

## CHARACTERIZATION METHODOLOGY

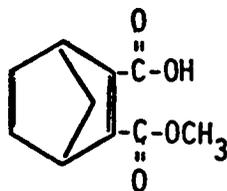
FOR PMR-15\*

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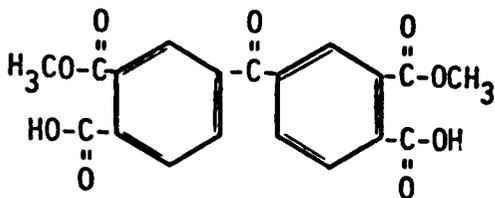
Characterization of model compounds, monomers, resin solutions and cure cycles of PMR-15 polyimide were performed. Successful separation of various reaction products were also accomplished by liquid chromatography. The PMR-15 cure analysis was performed by fourier transform spectroscopy and gas chromatograph - mass spectrometry. Characterization receiving inspection tests for Quality Control are recommended.

### INTRODUCTION

Within the aerospace industry polyimides are becoming increasingly important. One particular polyimide being developed for various uses is PMR-15 as developed by NASA-Lewis. PMR-15 consists of three monomers

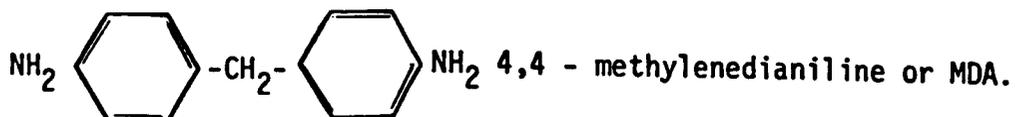


A monomethyl ester referred to as NE;



a dimethyl ester referred to as BTDE;

and



4,4 - methylenedianiline or MDA.

\*Work performed under contract NAS 3-22523.

The monomers polymerize under heat by the combining of BTDE and MDA with NE being an end cap. Final crosslinking occurs through the end cap. The material is usually received as a graphite prepreg and is then molded into part configuration under heat and pressure.

#### DEVELOPMENT OF METHODOLOGY

The starting materials for this polymer are 1) monomethyl ester of 5-norbornene -2, 3-dicarboxylic acid (NE), 2) Dimethyl ester of 3, 3', 4, 4' -benzophenone-tetracarboxylic acid (BTDE) and 3) 4, 4' - methylenedianiline (MDA). The two esters are synthesized from their respective anhydrides which are purchased commercially. The MDA is also purchased commercially. The starting products are then combined in a methanol solution to form the PMR resin. A suggested route for the polymerization of the resin system through the cure cycle is the formation of polyamide acid then polyimidization and finally the material becomes thermally crosslinked. Through the course of the reaction, water, methanol, and cyclopentadiene are evolved as reaction products.

The resin and starting materials were evaluated by liquid chromatography. Two modes were used as described below:

Mode	Adsorption	Reverse Phase
Columns	2 DuPont PSM60	Varian RP MCH10
Mobile Phase	1: THF:H <sub>2</sub> O with 0.01% Acetic Acid	Methanol Water
Program	Isocratic	Gradient 40:60 to 80:20 15 Min.
Detector	UV @ 210 and 254 NM	UV @ 210 and 254 NM

The isocratic method separates the esters their isomers and reaction products. (See Figure 1). One difficulty with this method is the MDA remains on the column and needs to be flushed out periodically to restore baseline. Another difficulty of the method is during the synthesis of the BTDE a small amount of triester is formed. The triester elution peak is sometimes poorly resolved with the NE peak. However, a quantitation can be made because the NE absorbs at 210 NM whereas the triester absorbs at both 254 and 210 NM. Figure 2 illustrates two batches of BTDE comparing a normal cook to one that has been overcooked. Figure 3 illustrates PMR resin with the formation of tetraester. The presence of tetraester has been correlated with a fall off in mechanical properties. The gradient method illustrated in Figure 4 separates the MDA from the esters. Although it does not show the detail of the isocratic method, it does permit quantification of the MDA. Also with this method a reaction product is detected as the resin ages, See Figure 5. Thermal analysis studies were also performed. Figure 6 illustrates a typical differential scanning calorimeter analysis performed in a pressure cell. One area of interest in the scan is the high temperature exotherm occurring at 587K denoting crosslinking taking place. The cure was also followed by infrared analysis which readily detects the disappearance of the MDA and formation of imide groups. In addition, the outgassing reaction products were monitored by

gas chromatography. Water, methanol and cyclopentadiene were all detected. Cyclopentadiene was first detected at 423K and as the sample reaches 573K a discontinuity occurs in the outgassing of cyclopentadiene that seems to correlate with the exotherm detected by DSC.

A number of methods were investigated to characterize the chemical and physical changes which occur during this cure cycle. The physical changes were found to be best characterized by dynamic mechanical analysis (DMA) using the DuPont compound pendulum method. Typical results are shown in Figure 7. The first three damping peaks occur at 373K (212°F), 423K (302°F) and 503K (446°F) and correspond very nicely with (1) the melting of the monomers, (2) the imidization reaction, and (3) the glass transition of softening and flow of the polyimide. The frequency curve, which is a measure of modulus, clearly shows that the first damping peak corresponds to a decrease in modulus (melting) while the second corresponds to the increase in modulus due to the imidization reaction. The third peak shows a frequency and damping relationship typical of the glass transition in a thermoplastic polymer. During the 30 minute holding period at 522K (480°F) both the damping and the frequency increase slightly which would be consistent with the completion of the ring closing imidization reaction and the continued flow of the thermoplastic polyimide. With the resumption of heating at the end of the 30 minute hold period, both the damping and the frequency decrease to a minimum at about 563K (554°F) and then increases as the crosslinking reaction caused by the thermal decomposition of the nadic ring begins to influence the flow properties of thermoplastic polyimide. Clearly the 30 minute hold period at 522K (480°F) is the proper point to apply pressure to effect the best possible consolidation of a composite material since it is just above the glass transition of the essentially complete polyimide and below the activation temperature for the crosslinking reaction.

Based on the characterization studies we have identified certain Receiving Inspection tests for Quality Control. The starting materials are controlled by liquid chromatography. The resin and prepreg are controlled by liquid chromatography, infrared analysis and gas chromatography. These tests have successfully identified non-processable material and materials with low mechanical properties during this contract.

#### LIQUID CHROMATOGRAPHY

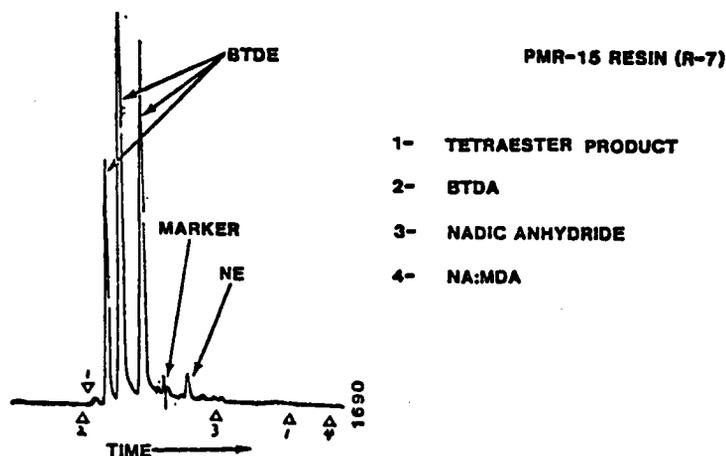


Figure 1

**LIQUID CHROMATOGRAPH  
BTDE**

**BATCH 5017**

**BATCH 4982**

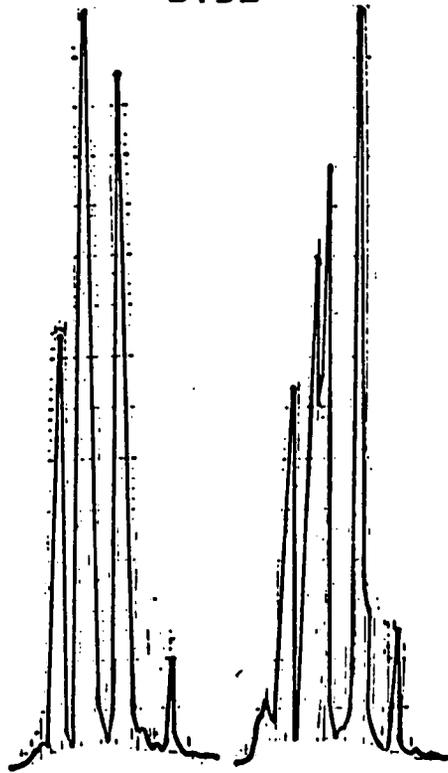


Figure 2

**LIQUID CHROMATOGRAPHY**

**PMR-15**

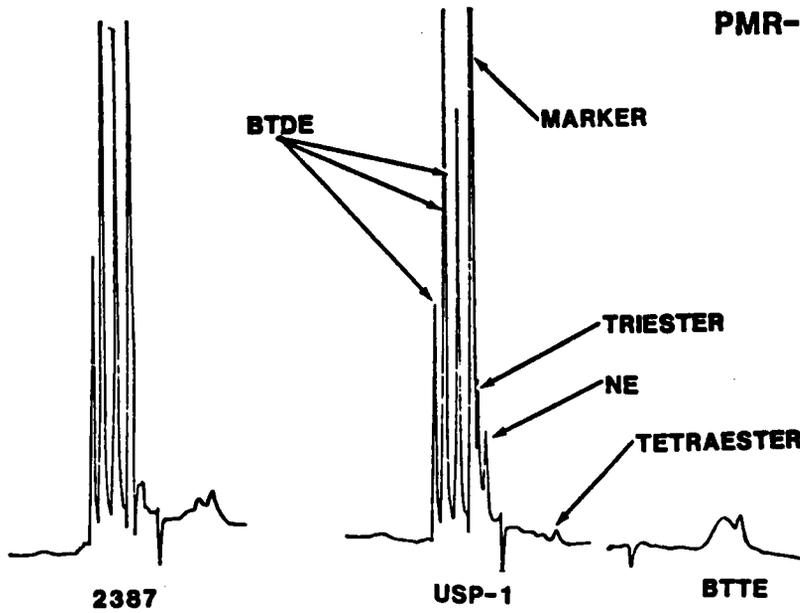
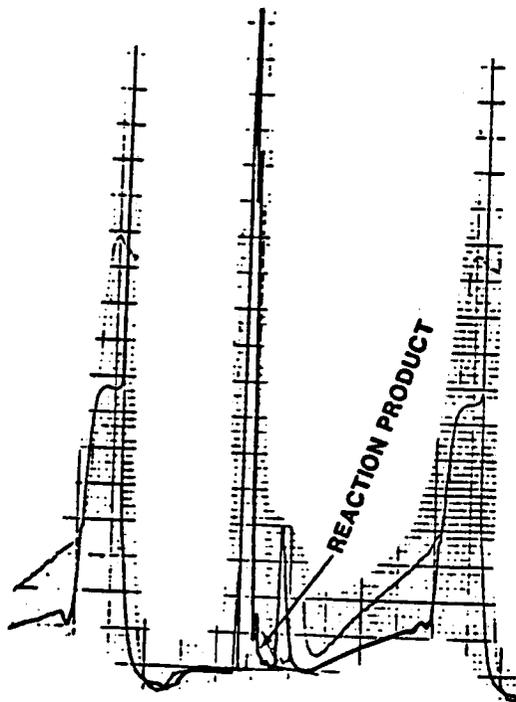


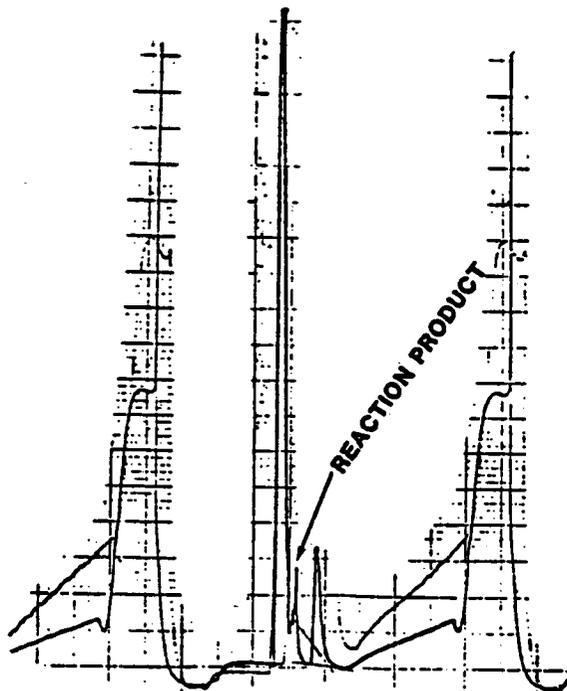
Figure 3



PMR-15

HPLC OF 67% SOLUTION RESIN - FRESH - UNAGED

Figure 4



PMR-15

HPLC SOLUTION RESIN AFTER 24 HOURS AT 316K(110°F)

Figure 5

Sample: PMR-15 LOT-G05244 R-2

Size: 13.22 AS RECD

Rate: 10C/MIN

DSC

Date: 7-Dec-82

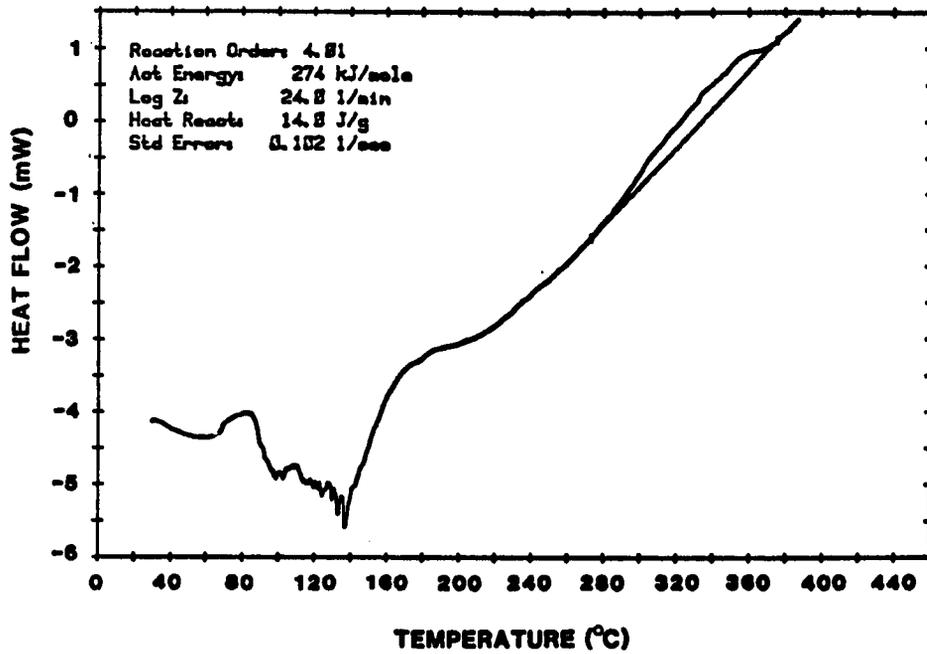


Figure 6

Sample: PMR-15 2187 3-PLY

Size: 18.7 X 6.35 X .33

Rate: 1.7

DMA

Date: 28-Oct-82

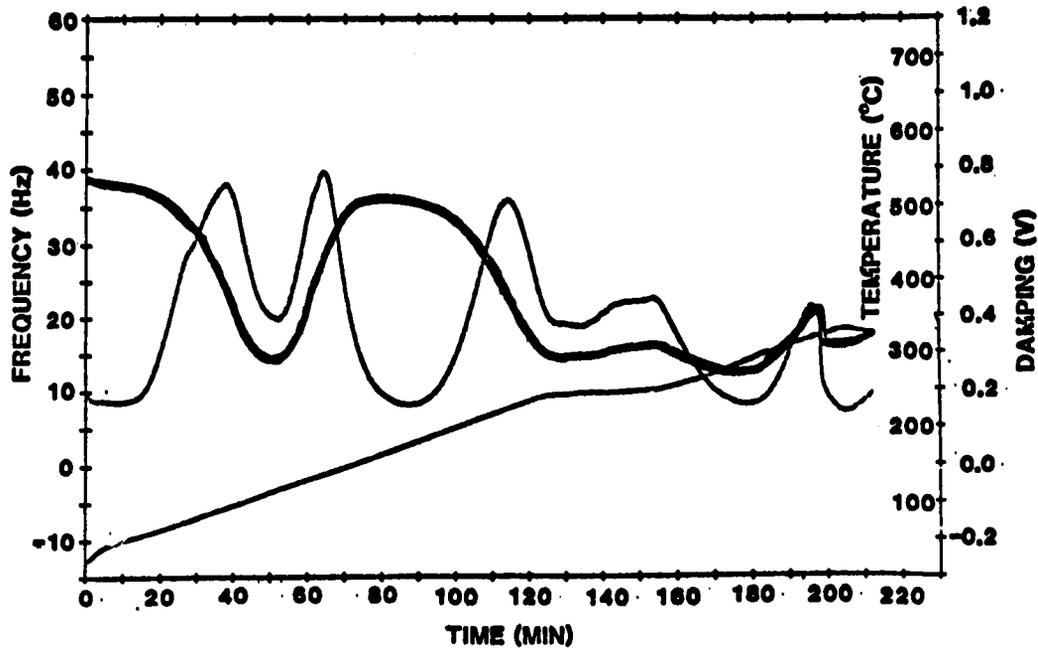


Figure 7