NOTES

Application of Infrared Spectroscopy to the Cure of Polyimide Laminates

INTRODUCTION

Boron fibers with a polyimide matrix are used in composite laminate form to produce such structures as airplane wings and radomes. Problems of bonding the laminates may occur during the cure of the polyimide matrix due to the outgassing of solvent. This work indicates how to circumvent this problem by utilizing infrared spectroscopic analysis to separate solvent emission from the imidization cure. As a result of this work the stepwise cure processes have been successfully modified to bond void-free laminates.

RESULTS AND DISCUSSION

Boron/polyimide prepreg used throughout this work was Skybond 703 produced by the Monsanto Company.

Polyimides are usually prepared in a two-step process.[1,2] The first step involves both the reaction of a primary diamide with a tetrabasic acid anhydride to form polyamic acids and the competing reaction of polyamic acid hydrolysis. The addition reaction is spontaneous and exothermic if the reactants are properly solvated. This is usually achieved by carrying out the reaction in a highly polar solvent such as dimethyl sulfoxide, dimethylformamide, or dimethylacetamide. The resulting polyamic acids, varying in color from yellow to dark amber or green, constitute the prepreg matrix. The second step consists of imidization which is a polycondensation reaction where two moles of water are split out of each polymeric unit. The reaction

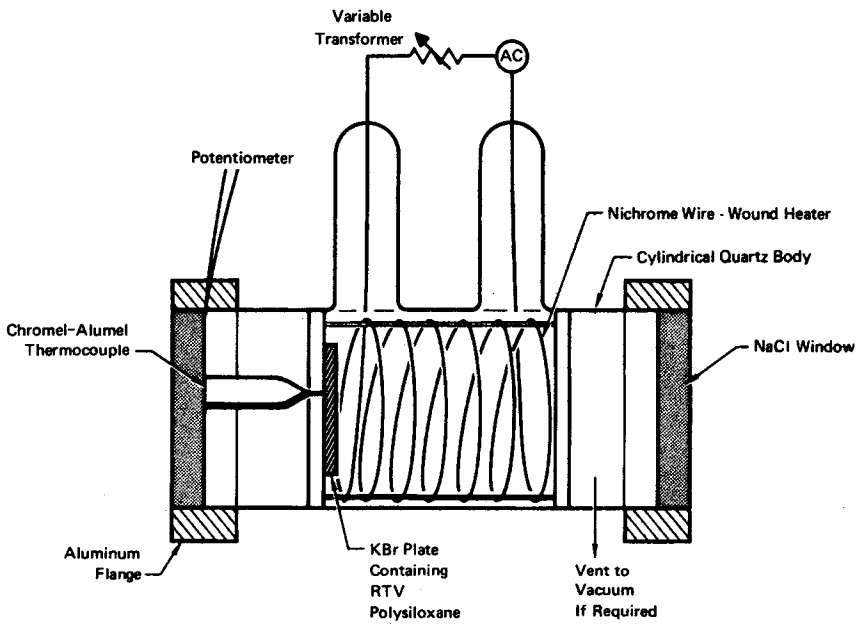
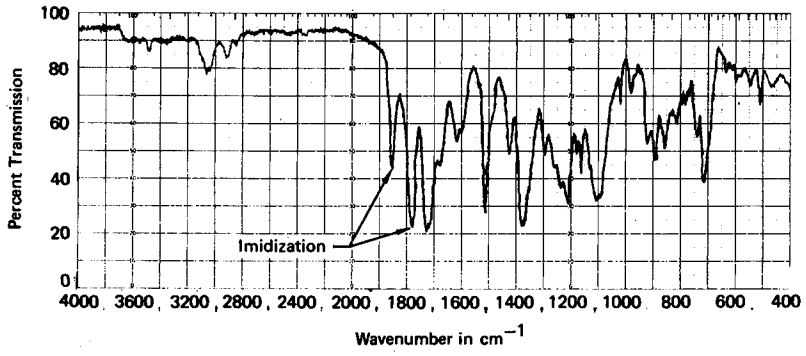
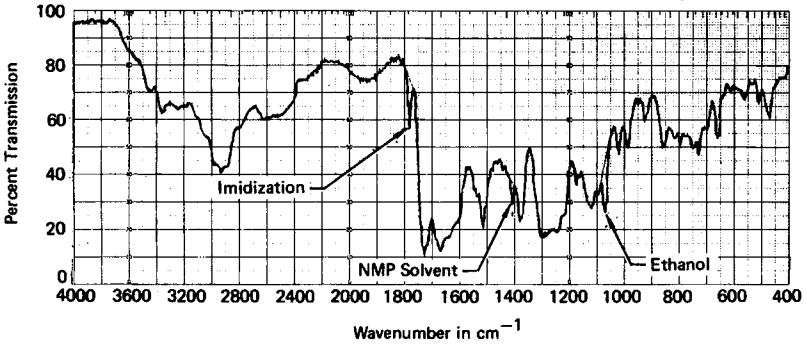


Fig. 1. Heated cell.



(a)



(b)

Fig. 2. Infrared spectrograms of polyimide matrix. (a) As-received "A" staged polyimide. (b) Cured polyimide resin.

rate is reported to be proportional to the reaction temperature and has been found to reach a maximum value of 120-140°C.[1,3] This direct intermolecular elimination of water constitutes the main imidization curing process.

In addition to imidization, a fourth reaction that occurs is the hydrolysis of the polyimide back to polyamic acids. Many times, green/yellow resin "precipitation" in the matrix has been observed in many boron/polyimide laminates after cure. Polyimide hydrolysis in the presence of moisture could explain this phenomenon. Anyway, low void content (less than 1%) laminates are required to achieve optimum mechanical properties.

A study was conducted to determine if infrared spectroscopic (IR) transmission analysis of the boron/polyimide laminate cure cycle could provide data to achieve this goal. A Beckman IR-9 was used at 80 cm^{-1}/min with the prepreg being contained in a heated cell as shown in Figure 1. Imidization and solvent emission were monitored by measurement of the absorption bands designated in Figure 2. For the given cure cycle, Figure 3 shows the emission of volatiles and onset of polymerization proceeding concurrently, resulting in the potential entrapment of volatile material in the matrix.[4] High void content in the finished laminates validated the inference drawn from Figure 3.

Examination of Figure 3 reveals that the bulk of polymerization occurred in the 2$^1/_2$-hour interval at 340°F (171°C). In addition, it can be seen that polymerization continued at a nearly constant rate in the postcure period, 400-600°F. The fact that a constant absorbance value is not reached indicates that longer postcure periods would be required to achieve maximum polymerization.

The initial absorbance value may be used to calculate the present advancement of resin. In the illustrated example of Figure 4, the initial absorption value was 0.075 and the maximum was

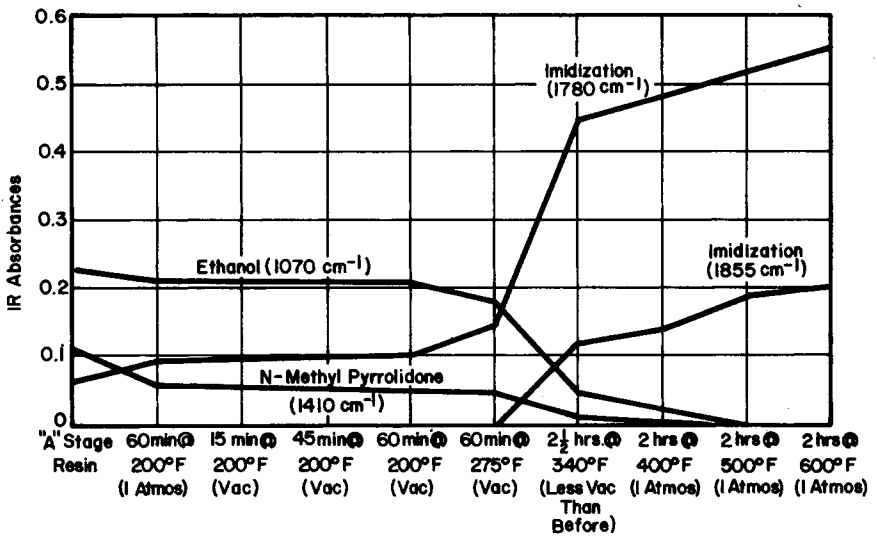


Fig. 3. Boron/polyimide prepreg—cure cycle. Use of IR for studying cure (solvent outgassing occurred simultaneously with final crosslinked polymer formation).

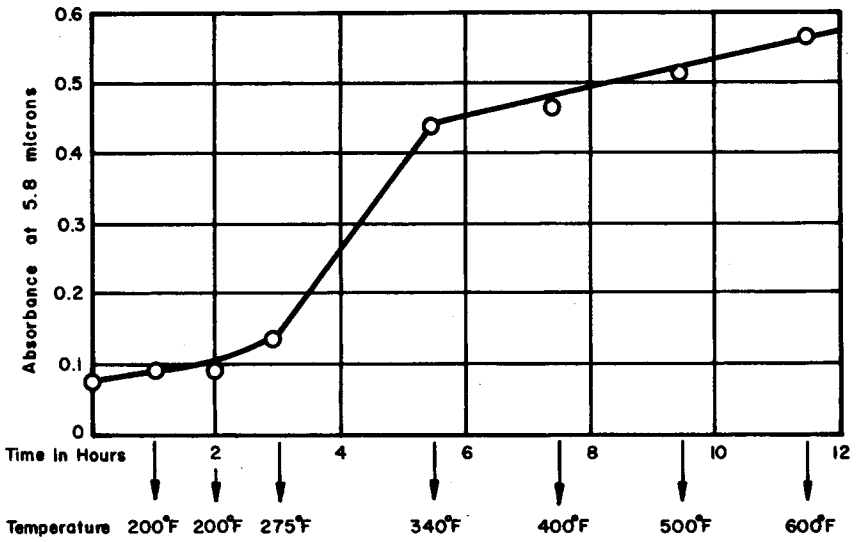


Fig. 4. Degree of polymerization of polyimide resin.

0.1565 at 600°F. The as-received resin consequently was imidized (polymerized) to 13.3% of the maximum possible polymerization obtainable with this cure schedule.

Figure 3 also shows the solvents present in this system and the absorption bands assigned to characterize them. From these data, it can be seen that all traces of detectable solvents were not removed until after the 500°F interval was completed in the postcure cycle. Curing for longer times at 200°F would eliminate more solvent prior to the onset of imidization which occurred during the range of 200-340°F. A change in the stepwise process to one with fewer steps of longer time duration, such as 2-3 hr at 200°F, followed by 1 hr at 275°F and the remaining times and temperatures of cure as determined in Figure 1, should prevent void formation because most of the solvent should have escaped prior to the onset of a high degree of imidization.

An approximate correlation with interlaminate shear was obtained with initial imidization in the prepreg as determined by the IR method (Fig. 5). This correlation shows that a low degree

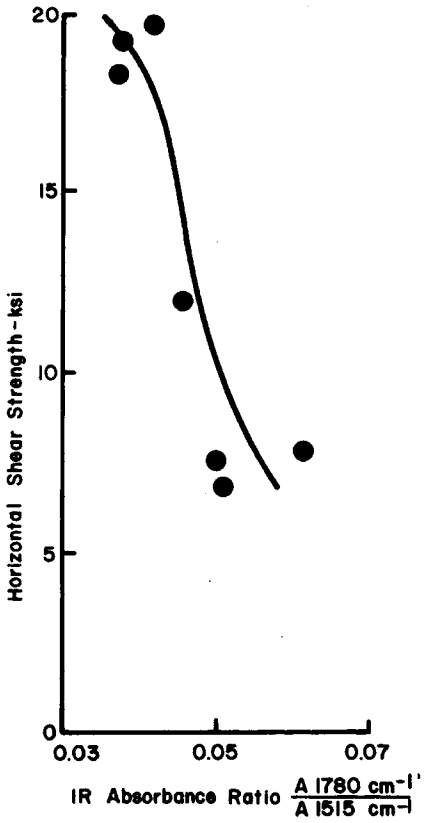


Fig. 5. Correlation between strength and prepreg cure advancement.

of imidization in the as-received prepreg is required to achieve higher interlaminar shear in the cured laminate. The lower the imidization in the prepreg, the greater chance there is of outgassing the solvent before the onset of sufficient imidization that would otherwise entrap the solvents and cause voids.

CONCLUSION

Void-free boron/polyimide laminates may be prepared by a stepwise cure cycle that has been determined by an infrared spectroscopic analysis of the matrix cure. Once the cure cycle is fixed to cure good laminates, this same IR method may be used to monitor the as-received prepreg material to ensure that the matrix is similar to that used to establish the cure cycle.

References

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Roger Fountain
Thomas W. Haas

American Standard, Inc.
P.O. Box 2003
New Brunswick, New Jersey 08903

Received August 27, 1974
Revised September 20, 1974