Microwave Irradiation of Nadic-End-Capped Polyimide Resin (RP-46) and Glass–Graphite–RP-46 Composites: Cure and Process Studies

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ABSTRACT: Microwave energy was investigated to cure nadic-end-capped polyimide precursors (RP-46 resin) using a Cober Electronics Model LBM 1.2A/7703 microwave oven at a frequency of 2.45 GHz. Both neat resin samples and glass cloth and hybrid glass cloth–graphite cloth–RP-46 resin composites were studied. For the resin studies, the effect of various parameters, such as power level, sample size, processing temperature, time, and graphite fiber absorber, were investigated. The variables investigated with the composite study were the power level, mold material, vacuum, and low pressure. The results showed that microwave energy was effective in curing both neat resin samples and composite specimens. The presence of a small quantity of absorber (chopped carbon fiber) accelerates the cure dramatically. Moreover, soapstone mold material was found to be an efficient absorber for glass and glass–graphite composite processing, causing an effective cure in less than 1 h. Glass and glass–graphite hybrid composites with flexural strengths of 372–588 MPa (54–85 ksi) and moduli of 28.7–31.7 GPa (4.2–4.6 Msi) have been fabricated. This is equivalent to 50 to 80% of the properties of composites fabricated by conventional means. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2391–2411, 1999

Key words: microwave; polyimide; composite; cure; crosslinking; nadic end cap; flexural properties

INTRODUCTION

Microwave energy is being applied in polymer processing, such as in epoxies, polyesters, polyurethanes, and, more recently, in polyimides, due to the potential for a shorter processing time, improved energy utilization, lower processing temperature, and product uniformity.[1–3] The microwave energy is absorbed by the molecules through the polarization or dipole reorientation of functional groups, which is consequently converted into thermal energy.[4] As a result, heat is generated within the molecule, and, thereby, a homogeneous heating pattern is created in the materials. In contrast, in conventional heating processes, the heat is transferred from outside to inside of the material by the conduction of the heating medium, resulting in a long processing time to achieve high product uniformity.

Fiber-reinforced polyimide materials have the potential to replace metals in many applications, such as in airframes, propulsion systems, missiles, and land vehicles, such as automobiles and armored tanks.[5] Processing of thick sections by conventional thermal processes requires slow ramp rates and, therefore, a long processing time. Since microwave processing heats the materials at a molecular level and the heat is generated

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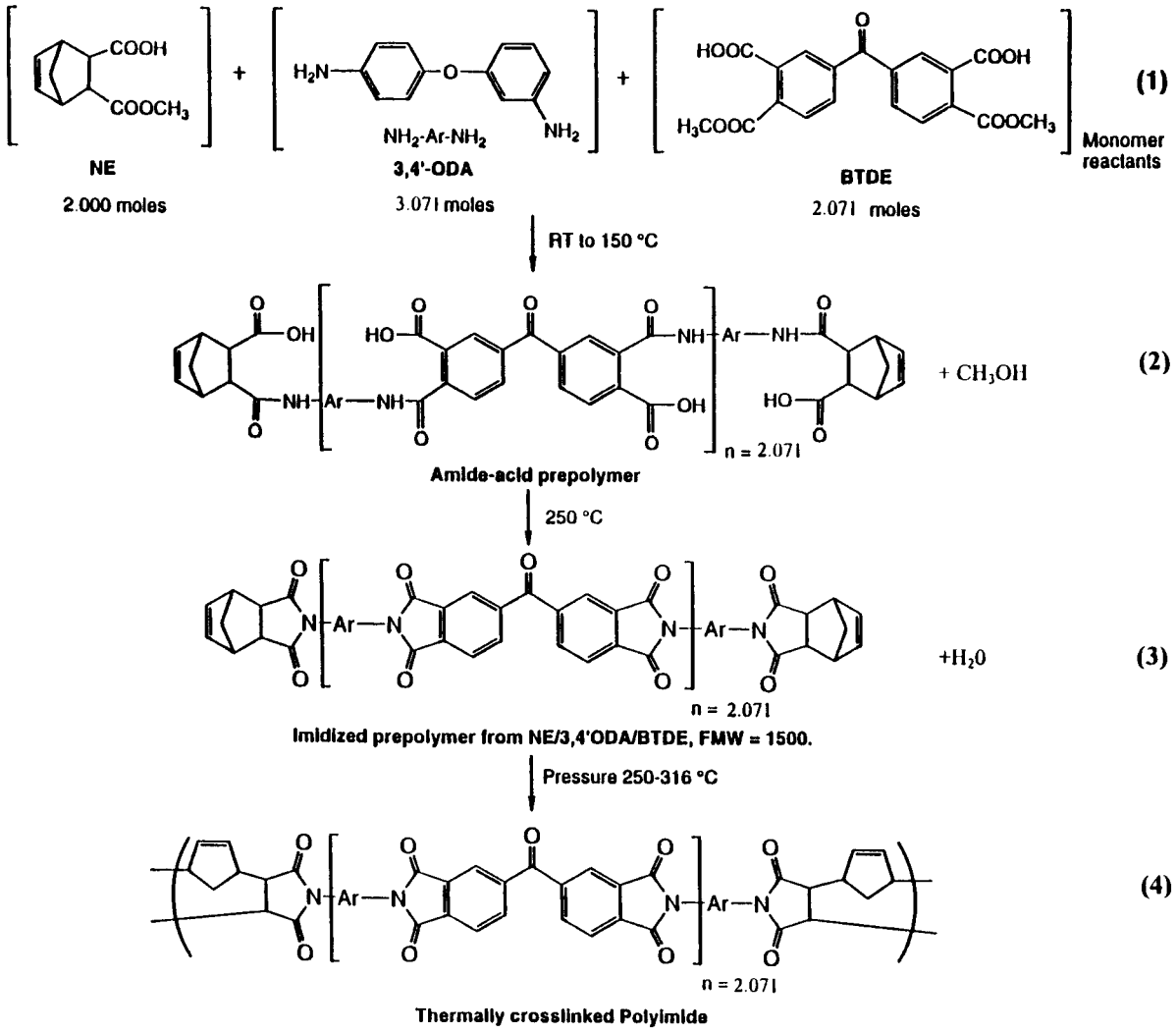


Scheme 1 RP-46 polymerization reaction.

within each molecule, a homogeneous heating pattern is created in the material even at the fast ramp rate. For electrically conducting fiber-reinforced polyimide composites, microwave processing could provide additional advantage since the electrically conducting fibers, such as graphite and carbon fibers, absorb the microwave energy more efficiently than the nonconducting materials; therefore, the composites containing conducting fibers could be heated by the microwave process to achieve inside to outside heating patterns and quick heat ramp rate. Additionally, microwave process may enhance the bonding between resin and fiber matrix.[6]

A microwave process is being investigated to develop an efficient method to fabricate polyimide composites. LaRC RP-46, a NASA-developed polyimide was initially selected for investigation.[7] RP-46 resin consists of polyimide precursors, 3,3′,4,4′-benzophenone tetracarboxylic acid dimethyl ester (BTDE), 3,4′-oxydianiline (3,4′-ODA), and an end-capping reagent, 5-norbornene-2,3-dicarboxylic acid monomethyl ester, in the ratio to yield imidized oligomers with molecular weight of about 1500 (Scheme 1). The cure process proceeds in the following three steps: (1) amidation, (2) imidization, and (3) a thermally induced crosslinking step (Scheme 1). The amidation and imidization steps can be achieved in a short time and by low-level microwave irradiation.[8–10] However, in our initial studies,[9] there was no strong evidence that the crosslinking reaction can be achieved by the microwave process, but subsequent studies[10] on a bisnadimide model compound revealed that crosslinking was achieved by microwave energy. Typically, crosslinked structures are cured ther-

mally above 300°C to obtain polyimide composites with high strength and stiffness. Our initial studies were performed on neat resin. These studies were extended to include glass cloth–RP-46 and hybrid glass cloth–graphite cloth–RP-46 composites.

MATERIALS

LaRC RP-46 provided by NASA Langley Research Center, contains 3,3′,4,4′-benzophenone tetracarboxylic acid dimethyl ester (BTDE), 3,4′-oxydianiline (3,4′-ODA) and 5-norbornene-2,3-dicarboxylic and monomethyl ester (NE) in a ratio to yield imidized oligomers with a theoretical molecular weight of 1500.[7] The mole ratio of NE–BTDE–3,4′-ODA used in the formulation is as follows: 1.0000/1.0356/1.5356. The material was provided as a powder in the uncured state and contained about 2% methanol which is the solvent used to prepare the resin. This was considered undried powder. The powder was vacuum-dried at 60°C for 2 days to remove residual methanol. Aremcolox™ machined ceramics was purchased from Aremco Products, Inc. High-temperature tacky tape sealant material was purchased from Northern Fiber Glass, Inc. (Hampton, NH). Kapton™ film (0.005 and 0.027 cm × 91.4 cm wide) were purchased from DuPont Co. Glass cloth (style 1675), and graphite cloth (G30-500 unsized), were donated by United Technologies Research Center (East Hartford, CT). Unidirectional G30-500 graphite fiber (2500 filaments/bundle) were also donated by United Technologies Research Center. The graphite tows were cut into 0.635 lengths (0.25/in.) for use in the resin cure studies.

Preparation of Resin Impregnated Fiber Cloth

The RP-46 resin-impregnated glass fiber cloth or graphite fiber cloth was prepared by immersing glass or graphite fiber cloth in a saturated (65 wt %) solution of RP-46 in methanol. The resin impregnated fiber was obtained after removal of methanol at 100°C for 7 min. This treatment yielded cloth fiber impregnated with uncured resin. Further treatment at 275°C for 15 min yielded imidized-resin-impregnated fiber.

Microwave Oven

The microwave oven used in this study is a Model LBM 1.2A/7703 Microwave and Convection Oven manufactured by Cober Electronics. The overall size of the microwave oven is 50.8 × 83.8 × 60.96 cm (20 × 33 × 24 in.). The size of the cavity is 27.94 × 39.4 × 42.54 cm ($11 \times 15\frac{1}{2} \times 16\frac{3}{4}$ in.) [1.65 ft^3]). The maximum output of microwave is 1200 W at 2.45 GHz frequency. The power output can be manually adjusted between 0 to 100%, the conventional thermocouple (type K) was used to record the temperature. To minimize the interference in temperature reading from the thermocouple caused by microwave absorption, the microwave power output was reduced to zero when the temperature was recorded.

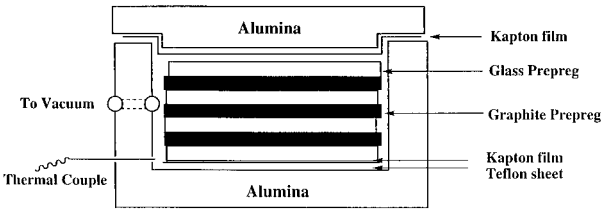


Figure 1 Schematic of alumina mold to fabricate glass–graphite–RP-46 polyimide resin composites.

Molds

An alumina mold 7.62 (l) × 7.62 (w) × 1.27 cm (thick) (3 × 3 × 0.5 in.) was initially used to fabricate composites. The inside of the mold cross-coated with a Teflon™ release agent. The lay-up of the plies is shown in Figure 1. The second type of mold consisted of sealing the composite lay-up inside Kapton film using tacky tape, with provisions for vacuum on the side of the tape. This sealed bag was sandwiched between two slabs of soapstone (Aremcolox™) 15.24 (l) × 15.24 (w) × 2.54 cm (thick) (6″ × 6″ × 1″), as shown in Figure 2. A Teflon mold with Kapton™ film seals was the third type of mold used to process the polyimide composites. The Teflon mold was made by cutting a cavity 15.24 (l) × 15.25 (w) × 2.5 (thick) (6 × 6 × 1 in.) in the Teflon block of 30.48 (l) × 30.48 (w) × 3.81 cm (thick) ($12'' \times 12'' \times 1\frac{1}{2}''$). Vacuum and thermocouple outlets were connected to the cavity (Fig. 3). Normally, the composite was inserted into the cavity, and a thin Teflon plate 20.32 (l) × 20.32 (w) × 0.32 cm thick ($8'' \times 8'' \times \frac{1}{8}''$) or Kapton™ film 20.32 (l) × 20.32 (w) × 0.013 cm thick (8″ × 8″ × 0.005″) covered the cavity with the high-temperature tacky tape as a sealant, then the system was evacuated for processing under vacuum. Kapton™ film was also used to form a vacuum bag in our early studies. In

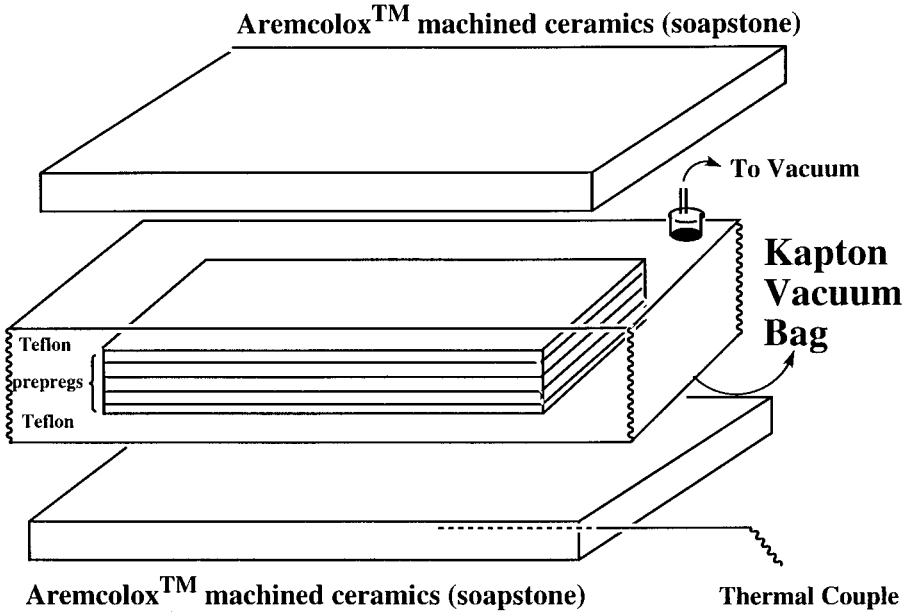


Figure 2 Schematic of vacuum bag laminate lay-up on soapstone molds.

this case, two layers of Kapton™ film and high temperature tacky tape were used as sealant.

Mechanical Properties

Three point bending tests were conducted on an Instron instrument, model TTCML according to ASTM D790M-84 method. The samples were cut into 6.35 (l) × .635 (w) × thickness (2.5 × 0.25 in. × thickness) specimens. A nominal span to depth ratio of about 16 to 1 was used for the three point bending tests. The crosshead speed was set at 1 mm/min, the maximum load was set at 22.7 to 90.9 kg (50 to 200 lb), and the recorder's chart speed was set at 10 cm/min.

CHARACTERIZATION

Density of Composites

The composite samples 6.35 (l) × 0.635 cm (w) thick (2.5 × 0.25 in. thickness) were weighed in isopropanol and air, respectively. The density of the sample was calculated as follows:

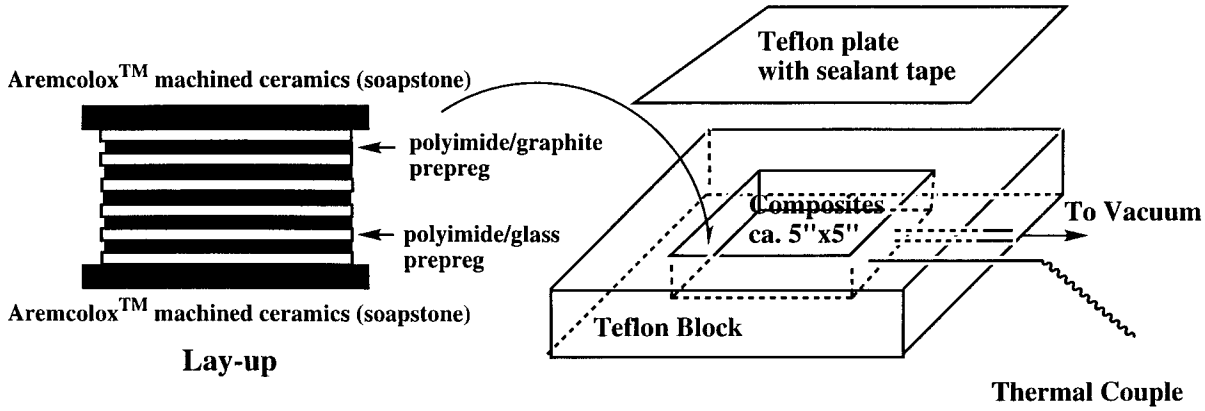


Figure 3 Schematic of the Teflon mold used in the microwave cure of RP-46 polyimide composites.

$$D = \frac{\text{wt in air}}{\text{wt in air} - \text{wt in isopropanol}} \times \text{density isopropanol}$$

Thermomechanical Analysis

The thermomechanical analysis was conducted on the Perkin–Elmer TMA-7 analyzer with a penetration probe on samples 0.635 (l) × 0.635 (w) × 0.254 cm (thick) (0.25″ × 0.25″ × 0.1″). The analysis was conducted from 30 to 400°C at the rate of 10°C per min.

Thermogravimetric Analyses

A DuPont Model 2950 thermogravimetric analyzer (TGA) at a heating rate of 10°C/min was used to measure weight losses of the microwave-treated resin samples. The dynamic TGA weight loss is defined as the loss in weight at the sample temperature of 325°C.

Infrared Spectroscopy

Infrared spectra of polyimides in KBr were obtained on a Nicolet 60SX Fourier transform infrared (FTIR) spectrometer.

COMPOSITE COMPOSITION

Void and Material Contents

Cross sections of each composite perpendicular to the fiber direction were cast into an epoxy resin and were polished with 1 μm polishing powder at the final stage. Void contents were obtained over an area of 1000 × 1000 μm at 57× magnification. The average of 10 areas was reported as the void content. Fiber and resin contents were determined by the burn-off method by subjecting the composite sample at 450°C for 5 h in a muffle furnace. To correct for loss of graphite or glass cloth during burn-off, weight loss of control specimens were also determined. The composite volume was determined from the density measurements, as described above.

MATERIAL LAY-UP AND PROCESSING

The material lay-up configuration, state of resin cure, and mold tool used for each composite is shown in Table I. The microwave process conditions used for each composite is listed in Table II. An example for a composite processed in the alumina ceramic mold with no vacuum is given for composite C1 (Fig. 1). An example for a composite processed in a Kapton™ bag is given below for composite C5 (Fig. 2). An example for a composite processed in the Teflon mold is given below for composite C11 (Fig. 3).

Composite C1

7628 glass cloth–RP-46 resin prepreg and G30-500 graphite cloth (8 Harness Weave)–RP-46 resin prepreg, both of which contain about 50 wt % RP-46 resin, were cut into 7.62 (l) × 7.62 cm (w) (3 × 3 in.) sections and stacked on a 7.62 (l) × 7.62 (w) × 1.27 cm thick (3 × 3 × 0.5 in.) alumina mold, covered with a 10 (l) × 10 (w) × 0.005 cm thick (4 × 4 × .002 in.) Teflon™ sheet. The stacking sequence was as follows: glass–graphite–glass–graphite–glass–graphite–glass. The top ply was covered with a (10 (l) × 10 (w) × 0.005 cm thick) sheet of Teflon, followed by an alumina top plate 7.62 (l) × 7.62 (w) × 1.27 cm (thick) (3 × 3 × 0.5 in.) (Fig. 1). An exhaust vent 22.86 cm in diameter (9 in.) was attached to the rear of the microwave unit to remove volatiles as they formed. The microwave power was then turned on and kept at 20% of power for 10 min, and then at 35% of power for 120 min. The temperature of the composite after this treatment was 300°C as measured with a thermocouple placed on the composite immediately after the run. The test data are listed in Table III.

Composite C5

Four layers of 7.62 (l) × 7.62 (w) (3 × 3 in.) RP-46-resin-impregnated G30-500 graphite cloth (RT-dried) and five layers of 7.62 (l) × 7.62 (w) (3 × 3 in.) RP-46 resin-impregnated 1675 glass cloth (about 57% wt of resin) were stacked together with alternate layers of glass and graphite. This composite was covered with Teflon sheet on both sides and placed in a vacuum bag fabricated from Kapton™ film and tacky tape. This lay-up was positioned between two pieces of Aremcolox™ machined ceramics [15.24 (l) × 15.24 (w) × 2.54 cm (thick), [6 × 6 × 1 in.]). Vacuum was applied to the bag lay-up and the vacuum bag was maintained at 3 mmHg (Fig. 2). The composite was heated in a microwave oven at power output of 20% initially for 15 min, 25% for 4 min, 30% for 1 min, 35% for 3 min, 40% for 3 min and 45% for 64 min. The total heating time was 80 min, and the

Table I Composite Lay-Up State of Resin, and Mold Set-Up

Composite No.	Lay-Up/Material/State of Resin	Mold Set-Up in Microwave Unit
C1	gl/gr/gl/gr/gl/gr/gl 7628 glass/G30-500 graphite/RP-46 uncured resin	Ceramic mold, Kapton film top and bottom, no vacuum
C2	gl/gr/gl/gr/gl/gr/gl 7628 glass/G30-500 graphite/RP-46 uncured resin	Ceramic mold, Kapton film top and bottom, no vaccum
C3	gl/gr/gl/gr/gl/gr/gl 7628 glass/G30-500 graphite/RP-46 uncured resin	Ceramic mold, Kapton film top and bottom, no vacuum
C4	gl/gr/gl/gr/gl/gr/gl 7628 glass/G30-500 graphite/RP-46 uncured resin	Ceramic mold, Kapton film top and bottom, no vacuum
C5	gl/gr/gl/gr/gl/gr/gl/gr/gl 1675 glass/G30-500 graphite cloth/RP-46 cloth uncured resin	Kapton bag, vacuum, on soapstone mold
C6	gl/gr/gl/gr/gl/gr/gl/gr/gl 1675 glass/G30-500 graphite cloth/RP-46 cloth uncured resin	Kapton bag, vacuum, on soapstone mold
C7	gl/gr/gl/gr/gl/gr/gl/gr/gl 1675 glass/G30-500 graphite cloth/RP-46 cloth uncured resin	Kapton bag, vacuum, on soapstone mold
C8	24 glass plies 1675 glass cloth/RP-46 imidized resin	Kapton bag, vacuum, on soapstone mold
C9	20 glass plies 1675 glass cloth/RP-46 imidized resin	Kapton bag, vacuum, on soapstone mold
C10	12 glass plies 7628 glass cloth/RP-46 imidized resin	Kapton bag, vacuum, on soapstone mold
C11	24 glass plies 1675 glass cloth/RP-46 uncured resin	Teflon mold on soapstone vacuum, Kapton seal
C12	20 glass plies 1675 glass cloth/RP-46 uncured resin	Teflon mold on soapstone vacuum, Kapton seal
C13	gl/gr/gl/gr/gl/gr/gl/gr/gl 1675 glass/G30-500 graphite cloth/RP-46 cloth uncured resin	Teflon mold on soapstone vacuum, Kapton seal
C14	12 glass plies/5 graphite plies 2gl/1g/2gl/1gr/2gl/1gr/2gl/1gr/2gl/1gr/2gl uncured resin	Teflon mold on soapstone vacuum, Kapton seal
C15	20 glass plies 1675 glass cloth/RP-46 imidized resin	Teflon mold on soapstone vacuum, Kapton seal
C16	30 glass plies 1675 glass cloth/RP-46 imidized resin	Teflon mold on soapstone vacuum, Kapton seal

processing pressure was 1.05 kg per cm^2 (15 psi). The temperature profile of this run is shown in Figure 4, and the test data are summarized in Table III. A temperature profile of the soapstone mold in the free state is shown in Figure 5. This mold is similar to what was used in the present study.

Composite 11

Twenty-four layers of 7.62 (l) × 6.35 (w) (3 × 2.5 in.) RP-46-impregnated 1675 glass cloth were inserted into two Aremcolox™ machined ceramics of 7.62 (l) × 12.70 (w) × 1.27 cm thick (3 × 5 × $\frac{1}{2}$ in.) interfaced with the Teflon sheet. This setup was inserted into the Teflon mold. Vacuum was applied and was maintained at 3 mm Hg (Fig. 3). The sample was heated by microwave oven at power output of 20% for 5 min, 30% for 3 min, 35% for 2 min, and 40% for 25 min. The total heating time was 35 min, and the processing pressure was 1.05 kg per cm^2 (15 psi). The composite was cut into 6.35 (l) × 0.64 cm (w) × thickness

Table II Microwave Irradiation Process Conditions: Time at Power in Minutes for Each Composite

% Output Power (Total Watts, 800)	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16
20					15	15		5	4		5		4		4	
25	10	10	10	5	4		5									
30					1	10		3	2		3		2		2	
35	120	110	80	65	3		62	2	2		2				2	
40					3		50	25	27		25	55	82	110	97	60
45					64	65				62						
Total Time	130	120	90	70	80	90	117	35	35	62	35	55	88	110	105	60

(2.5 × 0.25 in. × (thickness) pieces for mechanical test. The mechanical test data are summarized in Table III.

RESULTS AND DISCUSSION

Resin Studies: Effect of Residual Solvent (methanol) on Processing (Coupling)

The microwave cure process studies of neat resin are compared with the conventional thermal cure process (Scheme 1). The presences of residual methanol solvent 2 wt %) has a profound effect on the coupling efficiency between the RP-46 resin and microwave energy, as indicated in Table IV. For example, for 20 g of dried methanol-free resin, at 40% of power, foaming due to the release of methanol and water from the amidation and imidization reactions was observed after 360 s; while at 60% of power, foaming was observed in about 120 s. However, for an undried methanol containing specimen, at 60% of power, foaming for a 15 g specimen was observed in 20 s; while for a 15 g dried specimen, foaming was observed in 600 s. For the dried-methanol free powder, foaming is due solely to the gas released during amic acid and imide formation, as shown in Scheme 1. However, for the undried resin power, foaming is due to both residual methanol and gas released during the amic acid and imide reactions. Residual methanol solvent is a safety hazard in the microwave air environment because it can ignite spontaneously due to efficient coupling with the microwave energy. Therefore, in these experiments, a PVC exhaust tube located adjacent to the sample was used to remove methanol as it was formed during amic acid and imide formation.

Effect of Power Level on Processing (Coupling)

Scheme 1 shows the reactions which occur during thermal processing. Undried RP-46 resin powder

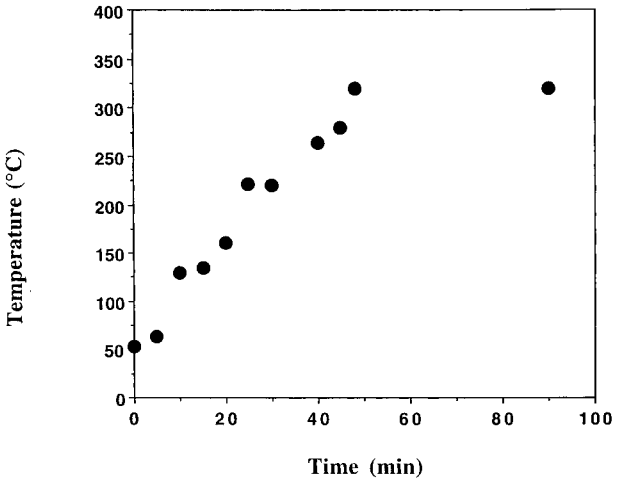


Figure 4 Temperature profile of a hybrid composite during the microwave process in the Teflon mold.

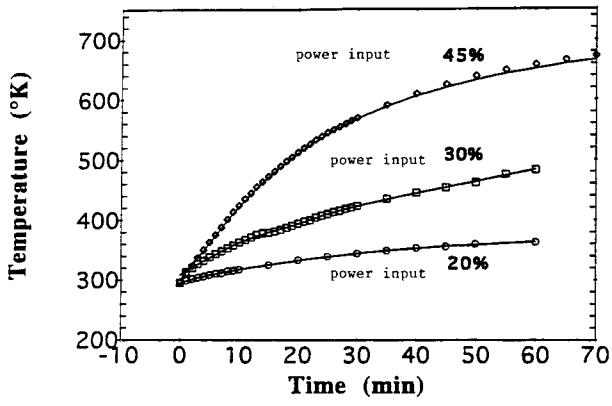


Figure 5 Microwave coupling with soapstone at 780 W: (○) 20%, (□) 30%, and (◇) 40% power.

Table III Properties of Microwave-Cured Glass and Glass–Graphite, Hybrid Polyimide Composites

Composite No.	C1	C2	C3	C4	C5	C6	C7
Microwave curing condition	see Table II	see Table II	see Table II	see Table II	see Table II	see Table II	see Table II
Curing time (h)	2.16	2.0	1.5	1.16	1.25	1.25	2.0
Fabrication pressure [kg/sq cm (psi)]	0.056 (0.8)	0.056 (0.8)	0.056 (0.8)	0.055 (0.8)	1.05 (15)	1.05 (15)	1.05 (15)
Flexural strength MPa (ksi)	499 (72)	438 (63)	395 (57)	386 (56)	453 (66)	396 (57)	271 (77)
Flexural modulus GPa (Msi)	24.7 (3.5)	23.3 (3.4)	21.6 (3.1)	19.4 (2.8)	24.7 (3.6)	10.2 (1.5)	21.0 (3.1)
Glass transition temperature T_g (°C)	289	284	284	267		302	256
Density (g/cc)	1.33	1.23	1.24	1.23			
Composition, void (vol %)	21	24	24	25	high	high	high
Glass (vol %)	24	26	23	22	8	8	33
Graphite (vol %)	34	26	32	33	39	39	9
Resin (vol %)	22	24	21	20	~43	~43	~59
Failure mode	interply delamination between gl/gr	tensile	interply delamination between gl/gr	tensile	interply delamination between gl/gr	interply delamination between gl/gr	interply delamination between gl/gr

samples (20 g) (contained 2% methanol) were placed in small beakers (50 mL), which were then loaded into the multiple mode microwave cavity. Samples were subjected to various power levels (ranging from 80 to 740 W) of microwave radiation energy to investigate the interaction between microwave radiation and RP-46 resin mixture. The correlation between microwave power and sample temperature after heating for 10 min in the microwave oven listed in Table V. Temperature was measured immediately after the 10-minute time period by placing a thermocouple into the sample after turning off the microwave power. Therefore, these temperatures do not reflect the true sample temperature. It is estimated that these temperatures have an accuracy of ±10%.

However, the trend of an increase in temperature with increase in microwave power indicates that coupling is induced between microwave energy and the nadic-end-capped polyimide resin monomers. Since considerable reflected power results in the process, the overall efficiency of the imidization reaction is only 44% at the 60% power level. The small sample size (20 g in a 50 mL beaker) may account for some of this low efficiency, as discussed below.

Effect of Sample Size on Microwave Processing (Coupling)

Sample size and geometry are important considerations in microwave processes. Changing the sample size from 5 to 15 g caused a temperature

Table IV Foam Formation of Dried and Undried RP-46 Resin

RP-46 Resin Sample	Sample Size (g)	Power (%)	Time to Foam (s)
Dried	20	40	360
Dried	20	60	120
Dried	15	60	600
Undried	15	60	20

C8	C9	C10	C11	C12	C13	C14	C15	C16
see Table II	see Table II	see Table II	see Table II	see Table II	see Table II	see Table II	see Table II	see Table II
0.6	0.6	1.0	0.6	0.91	1.5	1.83	1.75	1.0
0.81 (13)	0.91(13)	0.91 (13)	1.05 (15)	1.05 (15)	1.05 (15)	1.05 (15)	1.05 (15)	1.05 (15)
delaminated	delaminated	200 (54)	528 (77)	370 (54)	372 (54)	588 (85)	481 (70)	354 (51)
		14 (2.0)	21 (3.1)	14.3 (2.1)	28.7 (4.2)	31.4 (4.6)	19.0 (2.8)	11.8 (1.7)
329	326	305	267	261	252	307	283	311
				1.50	1.40	1.46	1.62	1.35
high	high	high	high	7.5 42	~20 ~20	8.7 ~24	~10 38	~15 42
0	0	0	0	0 45	~20 ~40	~24 ~43	0 52	0 53
not measured	not measured	interply delamination	interply delamination	interply delamination	interply delamination between gl/gr	interply delamination between gl/gr	interply delamination	interply delamination

increase of 32°C in 10 min at the same power level, as shown in Figure 6. Essentially, no coupling occurs between a 5 g mass of RP-46 resin and microwave energy, clearly showing that a critical mass is required to absorb the microwave energy with efficiency.

Effect of Processing Time on Level of Imidization

Table VI shows the correlation between weight loss change of undried nadic-end-capped polyimide resin monomers (RP-46) and processing time at a fixed power level. Within 60 min, the weight loss (15%) became constant, indicating that almost complete imidization had occurred. Dynamic TGA was used to determine the weight loss, defined as weight loss at the TGA temperature of 325°C. The theoretical weight loss for imidization and crosslinking is 17 wt %. This raises the question of whether or not the microwave process under these conditions induced the thermal crosslinking reaction, which is required

Table V Effect of Power Level on Microwave Processing of Undried RP-46 Resin

Power (%)	Time (min)	Temperature (°C)	Forward *P* (W)	Reflected *P* (W)	Efficiency (%)
20	10	36	80	70	12.5
30	10	50	240	180	25.0
40	10	57	430	300	30.2
50	10	60	610	350	42.6
60	10	60	740	400	44.0

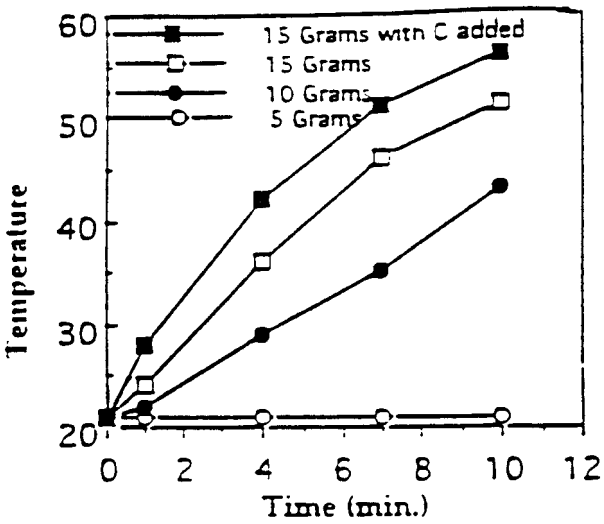


Figure 6 The effect of sample size on the microwave absorption of undried RP-46 resin.

for complete cure. A study of the crosslinking reaction using a bisnadimide model compound; namely, *N,N′*-(oxydi-3,4′-phenylene)di-5-norbornene-2,3-dicarboximide showed that microwave energy does induce the crosslinking reaction.[10] An interesting phenomenon in the present study is that the final temperature, about 60°C, does not change with increased processing time; and, yet, imidization becomes almost complete. With thermal processing, heating the undried monomer at 60°C for 2 days under vacuum only eliminates free methanol and does not cause imidization. Microwave processing for 10 min at 60% of power caused a 9.6 wt % loss, which matches the weight loss of thermal processing at 100°C for 60 min. The 15% weight loss after 60 min at 60% of microwave power is equivalent to thermal heating at 250°C for 1 h.

Effect of Graphite Fiber on Microwave Energy Coupling with Vacuum-Dried RP-46 Resin

To improve the microwave coupling, chopped graphite fiber was added in the vacuum-dried RP-46 monomer mixture and processed at different power levels. The results listed in Table VII show that graphite fiber greatly improved microwave coupling with the resin sample, as expected. With 2.9% of graphite additive, the high microwave absorption efficiency resulted in a temperature rise to 165°C, in only 11 s, resulting in a power efficiency of 78%. Clearly, power efficiency was much better with graphite fiber than without graphite fiber. With the size sample used in this study (20 g), without carbon fiber, the best efficiency was about 44%. For better process control, it was found that lower carbon levels (0.05 wt %) could be used to effectively convert monomer to imide at lower power levels (Fig. 7). At a power level of 220 W (30% of power), the measured temperature of the sample was 60°C, while at a power level of 760 W (60% of power), the measured sample temperature was 180°C. In both cases, complete imidization had occurred.

Characterization of the Cure Process

Infrared spectroscopy was used to characterize the changes due to amic acid and imide formation. Figure 8 compares the Fourier transform infrared (FTIR) spectra of uncured [Fig. 8(a)], thermally treated 200°C/1 h [Fig. 8(b)], and microwave-treated RP-46 resin [Fig. 8(c) and (d)]. Complete thermal imidization requires 1 h at 204°C [Fig. 8(b)]. Microwave treatment of air-dried powder at 60% of power (780 W) causes imidization [Fig. 8(c)], but this requires 2 h, showing the inefficiency of curing small quantities of resin and poor coupling efficiency of the resin with microwave energy. However, in the presence of only 0.05 wt % chopped carbon fibers, the imidization time was reduced to 6 min [Fig. 8(d)].

Comparison of the microwave cured specimens [Fig. 8(c) and (d)] with a thermally cured specimen (316°C/1 h) [Fig. 8(e)], reveals that, in both cases, the crosslinking reaction, as determined chemically by the disappearance of the sharp absorption peaks at 840 and 720 cm^{-1}, is incomplete. Complete crosslinking of the nadic end group requires thermal cure at 325°C for at least 12 h, illustrated in Figure 9(a) for postcured RP-46 resin and in Figure 9(b) and (c) for postcured bisnadimide model compound, *N,N′*-(oxydi-

Table VI The Correlation Between Weight Loss and Microwave Heating of Undried RP-46 Resin

Power (%)	Time (min)	Weight Loss (%)[a]
60	10	9.63
60	20	11.81
60	30	12.61
60	60	15.32
60	90	15.64

[a] Dynamic TGA weight loss at 325°C.

Table VII Effect of 2.9 Wt % Chopped Graphite Fiber on Microwave Energy Coupling with Vacuum-Dried RP-46 Resin

Power (%)	FP (W)	RP (W)	Time	Temperature (°C)	Efficiency (%)
20	80	30	5 (min)	128	62
30	220	60	3 (min)	228	73
40	430	100	80 (S)	348	77
60	760	180	11 (S)	165	76

3,4′-phenylene) di-5,6-norbornene-2,3-dicarboximide and in Figure 9(d) for uncured model compound, respectively. The peaks at 840 and 780 cm^{-1} become broadened, typical of a nadic-end-capped crosslinked spectrum. It is likely that other components formed during the postcure interfere with the ability to follow the disappearance of these peaks for an indication of the extent of crosslinking.

Composite Studies

The microwave oven used in this study is a conventional oven, Cober Electronic Model LBM, with a maximum output of 1200 W at 2.45 GHz frequency. The unit has no provisions for automatic temperature control, so that the power level was adjusted manually to reach a desired temperature range and heating rate. Samples were heated at a lower power level initially to prevent spark formation, especially for samples containing graphite cloth. In the cure of RP-46 resin, the following three reaction processes are involved: (1) the amidation step, which begins at about 100°C; (2) the imidization reaction, which initiates at about 150°C and above; and (3) finally, the crosslinking reaction, which initiates at about 275°C. For the vacuum-bag-processed composites, after the amidation and imidization steps, the composite was cured at a fast temperature ramp rate and at full vacuum to enhance the bonding between fiber and resin. In curing composites containing both graphite cloth with uncured resin (~ 35 wt %) and imidized RP-46 glass cloth (~ 50 wt % resin), a high temperature ramp rate and a constant full vacuum throughout the process were used, to remove volatiles and to minimize void formation. This is a critical step in the process since it determines the quality of the finished composite. In the studies described for neat resin, it was demonstrated that both amidation and imidization steps could be achieved in a short time and by low-level microwave irradiation. However, in these initial studies, there is no strong evidence that the crosslinking reaction was achieved by the microwave process.[9] However, subsequent studies on a bisnadimide model compound[10] showed that microwave energy effectively crosslinked the nadic-end-capped compound. We have investigated the microwave composite fabrication process with and without vacuum and with low pressure to assess the influence of vacuum on the process cycle. Other important parameters investigated in this work were the mold materials and substrates utilized in the composite fabrication process. A discussion of these parameters is given below.

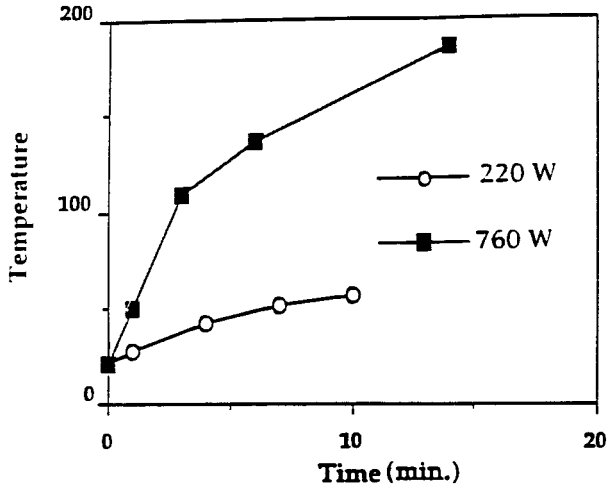
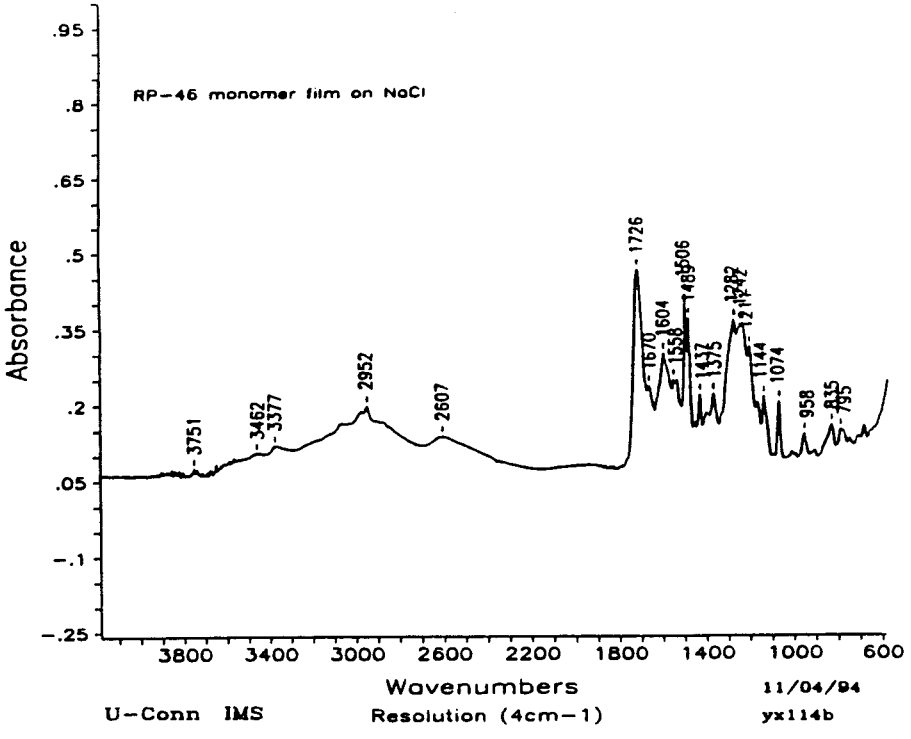


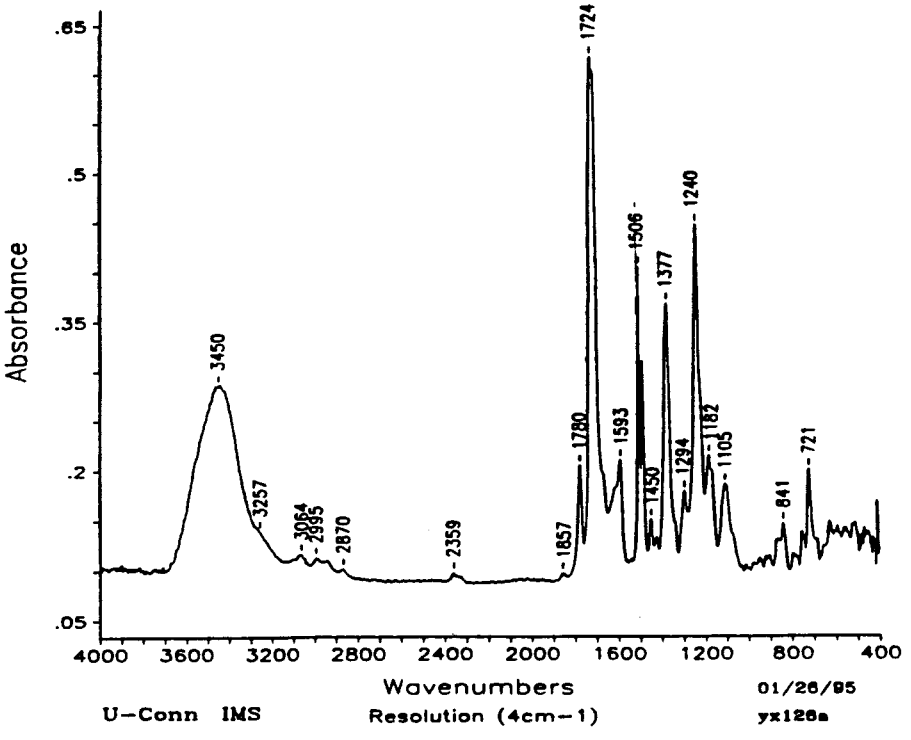
Figure 7 Temperature versus cure time of RP-46 resin containing 0.057 wt % chopped carbon fiber at (○) 220 and (■) 760 W.

Composites C1–4 Fabricated on Alumina Ceramic Molds Without Vacuum

Composites C1–4 were fabricated in an alumina ceramic mold at a pressure of 0.056 kg/cm^2 (0.8 psi) with no vacuum. The RP-46 resin in these

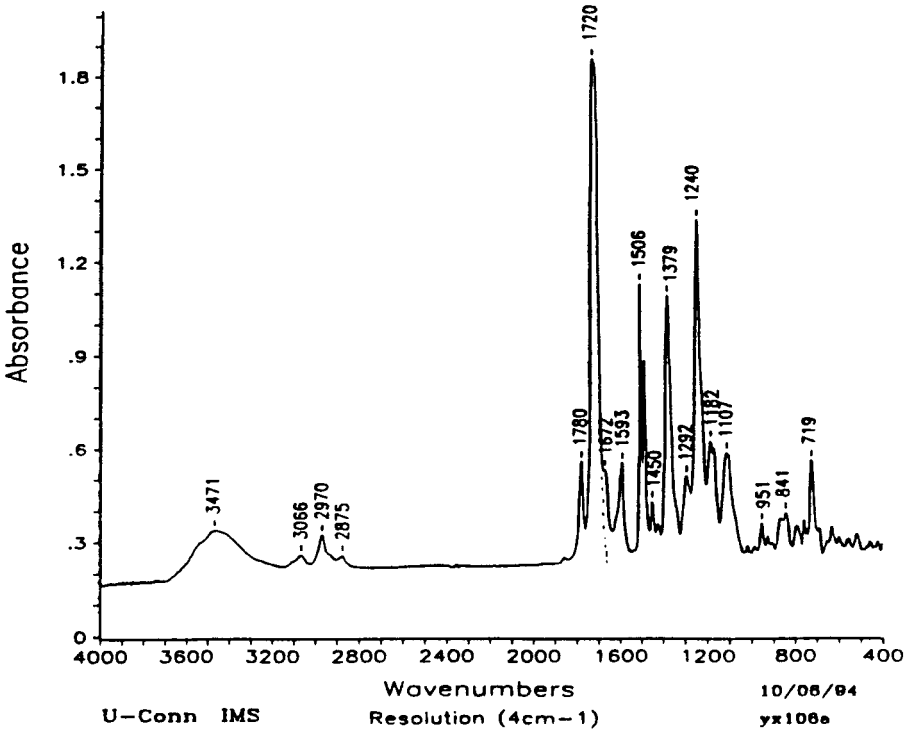


(a)

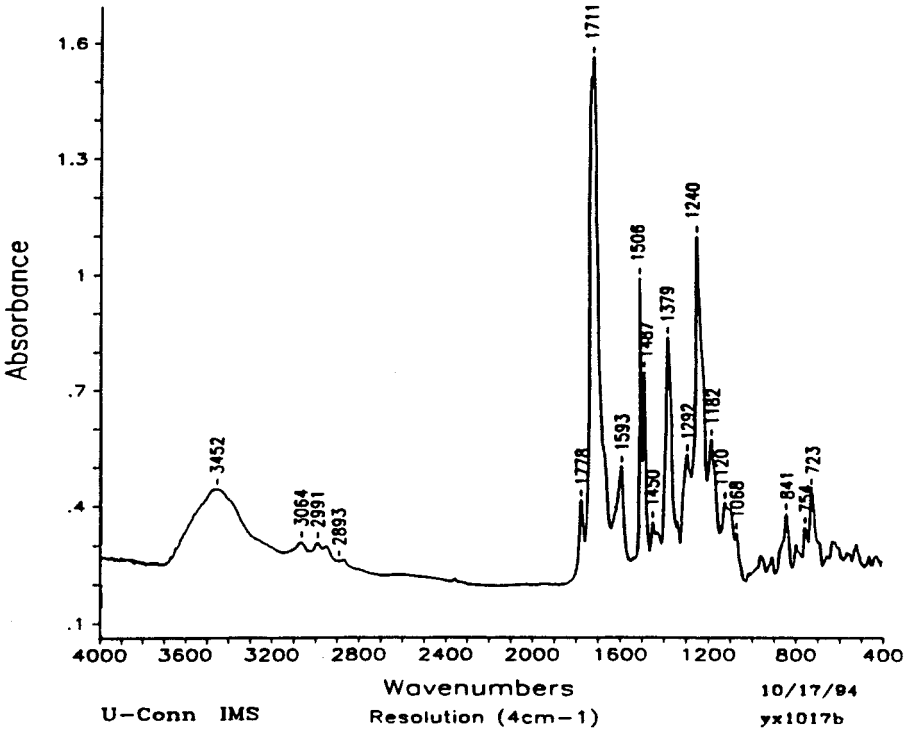


(b)

Figure 8 Infrared spectra of thermal and microwave-cured RP-46 resin: (a) RP-46 monomer resin; (b) RP-46, thermally cured at 204°C/1 h; (c) MW-cured 60% power, 2 h; (d) MW-cured 60% power, 0.057 wt % graphite fiber, 6 min; (e) RP-46, thermally cured at 316°C/1 h.

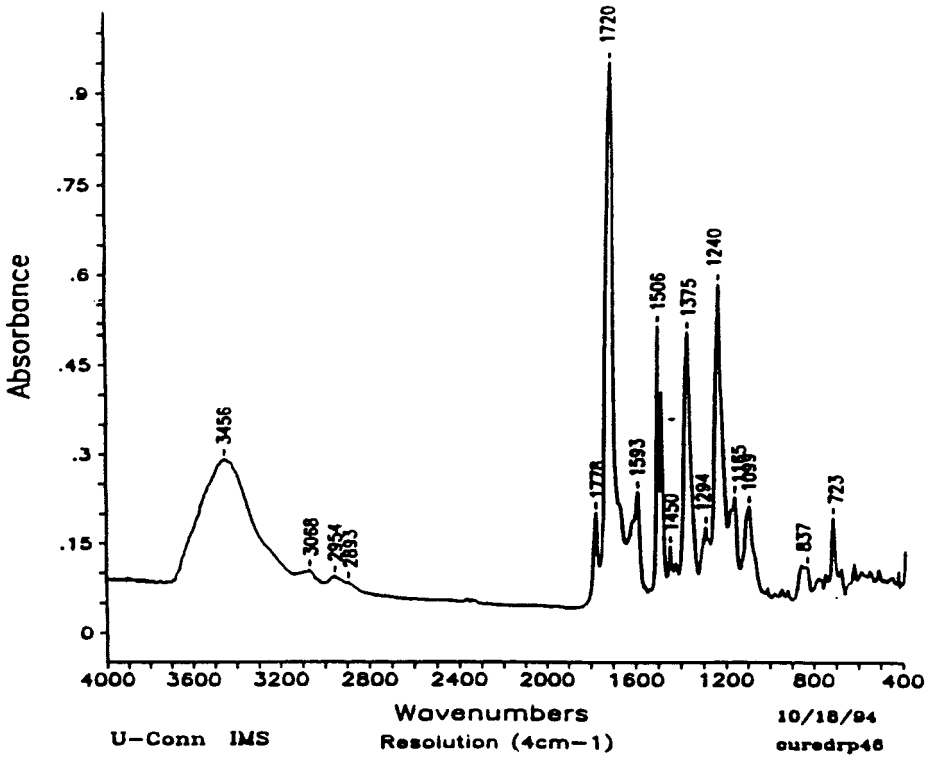


(c)



(d)

Figure 8. (*Continued from previous page*)

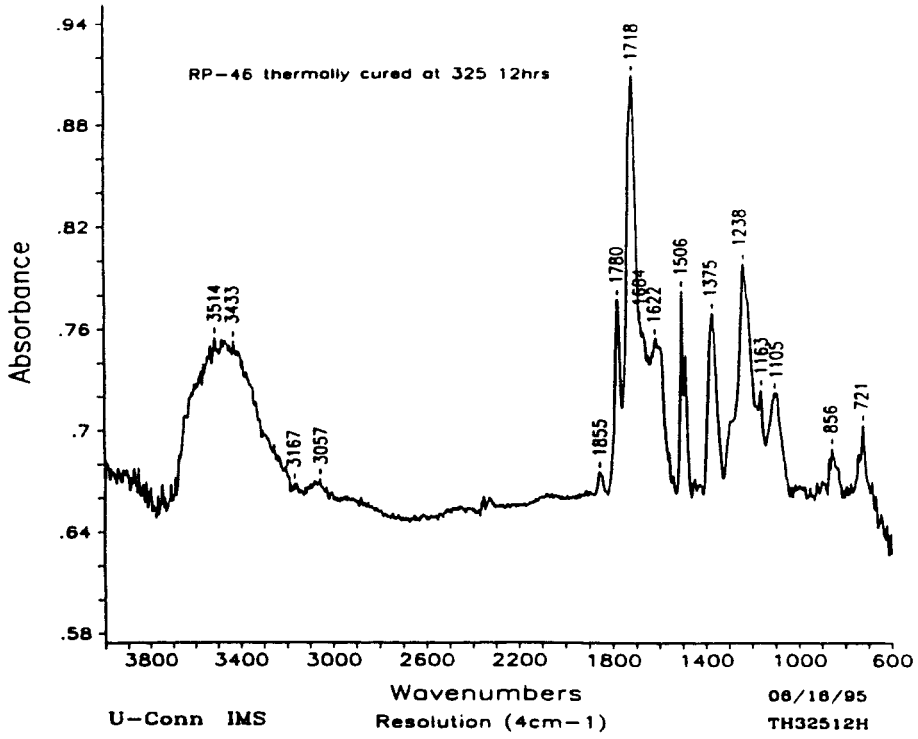


(e)

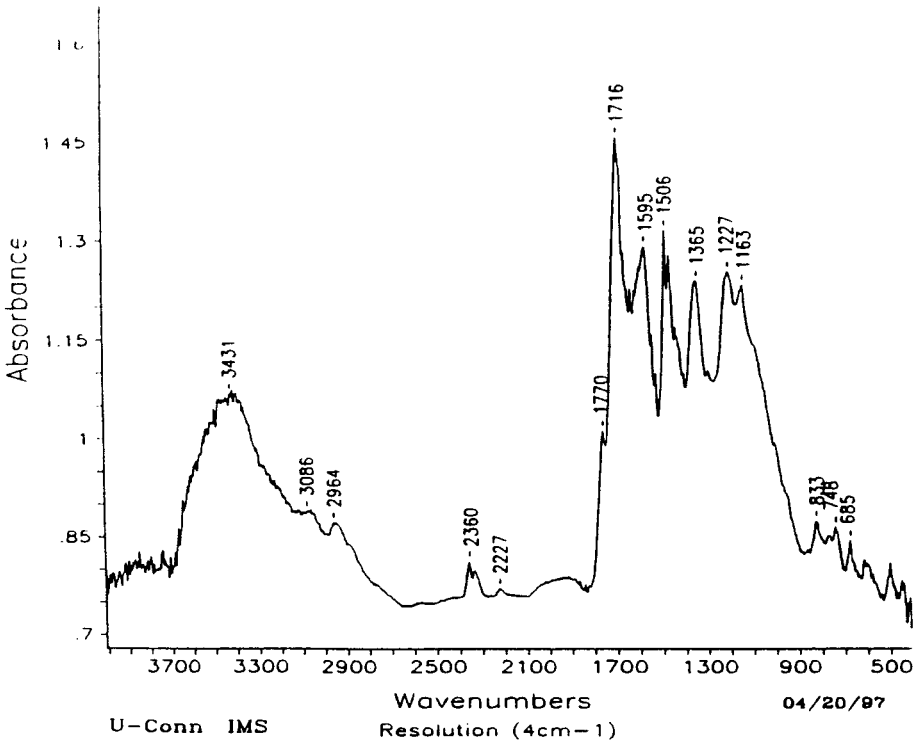
Figure 8. (*Continued from previous page*)

composites is in the uncured state, as noted in Table I. The lay-up for each laminate and microwave process parameters are listed in Tables I and II and in Figure 1. Characterization data, including T_g, composition, flexural strengths, and moduli, are shown in Table III. Infrared spectra of processed laminates C2, C3, and C4 are shown in Figure 10(a)–(c). The two key processes that are required to obtain good thermal and mechanical properties are (1) good interply adhesion and (2) complete resin cure. Good interply adhesion requires good resin flow within each fiber bundle and between ply layers. This can be obtained in the early stages of amidation and imidization in the temperature region at 125–150°C, and, later, during the crosslinking reaction in the temperature range of 275–300°C. However, even if these conditions prevailed during microwave irradiation, high resin viscosity requires significant force to consolidate the resin in order to promote interply adhesion. The low pressures of 0.056 kg/cm^2 (0.8 psi) utilized in this study therefore were not conducive for interply adhesion, as determined by the flexural properties and failure modes (Table III). Composite C4, which exhibited a flexural strength and modulus of 386 MPa (56 psi) and 19.4 GPA (2.8 msi), respectively, failed between plies. However, the process time for this composite was only 1.16 h, in contrast to composite C1, which exhibited better properties, but required a 2-h process time. The time required to process an RP-46 glass or graphite fiber composite with excellent mechanical and thermal properties by the thermal process is 16 h, including at least 10 h post-cure time.[12]

Complete cure must also be attained to exhibit good properties. In cases shown in Table III for composites C1–4 and others listed, the T_g's ranged from 267 to 300°C. RP-46 resin, cured at 316°C for 1 h, exhibits a T_g of 287°C. The IR spectrum of a sample cured in this manner [Fig. 8(e)] shows complete imidization. However, the presence of strong absorptions at 840 and 780 cm^{-1}, which is due to endo and exo isomers of the nadic-end-capped imide oligomers, clearly shows that thermal cure at 316°C for 1 h does not induce significant crosslinking. The IR spectra of composites C2, C3, and C4 are very similar to that in Figure 8(e), showing complete imidization and strong absorption at 840 and 780 cm^{-1}. There-

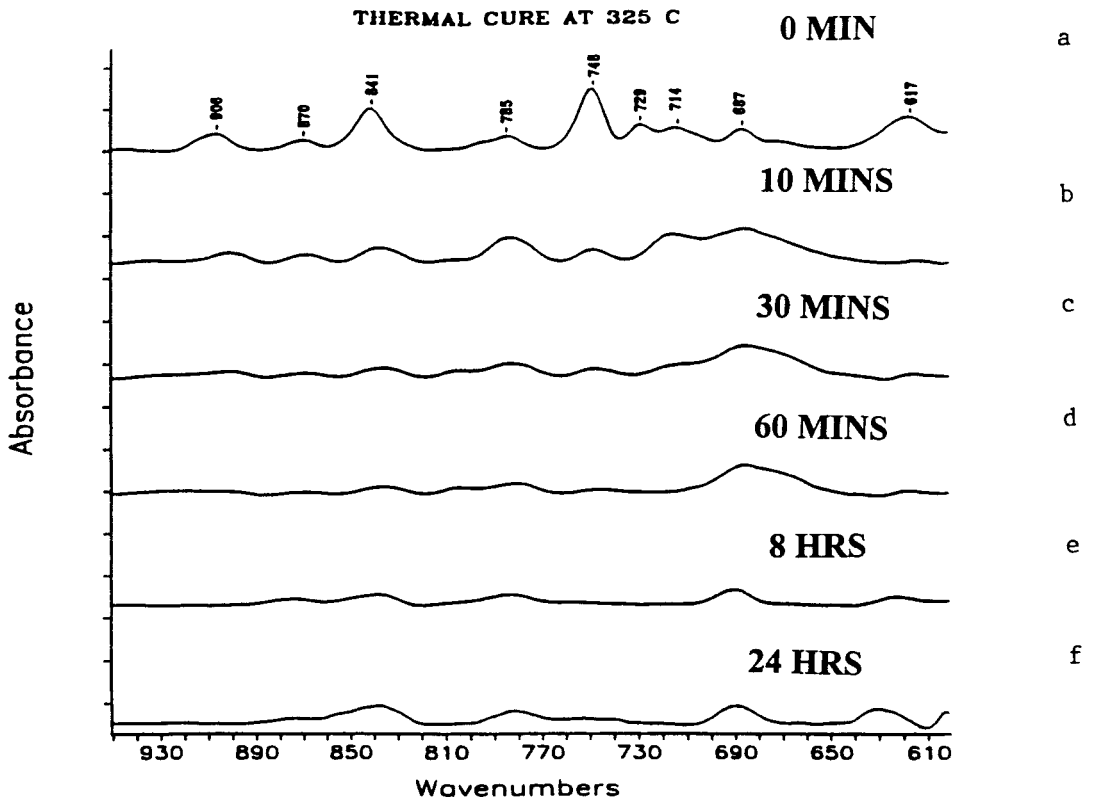


(a)

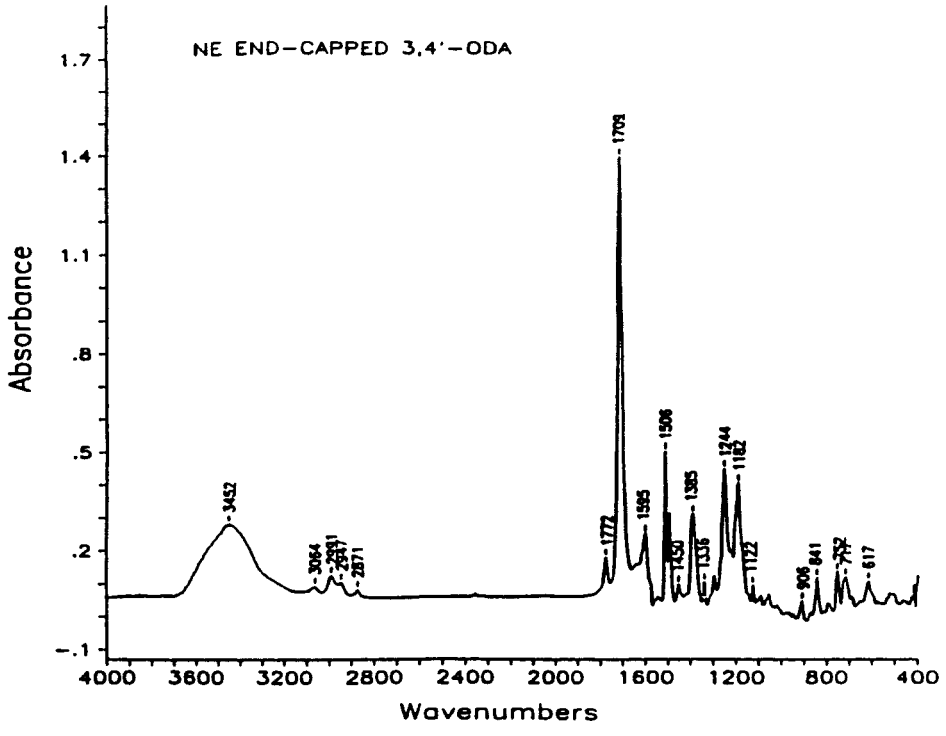


(b)

Figure 9 Infrared spectra: (a) RP-46 postcured at 325°C/12 h; (b) Model Nadimide compound *N′,N′*-(oxydi-3,4-phenylene)di-5-norbornene-2, 3-dicarboximide, postcured at 350°C/4 h; (c) Model Nadimide compound, postcured at 325°C, 0, 10, 30, and 60 min, and at 8 and 24 h; (d) Model Nadimide compound (uncured).

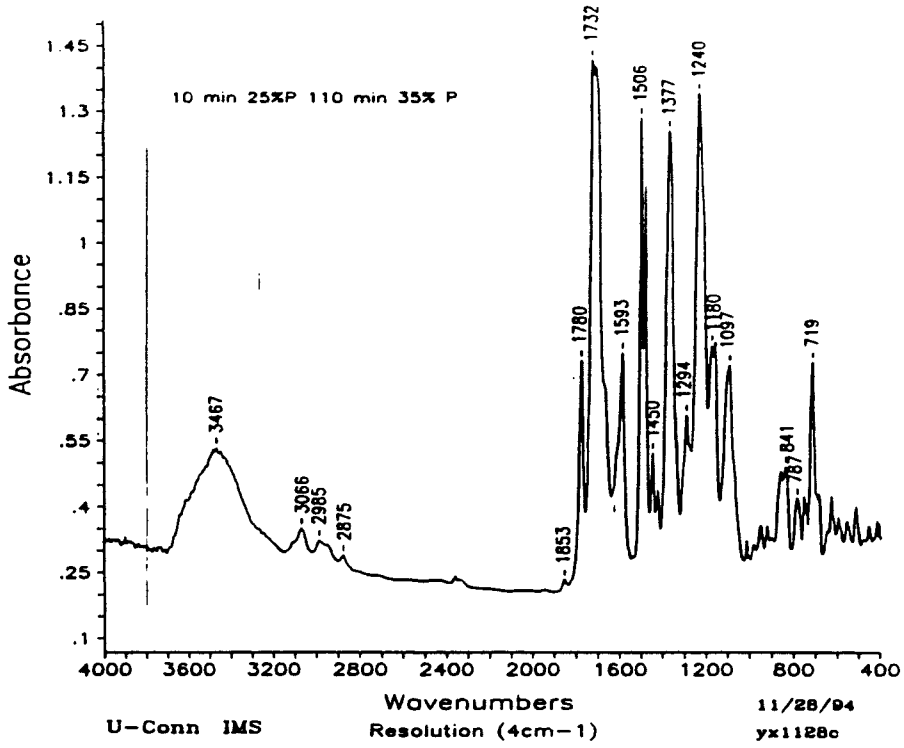


(c)

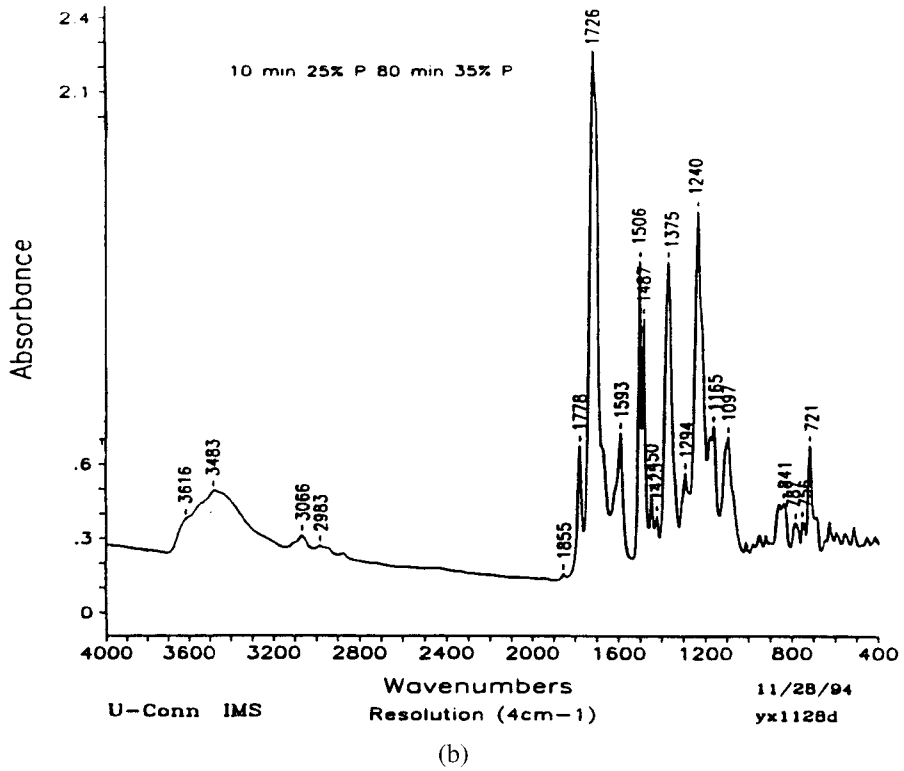


(d)

Figure 9. (*Continued from the previous page*)

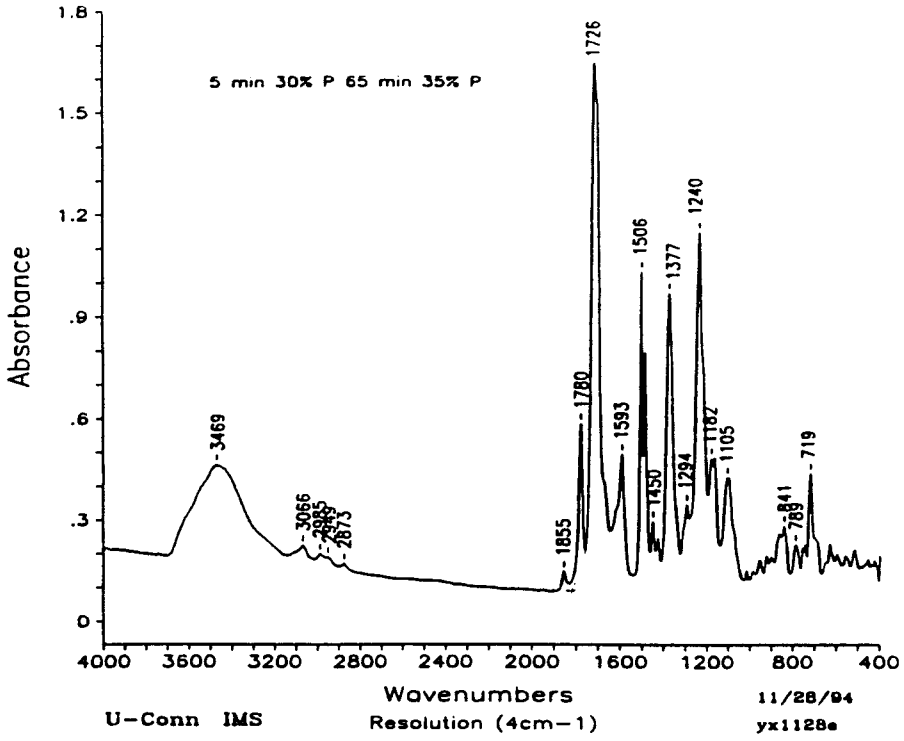


(a)



(b)

Figure 10 Infrared spectra of microwave-cured composites: (a) C2 (RP-46-24); (b) C3 (RP-46-25); (c) C4 (RP-46-27).



(c)

Figure 10 (*Continued from the previous page*)

fore, the T_g's exhibited by the microwave-cured composites indicate that insignificant crosslinking had occurred. As mentioned above, complete crosslinking is required for the resin to exhibit a high T_g (397°C) and good mechanical properties.[7,8]

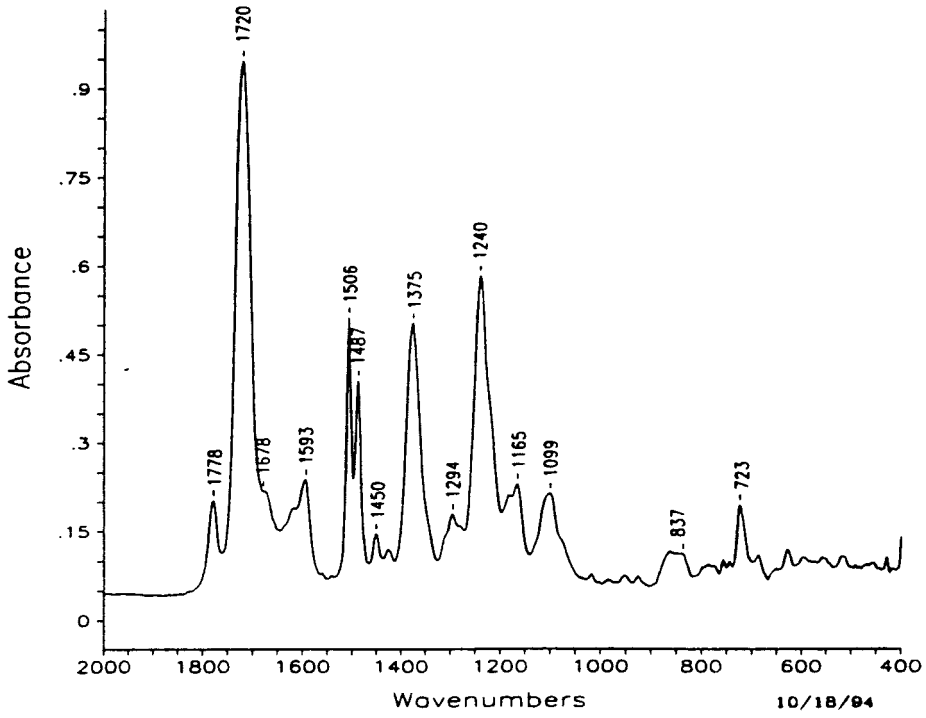
The low pressure used to consolidate the laminate was insufficient for resin flow, thereby leading to a highly porous structure. For this reason, most of the laminates contained high void content. The high void content and incomplete cure (crosslinking) therefore produces a system with low mechanical properties.

Composites Fabricated in Vacuum on Soapstone Molds at 1.05 kg/cm^2 (15 psi)

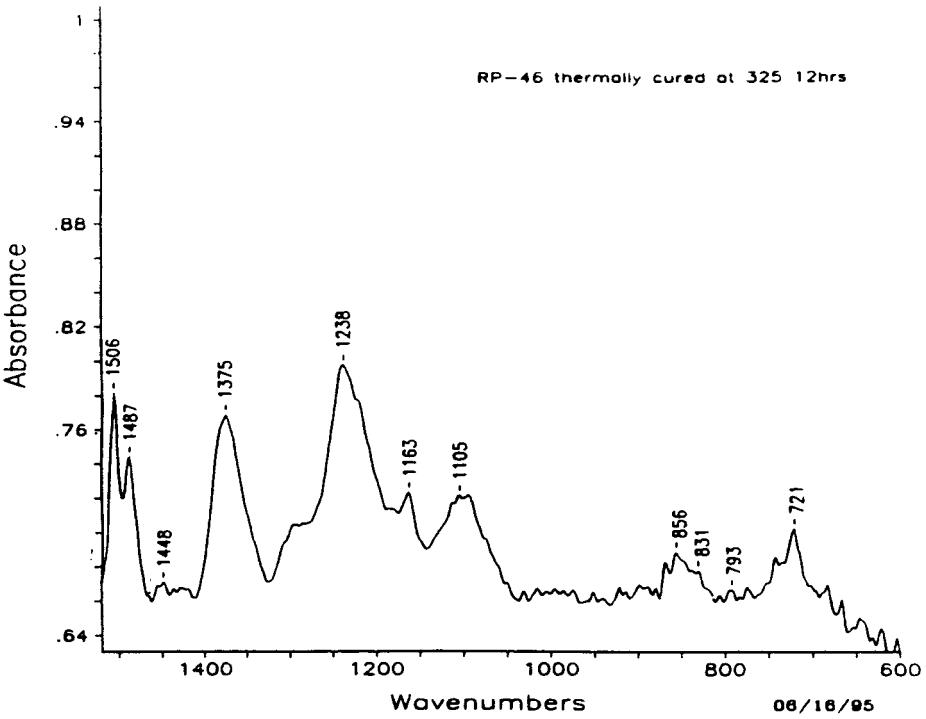
The composite series C5–C10 [Table III]), fabricated in vacuum on soapstone molds, exhibited similar properties as composites C1–C4 (Table III). Even though these composites were fabricated in full vacuum; and at a higher pressure than composites C1–C4, void contents were high. The relatively high T_g (302°C) for composite C6 is evidence of some degree of crosslinking, suggesting coupling of microwave irradiation with the composite mold set-up. The contribution of the soapstone to the cure process by absorption of microwave irradiation is significant. This is shown in Figure 5, a plot of temperature versus time at various power inputs. Clearly, within an hour at only 45% of power, the soapstone mold reaches a temperature of 360°C. Obviously, heat transfer from the soapstone to the composite plays a role in the cure of the RP-46 resin composite system. The extent of microwave absorption by the soapstone mold and by the resin laminate were not investigated in these experiments.

Composites Fabricated in a Vacuum in Teflon Mold at 1.0 kg/cm^2 (15 psi)

Composites C11–C15 containing uncured RP-46 resin were fabricated in a Teflon mold in vacuum, but with 0.63-cm-thick ($\frac{1}{4}$ in.) slabs of soapstone above and below the composite lay-up. These composites exhibited improvement in mechanical properties over the laminates cured on soapstone molds in Kapton vacuum bags (Fig. 2), showing the influence of the Teflon mold in this process. Both systems were processed at 1.05 kg/cm^2 (15 psi). Clearly, composite 13 exhibited good

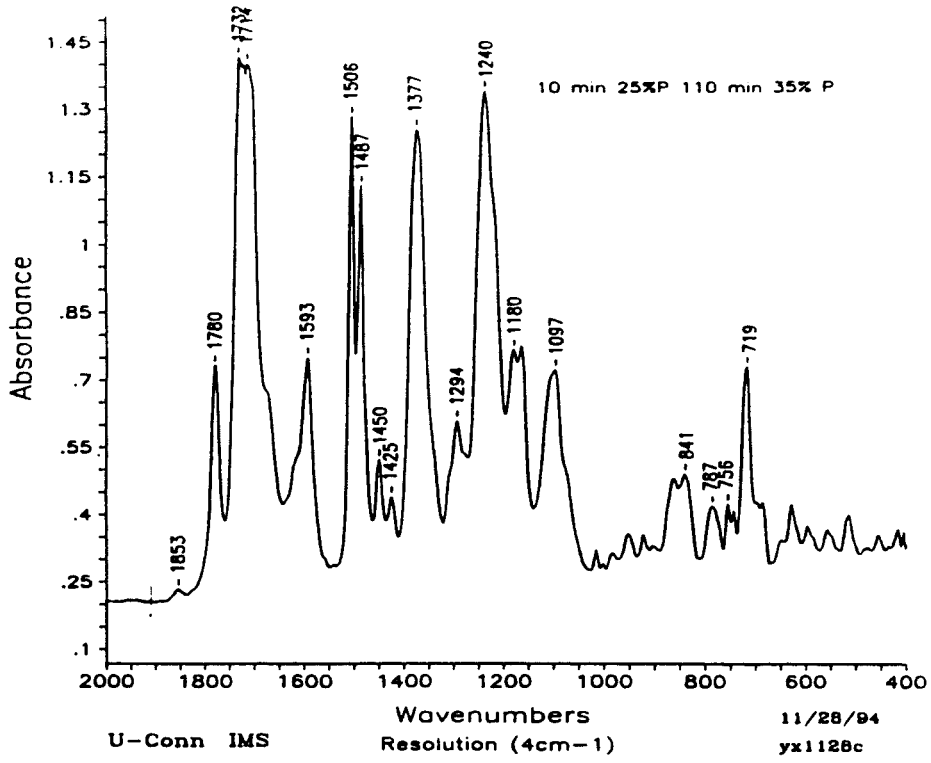


(a)



(b)

Figure 11 Infrared spectra of cured and postcured RP-46 resin composites: (a) RP-46, thermally cured at 316°C/1 h (wavelength region, 2000–400 cm^{-1}); (b) RP-46, thermally postcured at 325°C/12 h (wavelength region, 1450–600 cm^{-1}); (c) composite C2 (RP-46-24), microwave-cured (wavelength region, 2000–400 cm^{-1}); (d) composite C2 (RP-46-24), thermally postcured at 325 C/12 h (wavelength region, 1100–400 cm^{-1}).



(c)

Figure 11 (*Continued from the previous page*)

strength and modulus values [588 MPa (85 psi); 31.4 GPa (4.2 msi)], and thermal properties (T_g = 307°*C*). The densities of composites 11 and 13 systems (1.40–1.50) also indicate that these contain relatively low void content (7.5–8.7%) compared to the first two series described above. Therefore, the combination of Teflon mold, vacuum, 1.05 kg/cm^2 (15 psi), and soapstone served to produce composites with properties approaching those of thermally cured systems processed for 6.5 h at 17.5 kg/cm^2 (250 psi).[11] Soapstone has a profound effect on the process cycle, as illustrated in Figure 5. The temperature profile of the composite in the Teflon mold set-up (Fig. 3), which contains soapstone above and below the composite lay-up shows that within 50 min, the composite reaches cure temperature and appears to stabilize under the power output conditions noted in Figure 4.

Composites C11, C15, and C16 are glass–resin systems. Composite C11 exhibited good flexural strength and modulus, but poor T_g (267°C), indicating incomplete cure. This composite contained uncured resin, whereas composites C14 and C15 contained preimidized resin before microwave irradiation. The effect of preimidization on microwave irradiation gave conflicting results, as illustrated with composites C15 and C16. For example, composite C15 exhibited good strength 481 MPa (70 ksi) and stiffness properties 19 GPa (2.8 msi), high density, and low void. Therefore, it appears that coupling between the microwave energy and preimidized resin occurred to bring about consolidation of the plies. However, based on the low T_g (283°C), little or no crosslinking took place within this process time (1.75 h). However, the poorer strength properties, but higher T_g (311°C), exhibited by composite C16, suggests that poor consolidation occurred, but that some degree of crosslinking had occurred.

These preliminary experiments serve to show that nadic-end-capped polyimide resin and composite systems can be cured by microwave irradiation. The influence of pressure and other variables, such as time and power levels, on other microwave frequencies and fugitive absorbers and composite properties on the efficiency of microwave absorption require additional studies. These will be reported in subsequent publications.

Infrared Characterization of RP-46 Composites

Two composites, C1 and C13, were subjected to thermal postcure at 325°C/12 h. These showed a sharp increase in the glass transition temperature, from 289 and 284°C to 360 and 380°C, respectively. RP-46 resin thermally cured at 325°C/12 h generates a T_g of 393°C from 280°C after the thermal cure at 316°C/1 h. In both instances, initial cures were incomplete, clearly showing that crosslinking has not occurred to any great extent. The IR spectra support this view. The IR spectrum of thermal cure after 316°C/1 h and postcured at 325°C/12 h [Fig. 11(a) and (b)], in the absorption region of 1000 to 600 cm^{-1} are compared with microwave-cured composite C3 [Fig. 11(c)] and the same composite thermally postcured at 325°C/12 h [Fig. 11(d)]. The spectra of the thermal (316°C/1 h) and microwave-cured composite systems show complete imidization, but the presence of the absorption peaks near 840 and 780 cm^{-1} are strong indications that crosslinking has not occurred to any great extent. As mentioned previously, the IR spectra of the postcured composites, which show a broadening of absorptions in the 840 and 780 cm^{-1} regions, are most likely due to other components formed during postcure. This is typical of a highly crosslinked nadic-end-capped polyimide. Therefore, based on the T_g and IR data, under the conditions investigated in this study, only a small degree of crosslinking was induced by microwave energy.

CONCLUSION

Microwave energy was investigated to cure a nadic-end-capped polyimide resin, RP-46, and glass and graphite composites containing this resin. Under the conditions investigated, microwave irradiation caused complete imidization of neat resin and composites. Resin specimens containing only 0.057 wt % chopped graphite fibers exhibited complete imidization in 6 min. Microwave cure of glass and glass–graphite hybrid composites was accomplished over a period of 0.6 to 2.16 h, depending on the conditions. In both neat resin and composite studies in the absence of a soapstone absorber, under the microwave conditions investigated, crosslinking did not occur to any great extent. This was determined by glass transition temperature measurements and IR spectroscopy.

Soapstone mold material was found to be an efficient absorber for glass and glass–graphite composites, causing an effective cure in less than 1 h. Glass and glass–graphite hybrid composites with flexural strengths of 372–588 MPa (54–85 ks) and moduli of 28.7–31.4 GPa (4.2–4.6 Msi) have been fabricated by microwave irradiation. This is equivalent to 50 to 80% of the properties of composites fabricated by conventional thermal processes.

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