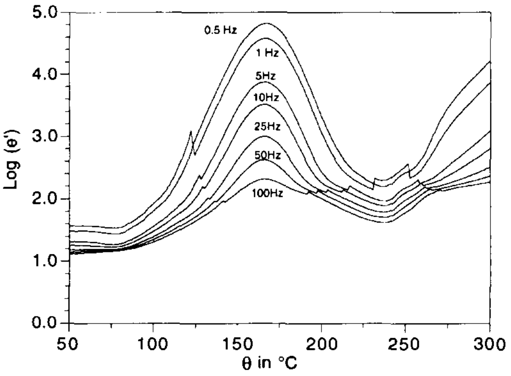

Fig. 7. Permittivities of the prepreg A, measured by varying the frequency from 0.5 to 100 Hz, with a heating rate of 2.5°C min^{-1}.

performed on prepreg B. The cure exotherm starts and ends during the ramping of the cure cycle, demonstrating an accelerated cure. The conversions for this material were 0.91 and 1.00 for the 121°C and the 177°C cure cycles, respectively (Table 1). In comparison, the conversion for prepreg A cured at the standard 177°C cure cycle was determined to be 0.84. Fig. 6 shows a DSC thermal curve for prepreg A cured at the 177°C cure cycle. Cure initiates during the ramping stage and continues well into the isothermal phase as indicated by the exotherm. This confirms the difference in curing mechanisms of these systems.

3.2. Dielectric analysis (DEA)

The permittivity (e') and loss factor (e'') from dielectric analysis provide valuable information pertaining to molecular behavior and material characterization. The permittivity (storage component of the dielectric constant) represents the measure of dipole alignments, while the loss factor (loss component of the dielectric constant) represents bulk ionic conduction and dipole orientations which dissipate stored energy. DEA offers the advantage of being able to test over a wide range of frequencies to observe molecular behavior and has also been used to determine kinetic parameters [5].

The permittivity profile obtained for prepreg A during its curing reaction is shown in Fig. 7. A frequency scan from 0.5–100 Hz range was used. During the initial heating period, the permittivity of the prepreg increased because of an increase in the polymer segment mobility from thermal energy. Once the thermosetting reaction dominated (~ 170°C), the

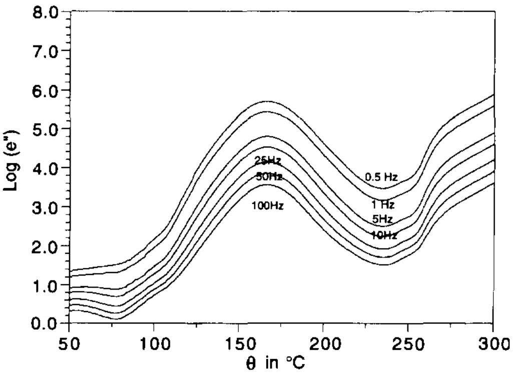

Fig. 8. Loss factors of the prepreg A, measured by varying the frequency from 0.5 to 100 Hz, with a heating rate of 2.5°C min^{-1}.

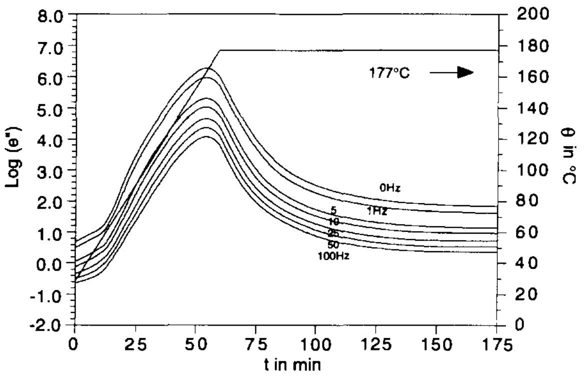

Fig. 9. Loss factors of prepreg A, obtained during a simulated autoclave cure process at 177°C.

segment mobility and permittivity showed a sharp decrease due to crosslinking.

Fig. 8 shows the results obtained for the loss factor of prepreg A through the curing reaction. These traces are similar in appearance to the permittivity results. The peak temperature for the loss factor can be seen to correspond well with that observed using DSC. In a manner identical to that illustrated in DSC analysis, activation energies for the cure reaction can be calculated from dielectric property measurements [5,6]. This method assumes a unique extent of reaction value corresponding to each peak position.

The activation energy for prepreg A generated by DEA using Kissinger's method was determined, and it should be emphasized that only one activation energy value was determined from this technique because of the DEA's inability to fully distinguish between multiple reactions. An activation energy of 89.4 kJ mol^{-1} was found for the prepreg which lies between the two activation energies, calculated for this material from the DSC results. The different activation energies between the two thermal techniques can be attributed to the different molecular response mechanisms. However, it can be seen that dielectric analysis can provide a means of obtaining kinetic parameters for a thermosetting system. DEA can therefore offer advantages in such areas as cure monitoring during processing.

An illustration of cure monitoring is shown in Fig. 9. As shown by the drop in the loss factors, the crosslinking for prepreg A initiates at the end of the 2.5°C min^{-1} heating ramp. After the long isothermal cure stage, the loss factors still exhibit a clear frequency dependence. This may be due to the material not being fully cured or possibly viscoelastic toughening activities that are between their respective glass transition and melting temperatures.

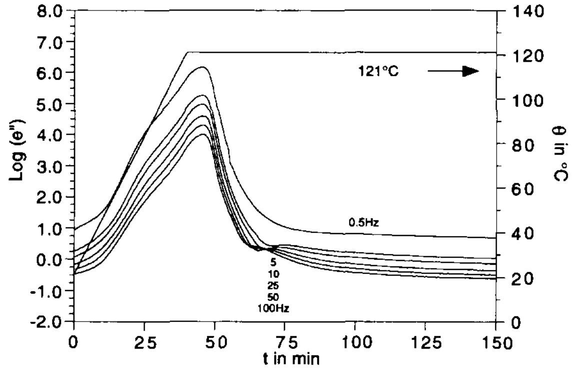

Fig. 10. Loss factors of prepreg B, obtained during a simulated autoclave cure process at 121°C.

The dielectric results for prepreg B are shown in Fig. 10. This figure shows the loss factors obtained for the sample with a 2.5°C min^{-1} heating ramp to a 121°C hold. The reaction initiation occurs just after the dwell temperature is reached, at which time the polymer chains begin to crosslink and in turn cause a drop in the loss factor values. Therefore, DEA provides a valuable tool for polymer material characterization both on kinetic and physical level.

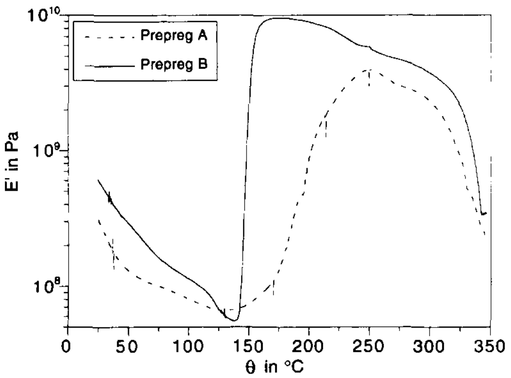

Fig. 11. DMA thermal curve of prepreg A and prepreg B during cure.

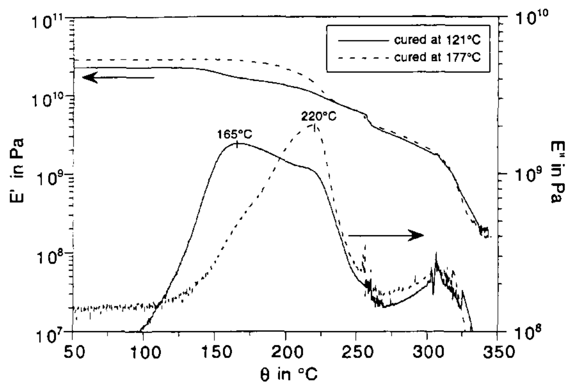

Fig. 12. Comparison of DMA thermal curves of prepreg B that had been previously cured at 121°C and 177°C.

3.3. Dynamic mechanical analysis (DMA)

Dynamic mechanical analysis was performed on the two systems, both in prepreg and cured composite form. the analysis of the prepreg was done to further investigate the gelation and curing of the matrices, while the cured composite analysis yielded information about the use temperature limits of each material.

Fig. 11 shows the relative rigidities of single plies of uncured prepreg A and B as they are heated from ambient to 350°C at 2.5°C min^{-1}. Upon initial heating, the rigidity of the prepreg decreased drastically as the viscosity of the matrix decreased. As the material was further heated, it began curing and eventually gelled. The gel point is marked by a sudden increase by a factor of 10 or more in prepreg stiffness. Prepreg B with its dual cure capability reached this gel point at a very low temperature (135°C) when compared to prepreg A (160°C). These temperatures correlate well with the ones achieved through dielectric measurements. Prepreg B also cured very quickly as it made the transition from a soft material with a low viscosity matrix to a rigid composite in a span of only 10 or 20°C, while prepreg A took ~ 50°C to make the same transition. Both systems show a large drop in stiffness after 250°C due to matrix degradation and cracking.

To investigate the validity of the dual temperature cure applicability of the prepreg B, laminates were cured at both 121°C and 177°C for 2 h in an autoclave and then thermomechanically tested to determine the resulting glass transition temperatures (T_g). The temperature at which the loss modulus (E'') was a maximum was assumed to be an indication of the T_g. As pointed out in [7], this method is more dependent on frequency and heating rate than using a fraction of the initial storage modulus, but it was assumed that the loss modulus peak was more consistent method and sufficient for comparison. Fig. 12 shows the relationship between E' (Storage modulus), E'', and the temperature for these two samples when heated at 5°C min^{-1}. Both laminates maintained a storage modulus of approximately 11 GPa until 150°C where the sample which had been cured at 121°C began to soften slightly. This decrease in storage modulus was accompanied by a sharp increase in the loss modulus and a peak in that value at 165°C. As the material transformed, into a rubbery solid, additional curing occurred. This region of curing is apparent by a broad almost flat region in the loss modulus curve between 165°C and 220°C. Following the completion of cross-linking, the loss modulus decreased sharply as the material completed its transition from a partially cured glassy solid to a fully cured solid at an elevated temperature. At roughly the same temperature (210–220°C), the sample which had been cured at 177°C softened. This sample did not show a flat region in loss modulus, having a single peak at 220°C, indicating that it was fully cured. Both samples showed a sharp decrease in storage modulus, a gradual increase in loss modulus, and noise in the loss modulus data beginning at 260°C. All of these phenomena may be attributed to the degradation of the matrix.

A laminate of prepreg A was made in the same autoclave as the 177°C cured prepreg B laminate and

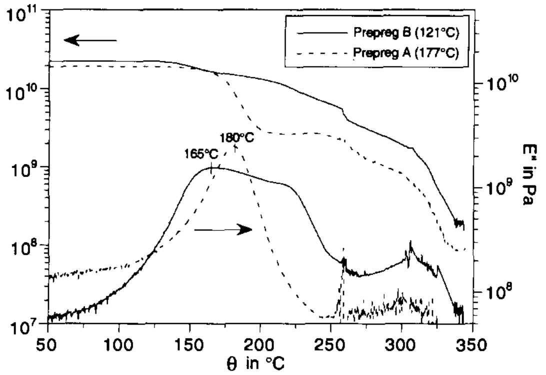

Fig. 13. Comparison of DMA thermal curves of prepreg B that had been previously cured at 121°C and prepreg A that had been previously cured at 177°C.

was tested in a manner identical to the previous prepreg B laminates. The DMA for prepreg A plot is shown in Fig. 13 along with the prepreg B cured at 121°C in order to illustrate the possibility of achieving similar thermal behavior with a lower temperature cure. The prepreg A laminate displayed a T_g of 180°C, only 15°C higher than prepreg B cured at 121°C and 40°C below that of fully cured prepreg B. At this temperature, the storage modulus decreased by almost a full decade as compared to the minimal, initial decrease in storage modulus in the prepreg B. Prepreg A began to degrade at 260°C, similar to prepreg B.

4. Conclusions

A prepreg system used in the commercial aircraft industry was compared with a prospective prepreg system which can possibly be used for the same applications. The commercial controlled-flow resin prepreg is a 177°C cure prepreg while the prospective dual temperature cure prepreg can be cured at both 121°C and 177°C. Specifically, DSC, DEA, and DMA were used to characterize and compare both of these prepreg systems. This investigation supports the conclusion that the dual temperature cure prepreg system can be cured at both 121°C and 177°C to give cured thermal properties equal or superior to the commercial prepreg system. These properties are attributed to the different cure characteristics of the two prepreg systems. Collectively, these results show that through thermal analysis, the characterization and comparison of prepreg system can be performed to fundamentally understand their process–structure–property interrelationships.

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