IN-SITU CURE MONITORING OF THE IMMIDIZATION REACTION OF PMR-15*

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Glass fiber reinforced polymer composites are becoming widely used in industry. With this increase in production, an in-situ method of quality control for the curing of the polymer is desirable. This would allow for the production of high-quality parts having more uniform properties.[1] Recently, in-situ fiber optic monitoring of polymer curing has primarily focused on epoxy resins and has been performed by Raman or fluorescence methods.[2-6] In addition, some infrared (IR) investigations have been performed using transmission or ATR cells.[7-9] An alternate IR approach involves using optical fibers as a sensor by utilizing evanescent wave spectroscopy.

Initial work at South Dakota School of Mines and Technology (SDSM&T) concerning the curing of epoxy adjacent an embedded silica optical fiber has been monitored in-situ by evanescent wave spectroscopy.[10] The epoxy studied was partially fluorinated and therefore had a refractive index lower than that of the silica optical fiber. The lower refractive index of the partially fluorinated epoxy allowed the fiber to be used as a waveguide for the internal reflection of IR light. This evanescent wave samples the polymer at the fiber/polymer interface. This combination of epoxy/silica served as a model composite system.

The bands used to monitor the cure of the epoxy were as follows: the C-N overtone absorbance band at 4725 cm^{-1} and the NH_2 combination band of the hardener at approximately 4925 cm^{-1}. It was found that the C-N band increased and the NH_2 band decreased over time. This result was expected, as epoxies react with the NH_2 in the curing agent to form C-N bonds while curing.

This method of cure monitoring has been applied to a PMR-15 composite system. Optical grade sapphire fiber has been chosen as the sensor due to its

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wide transmission range, high refractive index, and strength. The system will be used to determine the end of the immidization reaction or "gel point". It is important to know when the gel point has been reached because it is at this point that the Lewis Research Center Group increases the temperature and pressure applied in order to crosslink the polymer. Before the final product is made, PMR-15 can go through undesired temperature cycling simply through shipping and storing. This causes the polymerization reaction to be at different stages for different batches or lots of PMR-15. Because of this batch to batch variation, the time to reach the gel point can vary. By monitoring the reaction in-situ, the gel point can be found for each batch and variation in the quality of the final product may be reduced.

In order to monitor the PMR-15 reaction, we must first identify the bands present and determine which will be changing during the reaction. Spectra of the raw products of PMR-15 were collected using diffuse reflectance infrared Fourier transform (DRIFT) Spectroscopy. Spectra were also collected for the cured and uncured PMR-15 polymer. During the immidization reaction primary amines are converted to tertiary amines. Therefore, the reaction is complete when the primary and secondary amine bands have disappeared or stopped decreasing. Some examples of near-IR bands for the raw materials are as follows: 4,4'-methylene dianiline (MDA): amine stretching and bending combination 5000-5050 cm^{-1}, aromatic primary amines 6550-6850 cm^{-1}; 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA): aromatic CH stretch 5900-6100 cm^{-1}, carboxylic acid stretch 5300-5400 cm^{-1}; 5-norbornene-2,3-dicarboxylic anhydride (Nadic): carboxylic acid stretch 5300-5400 cm^{-1}. Complete identification of the bands is ongoing.[11-12]

Design of a curing cell to duplicate conditions at Lewis Research Center has been completed. The requirements of this cell were to maintain a temperature of 600 °F $\pm$ 1 °F for 60 to 90 minutes, to accommodate up to three 150 μm diameter sapphire fibers, and be easily cleaned without damage to the fibers. It was also designed to have a nitrogen blanket to prevent occurrence of oxidation reactions. Experiments to monitor the immidization reaction are currently being performed.

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Fig. 1

OUTLINE

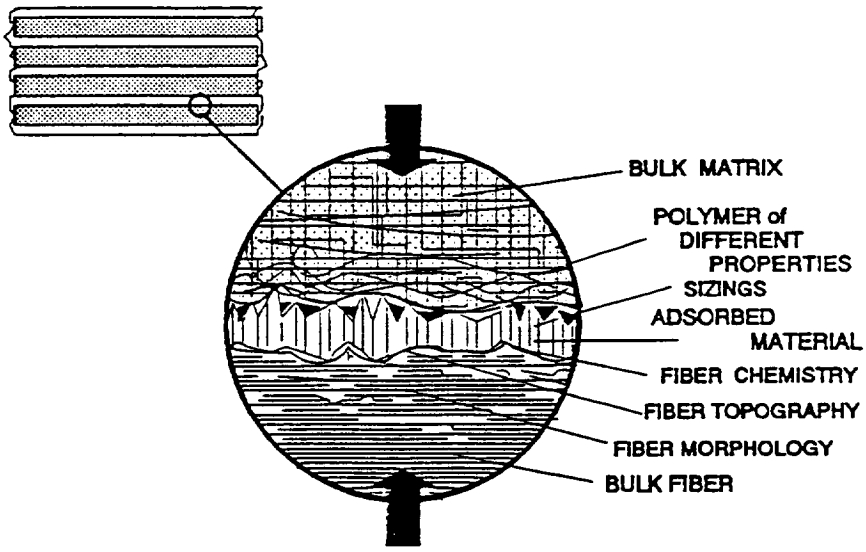
- Objectives
- Evanescent Wave Spectroscopy
- Silica Fiber Sensor
- PMR-15 Reaction
- IR Bands
- Summary of Results
- Conclusions
- Future Research

Fig. 2

OBJECTIVES

- Fiber selection
- Identification of PMR-15 IR bands
- Curing cell design
- Monitor immidization reaction of PMR-15

Fig. 3



FIBER-MATRIX INTERPHASE

P.J. Herrera-Franco and L.T. Drzal, Composites, 23, 1 (1992).

Fig. 4

FIBER OPTIC WAVEGUIDES

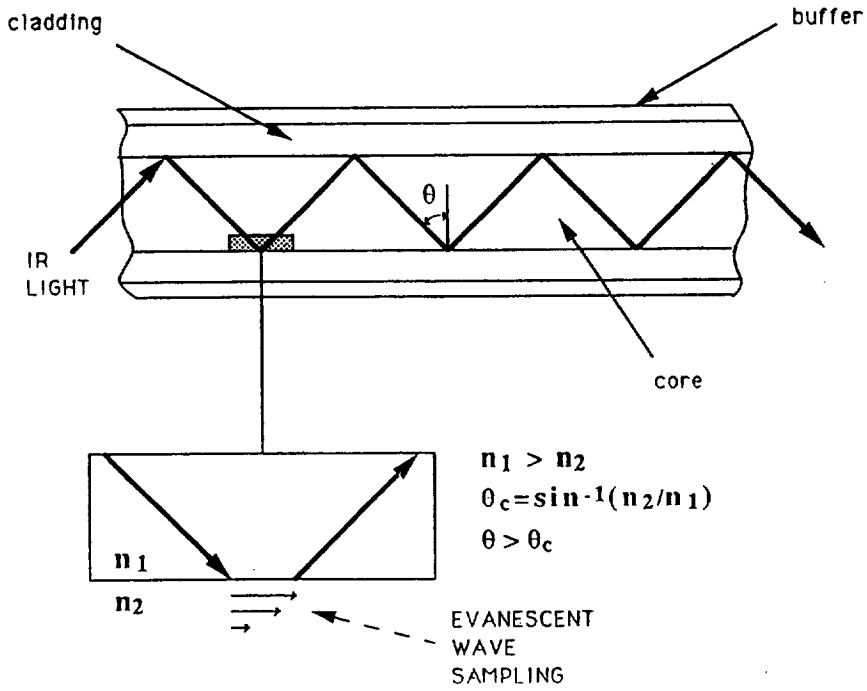


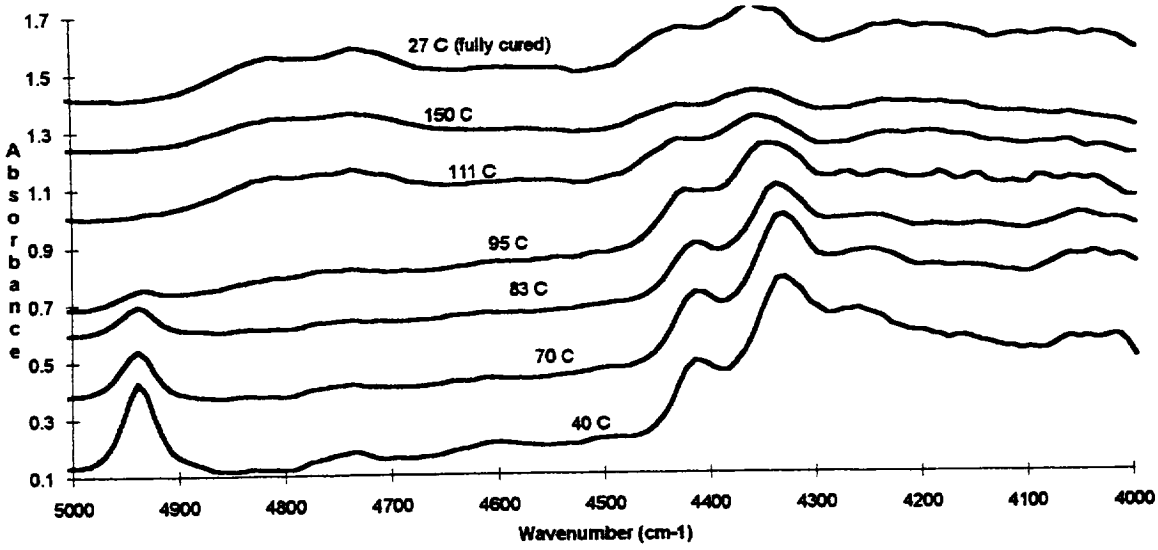
Fig. 5

SILICA FIBER SENSOR

- Create 1 cm sensing region in 140 μm diameter silica fiber
- Embed in Epo-Tek 328
- Heat to 150 °C for 1 hour
- Collect spectra during cure

Fig. 6

NIR Cure of Epo-Tek 328



Cossins, Connell, Cross, Winter, Kellar, Applied Spectroscopy, **50**, 900 (1996).

Fig. 7

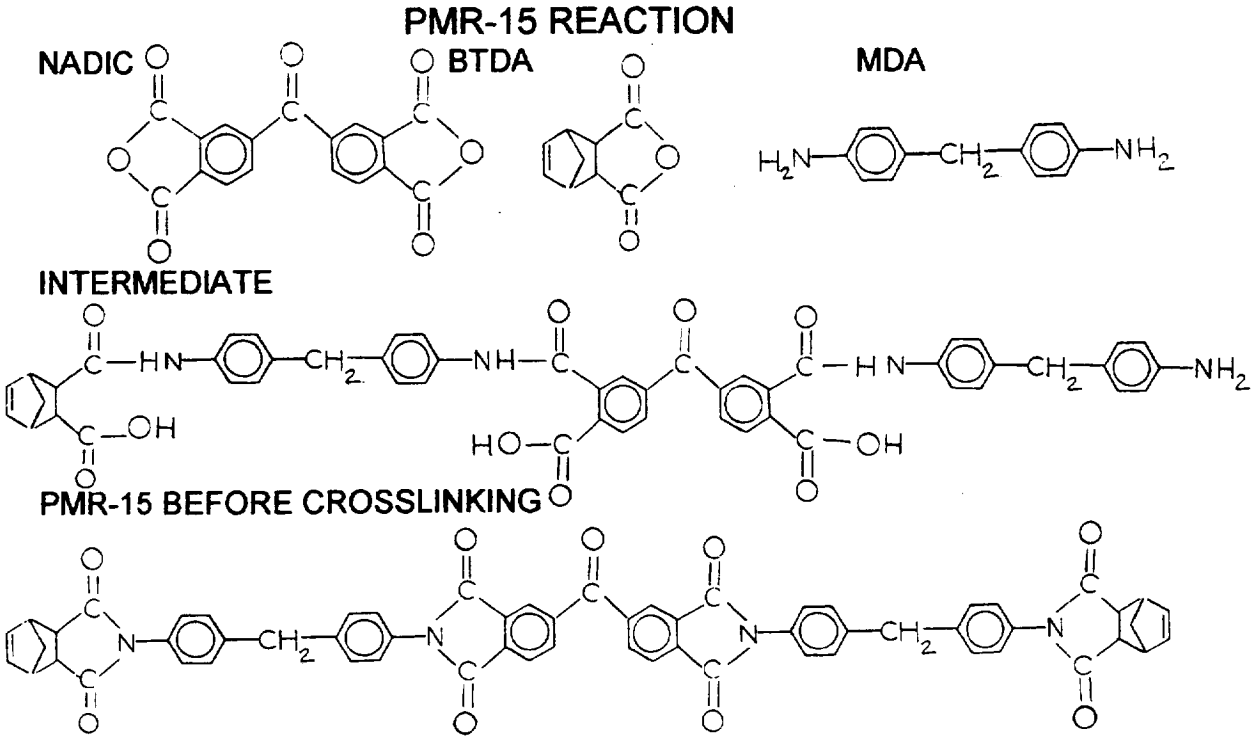


Fig. 8

Infrared Fibers and Their Transmission Ranges.

Fiber Type (core material)	Range (cm^{-1})
fused silica (ultra low -OH)	**26000-4000**
chalcogenide glass	**3333-1000**
zirconium fluoride	20000-2325
silver halide	3000-625
sapphire	**12000-2200**

Fig. 9

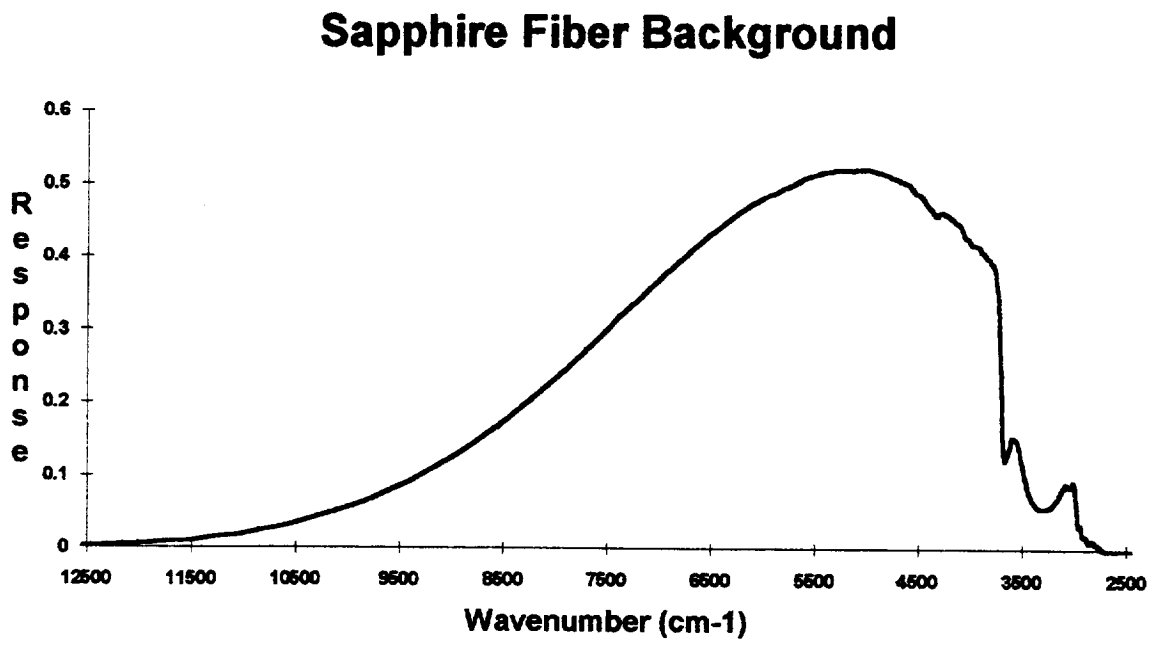


Fig. 10

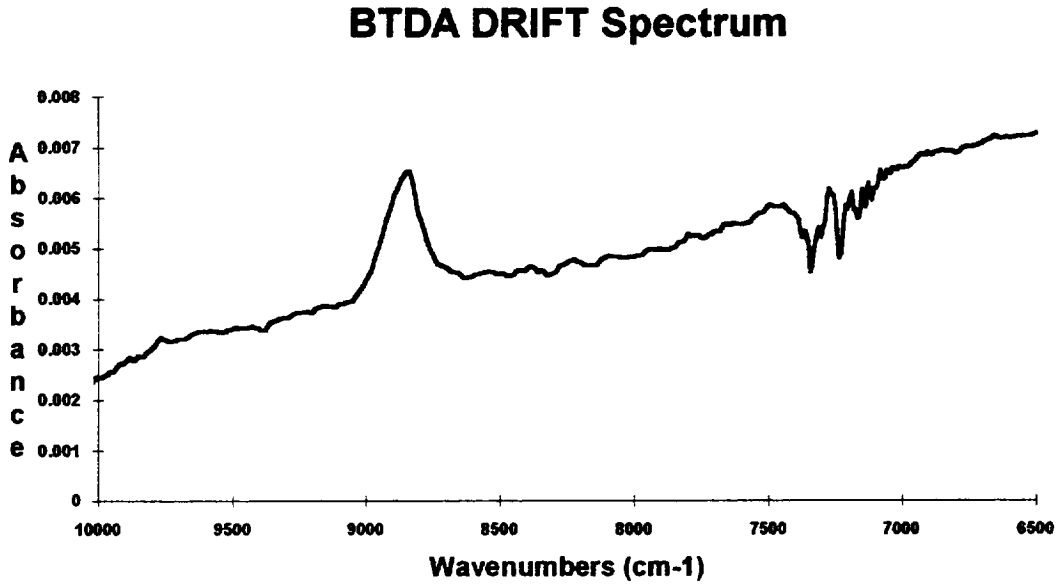

BTDA DRIFT Spectrum
Absorbance
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
10000
9500
9000
8500
8000
7500
7000
6500
Wavenumbers (cm-1)

Fig. 11

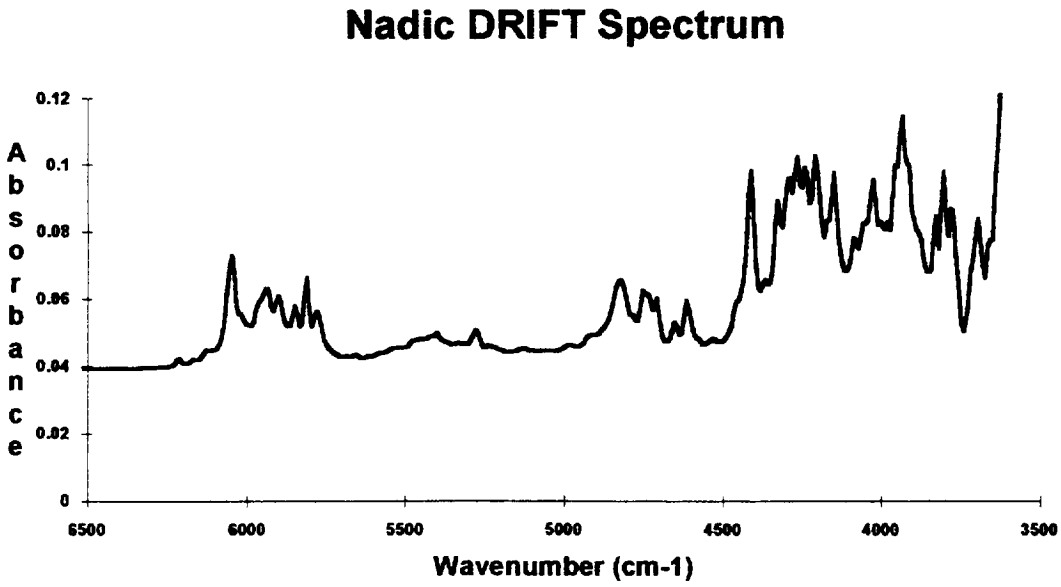

Nadic DRIFT Spectrum
Absorbance
0.12
0.1
0.08
0.06
0.04
0.02
0
6500
6000
5500
5000
4500
4000
3500
Wavenumber (cm-1)

Fig. 12

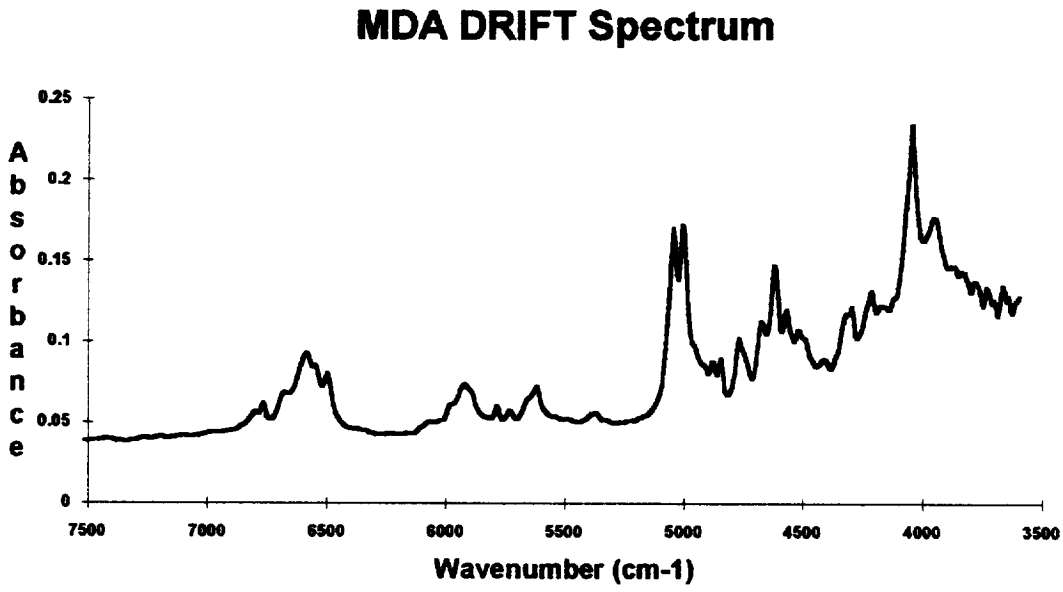

MDA DRIFT Spectrum
Absorbance
0.25
0.2
0.15
0.1
0.05
0
7500
7000
6500
6000
5500
5000
4500
4000
3500
Wavenumber (cm-1)

Fig. 13

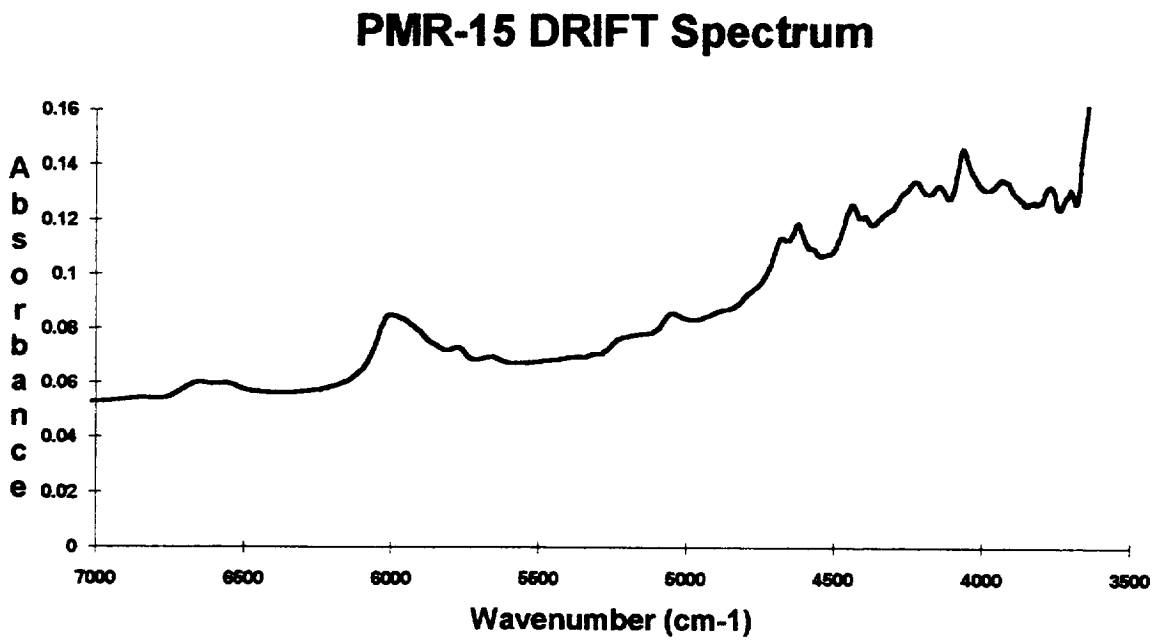

PMR-15 DRIFT Spectrum
Absorbance
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
7000
6500
6000
5500
5000
4500
4000
3500
Wavenumber (cm-1)

Fig. 14

SUMMARY OF RESULTS

- Sapphire fiber chosen
- Heating cell designed
- Possible IR bands for cure monitoring identified

Fig. 15

CONCLUSIONS

- Monitoring of the immidization reaction of PMR-15 is possible

Fig. 16

FUTURE WORK

- Obtain fiber spectrum and compare to DRIFT
- Identify and monitor IR bands changing with cure
- Develop correlation of band change to gel point

Fig. 17