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Abstract

The contributions of individual resin components to total resin weight loss in 600°F air aged Celion 6000/PMR-15 polyimide composites were determined from the overall resin weight loss in the composite by chemically separating the PMR-15 matrix resin into its monomeric components. The individual resin components were also analyzed by spectroscopic techniques in order to elucidate curing and degradation mechanisms of the PMR-15 matrix resin. The isothermal weight loss of the individual resin components during prolonged 600°F thermo-oxidative aging of the composite was correlated to the changes observed in the Fourier Transform infrared spectra and Fourier Transform nuclear magnetic resonance spectra of the individual resin components. The correlation was used to identify the molecular site of the thermo-oxidative changes in PMR-15 polyimide matrix resin during 600°F curing and prolonged 600°F thermo-oxidative aging.

1. INTRODUCTION

The study of curing and thermo-oxidative degradation of high temperature resins and their composites is usually attempted by thermomechanical, thermogravimetric and spectroscopic techniques. However, thermomechanical techniques only provide curing and degradation data in a "cause and effect" manner by observation of changes in physical characteristics such as mechanical properties or glass transition temperatures. Similarly, thermogravimetric techniques only serve to quantify the net overall result of degradation as a thermal or thermo-oxidative weight loss. In reality, a considerable quantity of thermal or thermo-oxidative molecular changes may have occurred in the resin before detection of their effects by thermogravimetric techniques is possible. Presently, spectroscopic techniques are probably the best method for reducing the "cause and effect" limitations imposed in determining the mechanism of curing and the occurrence of degradation in a resin or its composite. However, the elucidation of curing mechanisms and degradation pathways is complicated in spectroscopic techniques by technical limitations such as interfering absorbances or resonances, incompatible physical sample state for analysis and data complexity. The application of any of the three methods to model compounds has the same limitations, but in addition, a further margin for error is introduced by the question of whether the model accurately represents the desired polymer system.

The purpose of this study was to characterize in a less equivocal manner the compositional changes, curing mechanisms and degradation mechanisms of PMR-15 polyimide matrix resin during curing and prolonged thermo-oxidative exposure of graphite fiber composites. In order to avoid the pitfalls inherent with the thermomechanical, thermogravimetric and spectroscopic techniques, the bulk resin and composite samples were chemically separated into gravimetrically determinable monomeric components. These components were then characterized by application of the routine accepted techniques of Fourier Transform infrared spectroscopy (FT-IR), Fourier Transform nuclear magnetic resonance spectroscopy (FT-NMR), liquid chromatography (LC) and elemental analysis. The results of the characterization are discussed in terms of molecular sites for curing and thermo-oxidative degradation. The individual resin component isothermal weight losses were calculated and their contributions to overall resin isothermal weight loss were empirically correlated to observed composite thermo-oxidative performance. The correlations of the individual resin component weight loss to the resin component molecular degradation characterization are also presented.

2. EXPERIMENTAL

2.1 MATERIALS AND WEIGHT LOSS DATA

The neat resin plug used in this investigation was prepared under high pressure from PMR-15 molding powder cured for one hour at 600°F as described in reference 1. The Celion 6000/PMR-15 composites used in this investigation were the mechanical test specimens that had been fabricated, aged and tested in earlier studies.[2] The 600°F air weight loss data for the composite and the PMR-15 resin in the composite were the weight losses from the above laminate.[3]

2.2 RESIN COMPONENT SEPARATION

The PMR-15 polyimide neat resin plug (2.5984 gm.) was first broken into pieces and then digested in warm hydrazine hydrate (20 ml. of 85% solution at 80°C for 72 hours). The dark solution was acidified by slowly adding it to 200 ml. of 6N hydrochloric acid. The resultant bishydrazide derivative of 3,3',4,4'-benzophenonetetracarboxylic dianhydride was collected by suction filtration, water washed and air dried at 60°C to yield 1.3285 gm. (105.1%) of brown powder. The filtrate was made basic by slowly dissolving sodium hydroxide pellets. The resultant black precipitate was collected by suction filtration, water washed and air dried at 60°C to yield 0.0255 gm. (2.0%) of partially hydrolyzed bishydrazide. These two precipitates were combined, redigested in 10-15 ml. of 85% hydrazine hydrate (80°C for 6 hours) and reisolated from acid solution as described above to yield 1.2782 gm. (101.1%) of brown bishydrazide derivative, m.p. >360°C. A precipitate was not obtained when the filtrate was made basic. This basic solution and the earlier basic solution were combined, heated to 60°C for one hour, cooled to 25°C and extracted four times with 40 ml. portions of chloroform. The combined yellow chloroform layers were washed twice with 20 ml. portions of water, dried over magnesium sulfate, gravity filtered, evaporated and air dried at 40°C to yield 0.9814 gm. (92.7%) of brown 4,4'-methylenedianiline (MDA), m.p. 85-88°C. The aqueous layer was acidified to pH 4-5 by addition of 6N hydrochloric acid and then allowed to evaporate to dryness at room temperature. Acetic anhydride (100 to 125 ml.) was cautiously added to the resultant brown sodium chloride mass (1/2 to 1 inch in bottom of the one liter evaporation breaker). This was heated at 100°C for six hours during which time the salt residue changed to fine white granules and the acetic anhydride/acetic acid solution turned brown. The slurry was cooled to 40°C and the excess acetic anhydride was cautiously hydrolyzed by dropwise addition of 400 ml. of water over a three hour period. The resultant brown and white precipitates were collected by suction filtration and washed with hot water until the white precipitate (acetylhydrazine) had dissolved. The brown product was air dried at 60°C to yield 0.5985 gm. (78.5%) of polymerized nadic crosslinker, m.p. 280-300°C. The filtrate was extracted six times with 100 ml. portions of chloroform. The combined yellow chloroform layers were washed three times with 50 ml. portions of warm water, dried over magnesium sulfate, gravity filtered and air dried to yield 22 gm. of white acetylhydrazine. This was dissolved in 100 ml. of warm water, suction filtered, water washed and air dried at 60°C to yield an additional 0.0688 gm. (9.0%) of polymerized crosslinker, m.p. about 150°C. This filtrate and the above filtrate were combined, evaporated to about 300 ml. and re-extracted three times with 20 ml. portions of chloroform. The combined yellow chloroform layers were washed three times with 10 ml. portions of hot water, dried over magnesium sulfate, gravity filtered evaporated and air dried to yield 3.0 gm. of white acetylhydrazine. This was dissolved and decanted four times with 20 ml. portions of warm water to leave 0.0316 gm. (4.2%) of polymerized crosslinker which solidified upon standing, m.p. about 130°C. The total yield of crosslinker recovered was 0.6989 gm. (91.7%).

Elemental Analysis, % C, H, N
Calc. for $(C_{11}H_{12}N_2O_3)_n$
amide-imide C=59.99,H=5.49,N=12.72
Found-crop 1 C=56.13,H=5.42,N=12.04
-crop 2 C=59.09,H=6.09,N=8.88
-crop 3 C=62.18,H=7.80,N=8.34

For chemical separation of cured and 600°F air aged composites, the above neat resin separation scheme was used except, that in addition, first the graphite fiber was isolated as described in reference 3. The procedure for the composite separation also differed from the neat resin procedure as follows: (1) the initial composite digestion proceeded in 8 hours instead of 72 hours, (2) the amount of resin in the composite sample was 5 or more times smaller, (3) larger water and neutralization salt volumes were handled (resulting from the fiber washings), and (4) 5 to 10 times more hydrazine hydrate per gm. of PMR-15 resin in the composite vs. neat resin was used (to immerse the resultant fiber mass during digestion). In all the composite digestion/separations the bishydrazide precipitates were redigested as was done in the described neat resin procedure in order to lower the yield of the partially hydrolyzed bishydrazide precipitate (from basic solution) to less then 0.001 gm.

2.3 RESIN COMPONENT WEIGHT LOSS

The individual resin component weight losses were calculated according to the following equations:

(1) Percent weight recovered of PMR-15 components = (component weight isolated x 100)/component weight initially in sample = (component weight isolated x 100 x 1500)/(initial sample weight x initial resin weight fraction x n x mw), where mw = molecular weight of isolated derivative and n = stoichiometry in PMR-15; 2.087 for bishydrazide derivative, 3.087 for diamine and 2.000 for crosslinker.
(2) Percent weight loss = 100 - percent weight recovered.

The theoretical amount of crosslinker percent weight loss was also calculated with equations 1 and 2 using as the component weight isolated the maximum crosslinker weight possible at each exposure time equal to (aged sample weight x aged resin weight fraction) - (diamine weight isolated x [mw diamine - 4 hydrogen mw]/mw diamine) - (bishydrazide weight isolated x [mw bishydrazide - mw 2 hydrazine]/mw bishydrazide). All weight loss determinations were calculated from single data points except for zero exposure time composites, which were digested in triplicate. The overall percent resin weight losses in the composite were from same composite samples as reported in reference 3.

2.4 INSTRUMENTAL EQUIPMENT

Nuclear magnetic resonance spectra were obtained on a commercial 80 MHz Fourier Transform instrument. Resonances were referenced to an internal tetramethylsilane standard or the chloroform peak. NMR samples of model compounds and separated PMR-15 resin components were prepared in deuterochloroform or trifluoroacetic acid for proton measurements and in trifluoroacetic acid for carbon measurements, both at a 10 percent concentration or less if solubility was limited. All proton data were electronically integrated. Infrared spectra were obtained on a commercial Fourier Transform spectrometer. Model compounds and separated PMR-15 resin components were examined as solids in potassium bromide pellets. Liquid chromatographic separation of the polymerized crosslinker (before and after acetic ahydride treatment) was done on a commercial HPLC with a 60 x 60 x 125 Å microporasil column set using a 50/50 water/methanol solvent and a refractive index detector followed by a 254 nm ultraviolet detector.

3.0 MODEL COMPOUNDS AND REACTIONS

Spectral standards of the bishydrazide derivative of 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were prepared by treatment of the dianhydride with hydrazine hydrate ($N_2H_4 \cdot H_2O$) and with $N_2H_4 \cdot H_2O$ in acetic acid to yield 95.0% of a yellow brown powder, m.p. $>$ 360°C and 98.5% of a light yellow powder, m.p. $>$ 360°C, respectively. The infrared spectra were identical.

Spectral standards of the diamines were the as received, commercially available, highest purity, white 4,4'-methylenedianiline (MDA) and the as received commercially available, white 4,4'-diaminobenzophenone (BDA), m.p. 245.5-247°C. Both diamines were treated in $N_2H_4 \cdot H_2O$ at 80°C to show that: (1) MDA is recovered in 98.9% yield without undergoing any oxidation during digestion conditions, and (2) BDA forms an 83.9% yield of the hydrazone derivative, m.p. 161.5-162°C, during digestion conditions but hydrolyzes during the dilute acid digestion/isolation conditions to reform BDA in a 97.1% yield.

Model reactions of the aliphatic nadic anhydride crosslinker (NA) showed the adduct of $N_2H_4 \cdot H_2O$ with NA was a 75.9% yield of the 5 membered ring, N-amino imide, m.p. 138-140°C (rather than the 6 membered ring, aliphatic hydrazide). The literature supports 5 member ring formation from aliphatic anhydrides and 6 member ring formation from ortho substituted aromatic anhydrides for their reactions with hydrazine.[4,5] The 5 membered ring N-amino imide was characterized by IR, NMR, elemental analysis and reaction with acetic anhydride to give a 63.6% yield of the acyclic/cyclic bisimide derivative, m.p. about 110°C. The IR, ^{1}H-NMR and ^{13}C-NMR spectra of both agreed with the assigned structures.

Elemental Analysis, % C, H, N

Calc. for $C_9H_{10}N_2O_2$	
Amine-imide	C=60.67,H=5.66,N=15.72
Found	C=60.80,H=5.37,N=15.17
Calc. for $C_{13}H_{14}N_2O_4$	
Bisimide	C=59.53,H=5.38,N=10.68
Found	C=59.31,H=5.50,N=10.80

Model digestions of N-phenyl nadimide were performed to show that the low molecular weight PMR-15 crosslinker fractions would not be lost as result of solubility in water during the digestion procedure. Thus, the recovery of the model crosslinker after digestion was 87.9% of a mixture of N-amino imides and N-amino amide acids, m.p. 85-100°C. These crosslinker digestion products were reacted with acetic anhydride to show the low molecular weight PMR-15 crosslinker products would not be lost due to water solubility during the isolation of the digested crosslinker products. Thus, the recovery of these digested hydrazine derivatives after treatment with acetic anhydride was 88.5%, calculated as the acyclic/cyclic bisimide, m.p. about 110°C.

4. RESULTS AND DISCUSSION

4.1 PMR-15 DIGESTION/SEPARATION

Figure 1 illustrates the digestion/separation scheme used to isolate the three resin components and fiber (if any) of cured PMR-15 resin and postcured/thermo-oxidatively aged PMR-15 composites. The digestions were done using hydrazine hydrate with a procedure similar to the one originally used for condensation polyimides.[6] A subsequent procedure reported[7] for separating the digested condensation polyimide resin components was modified in this study in that the dianhydride was isolated as the biscyclohydrazide derivative (instead of as 3,3',4,4'-benzophenonetetracarboxylic dianhydride, BTDA). Also several additional new steps were developed to isolate the addition cured nadic anhydride crosslinker (polymerized NA). During the process of verifying these modifications of the developed analytical procedure, the following conclusions were made:
(1) The modified procedure can be successfully used to separate and isolate the three components of cured PMR-15 resin.
(2) Redigestion of the bishydrazide precipitates is required to obtain representative gravimetric results and to obtain no more than three types of isolated components.
(3) Some intermixing of the components is present even after redigestion.
(4) The modified separation procedure is quantitative for all three components except when isolating the crosslinker from postcured and aged composite samples.

4.2 RESIN COMPONENT WEIGHT LOSS

Using the modified separation procedure on Celion 6000/PMR-15 composite specimens fabricated and tested for previous studies[2,3] with the 600°F resin weight loss data and the calculations described in section 2.3, the 600°F weight loss of the three resin components and the theoretical 600°F weight loss of the crosslinker component were determined. The 600°F composite weight loss and the overall 600°F resin weight loss data shown in figure 2 for these composites were taken from reference 3. Figure 3 shows the 600°F weight loss of the BTDA and 4,4'-methylenedianiline (MDA) components of these composite samples. A weight loss for the BTDA component was not observed throughout the exposure time. Instead, the weight of the BTDA bishydrazide recovered was consistently greater than the theoretical amount based on BTDA initially formulated. This strongly suggests that the digestion procedure did not provide a clean separation, and accordingly the weight of undigested MDA raised the recovery of the bishydrazide consistently above 100%. More importantly from the minimal slope of the BTDA curve it may be concluded that the BTDA component does not significantly contribute to the weight loss of the PMR-15 composites in a 600°F air environment. The weight loss of MDA from PMR-15 samples was approximately 10% from cured resin and postcured composites. The 10% weight loss slowly increased to more than 50% weight loss after 2100 hours of 600°F air exposure. The overall position of the MDA weight loss curve is probably not exact because of the inherent difficulties in completely separating the MDA from the BTDA and crosslinker components. However, in spite of these difficulties, a uniform weight loss behavior for MDA was found. Also, as can be seen in figure 4, when these data were plotted as a function of the square root of exposure time, a straight line was obtained which could be extrapolated to zero weight loss at zero exposure time. The linear dependence of MDA weight loss on square root of exposure time indicates that the weight loss is diffusion controlled. More importantly, the levels of MDA lost clearly indicate that MDA is a major contributor to observed resin weight loss.

Figure 5 shows the experimentally determined (chemical separation) and theoretical weight loss curves of the NA crosslinker component. The wide scatter of the experimentally determined data indicates that the crosslinker component was not quantitatively isolated from the postcured and aged PMR-15 composite samples. The limits of the isolation procedure were exceeded because of the need to work with small samples and large quantities of reagents and solvents. In two instances where the experimental data points were nearly equal to or greater than the theoretical values, infrared analysis showed that the isolated crosslinker also contained other compounds. Thus, it may be concluded that the amount of crosslinker isolated represented only a fraction of the total crosslinker present at each exposure time.

In order to determine the actual amount of 600°F crosslinker weight loss the assumption was made that the exposed sample weight minus the combined weights of the BTDA and MDA isolated was equal to the theoretical crosslinker weight. The amount of crosslinker present at each exposure time and its weight loss were then calculated as described in section 2.3. The theoretical crosslinker weight loss, shown in figure 5, indicates that after an initial weight loss of about 15% in 300 hours the crosslinker weight remains fairly constant out to 1200 hours. Although the crosslinker does degrade and loses weight during the 300 to 1200 hour time interval, any loss in weight is offset by competitive weight gaining thermo-oxidative molecular changes. After 1200 hours of exposure degradative molecular changes predominate and rapid weight loss occurs. This finding correlates with the overall 600°F performance of PMR-15 composites. Excellent retention of mechanical properties and a surprisingly low composite weight loss are observed for up to 1200-1500 hours of 600°F air exposure.[2] After 1200-1500 hours of exposure the degradation rate of the PMR-15 composite and the crosslinker component increased significantly. The BTDA component showed virtually no weight loss and the MDA component showed a leveling off of its contribution to resin weight loss as exposure time increased. The three resin component weight loss curves and the overall resin weight loss curve are plotted in figure 6 for visual comparison.

4.3 RESIN COMPONENT ANALYSIS

The bishydrazide, diamine and crosslinker resin components were analyzed by a variety of techniques, including FT-IR, FT-NMR, LC and elemental analysis. The infrared spectra of the first component isolated, the biscyclohydrazide, are shown in figure 7. No significant changes were observed in the infrared spectra going from the model compound, to bishydrazide isolated from cured, postcured and aged composite specimens. The ^{1}H-NMR spectra of the bishydrazides showed only a broad complex multiplet from 6.5 to 8.3 ppm. The m.p. were all $>$ 360°C, however, the colors of the bishydrazides were as follows: (1) yellow for the model compound, (2) brown from the staged and cured resin, and (3) black from the postcured and aged composite specimens. The color change (and weight gain - section 4.2) may be partially due to colloidal graphite absorbed on the bishydrazide because treatment of yellow model compound with hydrazine and graphite fiber produced brown bishydrazide. However, most of the color change (and weight gain) was probably due to the undigested MDA residues on the bishydrazide. These residues generally caused a high C, high H and low N elemental analyses:

Calc. for $C_{17}H_{10}N_4O_5$, % C, H, N
Bishydrazide C=58.29, H=2.88, N=15.99
Found-cured C=58.94, H=4.40, N=14.45
post cured C=57.77, H=4.27, N=12.82
prolong aged C=60.18, H=3.94, N=13.27

The infrared spectra of the second component isolated, the MDA, are shown in figure 8. The only significant change from as received MDA was the presence of weak imide bands (1696 and 1772 cm^{-1}) representing undigested BTDA and/or crosslink residues in the MDA isolated from cured, postcured and aged composite specimens. The presence of undigested BTDA residues was further verified by subtracting the as received MDA spectrum from the isolated MDA spectra. The difference was identical to the spectra of the bishydrazides precipitated from basic solution. However, the concentration of BTDA residues in MDA was too low for detection by ^1H-NMR as the NMR spectra of isolated MDA showed only resonances consistent with the as received MDA. These residues are probably the cause of a color change and m.p. lowering observed in the recovered MDA samples. The as received cream colored MDA is isolated from cured and aged matrix resin as dark brown MDA melting 3-4°C lower. However, some of the color change and m.p. lowering could also be due to impurities initially present in the as received MDA. Treatment of as received MDA with hydrazine yields two crops of MDA; the first crop (72% recovery) was more pure than the as received and the second crop (27% recovery) of dark brown MDA with a 5°C m.p. lowering represented a concentration of the impurities in as received MDA.

Oxidation of MDA to 4,4'-benzophenone diamine (BDA) during curing and aging of polyimide resins, (reference 8 and references cited therein) as another possible source of the impurities was ruled out as a factor in this case. First, both MDA and BDA were shown not to be altered during the digestion conditions (section 3). Second, an infrared study showed that as little as 0.8% BDA could be detected in MDA by the presence of the strongest BDA absorbances appearing as minor absorbances through the MDA FT-IR spectra at 3373, 1582, 1551, 1155 and 926 cm^{-1}. It may be concluded that oxidation of the methylene bridge to form BDA does not occur during 600°F air exposure of PMR-15 composites because of the following: (1) MDA and BDA are not affected by the digestion conditions, (2) BDA IR bands were not present in the isolated MDA spectra in figure 8, and (3) the NMR and m.p. data showed the isolated amine fraction was still MDA. If this oxidation occurs, it can only happen on the composite surface <u>and</u> the resulting BDA must undergo weight loss along with the MDA weight loss as fast as BDA forms. This is in direct contrast to the literature (reference 8 and others cited therein) which report as much as 12% benzophenone structures are formed during thermo-oxidative aging of condensation polyimide films containing arylmethylene linkages. However in this case, the lower surface area/resin content of composites vs. films (used in reference 8) and the presence of more easily oxidizable structures (polymerized NA acting as an oxygen sink) could suppress the oxidation of MDA to BDA to well below the detection limits of FT-IR spectroscopy.

The infrared spectra of the third component isolated, the acetylated polymerized nadic crosslinker, are shown in figure 9. The only major differences observed between the spectrum of cured NA crosslinker and postcured or aged NA crosslinker are the formation after postcuring/aging of a very strong broad band in the 1000-1200 cm^{-1} region and a medium intensity sharper band in the 450-470 cm^{-1} region. These absorbances are probably due to the formation of carbon-oxygen ether linkages (thermo-oxidative crosslinking) during postcure and aging at 600°F. Thus, it may be concluded that thermo-oxidative crosslinking initiates during postcuring. The crosslinker weight change data (section 4.2) suggest that thermo-oxidative crosslinking continues throughout the useful lifetime of the composite until finally crosslinker weight loss becomes predominant after about 1200 hours of 600°F aging. The regions other than 1000-1200 and 450-470 cm^{-1} of these two spectra are similar to the spectrum of crosslinker isolated from cured resin. Some minor differences in the amount of carbonyl and imide bands (1650-1770 cm^{-1} region) and amide and carboxyl bands (3200-3400 cm^{-1} region) are observed which probably represent undefined differences in the degree of imide ring formation (amide-acid ring closure) and secondary amide formation during the acetic anhydride treatment step of the crosslinker isolation procedure.

The ^{1}H-NMR spectra of these three crosslinker samples are shown in figure 10. The spectrum of the cured crosslinker showed a broad amide N-H peak centered at 9.12 ppm, very minor singlets at 2.88 and 2.43 ppm, one strong singlet peak for the amide acetyl group at 2.09 ppm and polymer methylene chain at 1.25 ppm. The spectrum of the postcured crosslinker showed downfield shifts to form new peaks at 4.82, 4.13 and 3.59 ppm; intensified peaks at 2.92, 2.84, 2.35 and 2.26 ppm; amide acetyl group as a weakened singlet at 2.09 ppm, intensified methylene polymer chain at 1.26 ppm, and a new methylene polymer chain as a singlet at 0.89 ppm. The spectrum of crosslinker isolated from aged composites was basically identical to the postcured crosslinker spectrum except, that in addition, a clearly defined strong peak has formed as a downfield shift at 1.66 ppm. This is probably the result of the formation of more alpha-methylene groups next to the thermo-oxidatively formed carbon-oxygen crosslinking sites. Two things should be noted about the ^{1}H-NMR spectra shown in figure 10. None of the spectra exhibit a carbon-carbon double bond (olefinic) peak. Thus, it can be concluded that the olefin in the polymerized crosslinker is consumed during the 600°F curing step by some undefined mechanism. However, consumption of the olefin during postcuring, instead of curing, would seem more plausible because then the consumption would correlate with the appearance of the strong carbon-oxygen bands, centered at 1087 and 462 cm^{-1}, in the IR of crosslinker isolated from postcured and aged composites (figure 9). The second thing to note about the ^{1}H-NMR spectra in figure 10 is the apparent intensity reversal of the acetyl peak (2.09 ppm) and the major methylene polymer chain (1.25 ppm) in cured vs. postcured/aged crosslinker. This reversal is considered to be due only to a reduced number of sites for reaction with acetic anhydride as thermo-oxidative crosslinking increased in the polymerized NA component of postcured and aged composites.

The results of the ^{13}C-NMR spectrum of the crosslinker isolated from cured PMR-15 composite were consistent with either a cyclic imide/N-amino amide or the acyclic/cyclic bisimide polymer structures. The following were observed: (1) two types of carbonyl singlets at 176.34 and 174.42 ppm for the cyclic imide and acyclic amide (or imide), (2) a weak aromatic peak at 130.2 ppm for MDA residue, (3) a broad weak resonance region at 49-36 ppm for branched polymer carbons, and (4) a weak singlet at 29.59 ppm for acyclic amide (or imide) acetyl group(s). Again, an olefin peak was not observed (generally about 135 ppm). The crosslinker samples isolated from postcured and aged composites were too insoluble in NMR solvents for an acceptable ^{13}C analysis. This decreased solubility is additional evidence that thermo-oxidative crosslinking occurs in nadic crosslinker resin component, and the crosslinking is initiated during the postcuring.

LC analysis with a 254 nm UV detector of the crosslinker solution before the acetic anhydride treatment showed at least 4 weak peaks and one sharp strong peak. Analysis after isolation of the crosslinker by the acetic anhydride procedure showed 3 sharp strong peaks and one strong broad complex peak. The chromatograms are shown in figure 11. The presence of only one strong peak in the LC of untreated crosslinker suggests a strong UV absorbing MDA residue is attached to the crosslinker component. Treatment with acetic anhydride increased the absorbances of the weak UV absorbing crosslinker components to provide the strong peaks observed in the LC of acetylated crosslinker. The chromatogram of the acetylated crosslinker may be roughly divided into two portions; first, the higher molecular weight region consisting of three sharp peaks and second, the more slowly eluted region consisting of one broad complex peak with at least three shoulders or peaks on the low molecular weight tail of the broad peak. Because of the decreased solubility and the less than theoretical yield of crosslinker isolated from postcured and aged PMR-15 composites, solutions of these crosslinker samples were not investigated by LC.

The two elution regions of the cured crosslinker were collected and analyzed with FT-NMR (microcapillary tube). The NMR spectra are shown in figure 12 and are consistent with the spectrum of crosslinker isolated from cured resin that was described earlier. For low and high molecular weight portions of the chromatogram, respectively, the following was observed: N-amino acetyl as a sharp singlet at 2.06 and 2.13 ppm, alpha methylene as a sharp singlet at 1.60 and 1.57 ppm, polymer chain as a weak singlet at 1.25 and 1.27 ppm and both at 0.75 ppm, and branched polymer chain as a broad weak raised baseline for both molecular weights from the acetyl 2.1 ppm region to about 4.0 ppm. The major difference between the low and high molecular weight fractions was the lower intensity of the N-amino acetyl peak in the 2.1 ppm region in the low molecular weight sample. The major differences between the spectra of the two fractionated crosslinker samples and the spectrum of the entire crosslinker (described earlier) were that the fractionated crosslinker samples exhibited additional very weak peaks at 0.75 ppm and more intense alpha methylene peaks in the 1.6 ppm region.

5. CONCLUDING REMARKS

The degradation of PMR-15 matrix resin was found to occur primarily through weight loss of the 4,4'-methylenedianiline component. The observed weight loss of the 4,4'-methylenedianiline is linear with the square root of the 600°F exposure time which suggests a thermo-oxidatively diffusion controlled reaction. Intermediate oxidation products such as 4,4'-benzophenone diamine were not found in the composite. Degradation of PMR-15 matrix resin was also found to occur in the nadic anhydride crosslinker component. During 600°F isothermal exposure, the crosslinker component does initially lose weight but later the competition of thermo-oxidative weight gain and weight loss provides a net balance of no observed weight loss for about 1200 hours. Thereafter, the crosslinker component rapidly loses weight to become a significant contributor to overall resin weight loss. The mechanism for the weight gain of the crosslinker component during 600°F exposure entails the generation of carbon-oxygen thermo-oxidative crosslinks. The thermo-oxidative crosslinking initiates during the postcuring and probably continues throughout the useful 600°F composite lifetime. The carbon-carbon double bond in the polymerized crosslinker was found to disappear primarily during initial curing, rather than postcuring. The 3,3',4,4'-benzophenonetetracarboxylic dianhydride component did not significantly contribute to the weight loss or degradation of PMR-15 matrix resin.

The hydrazine digestion/separation procedure developed was successful in isolating the resin components (and fiber) of PMR-15 resin and composites. The separations were essentially quantitative except for the crosslinker component when isolated from postcured and aged PMR-15 composites.

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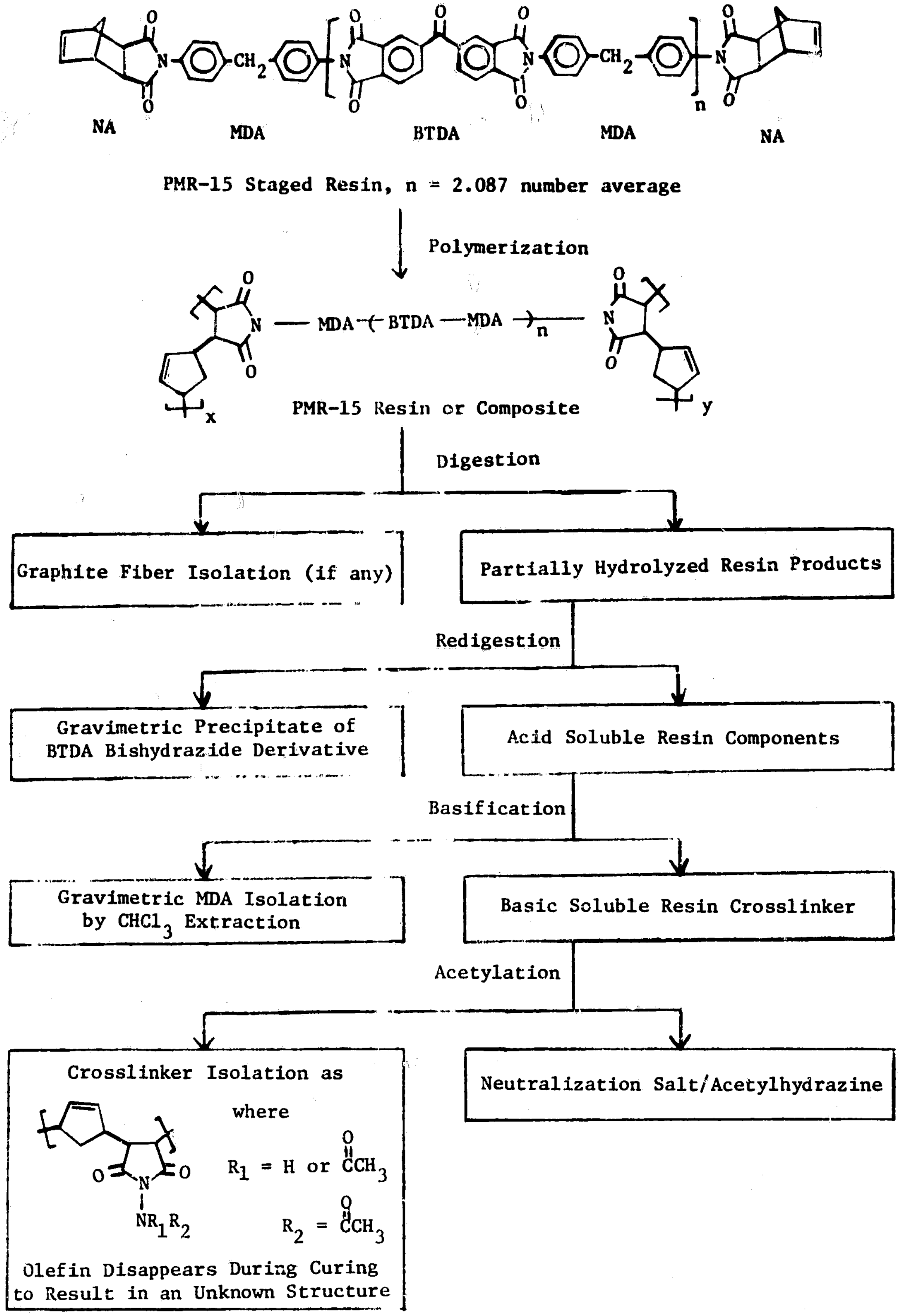

Figure 1.- PMR-15 Matrix resin digestion/separation.

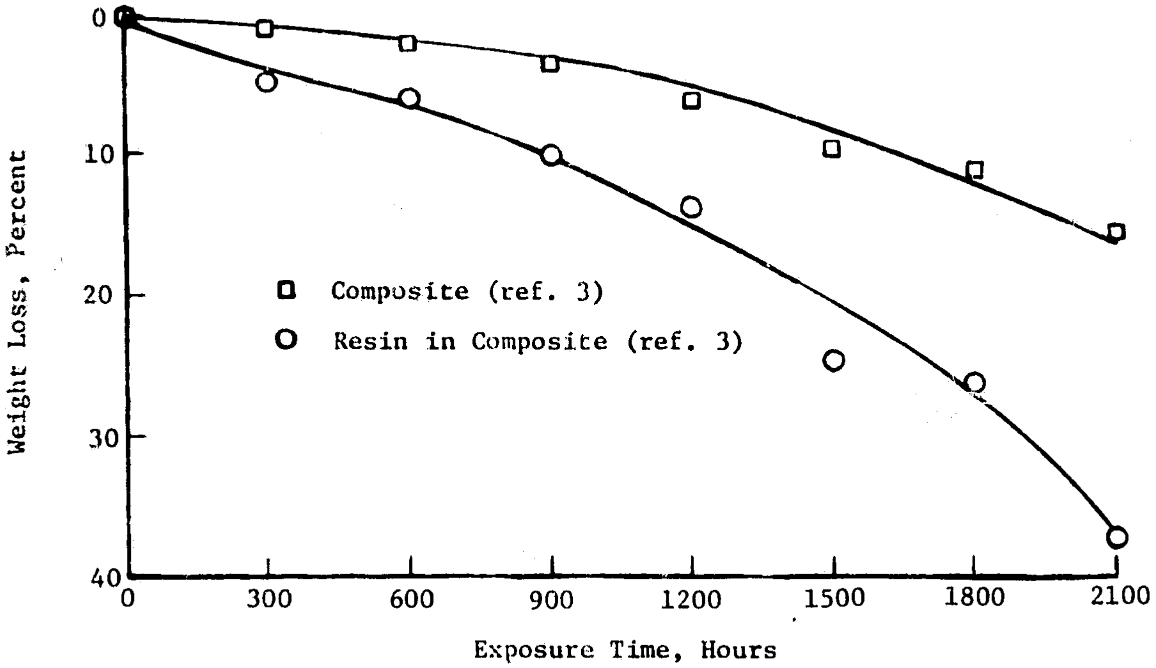

Figure 2.- Composite and resin weight loss of Celion 6000/PMR-15 composite as a function of 600°F air exposure time.

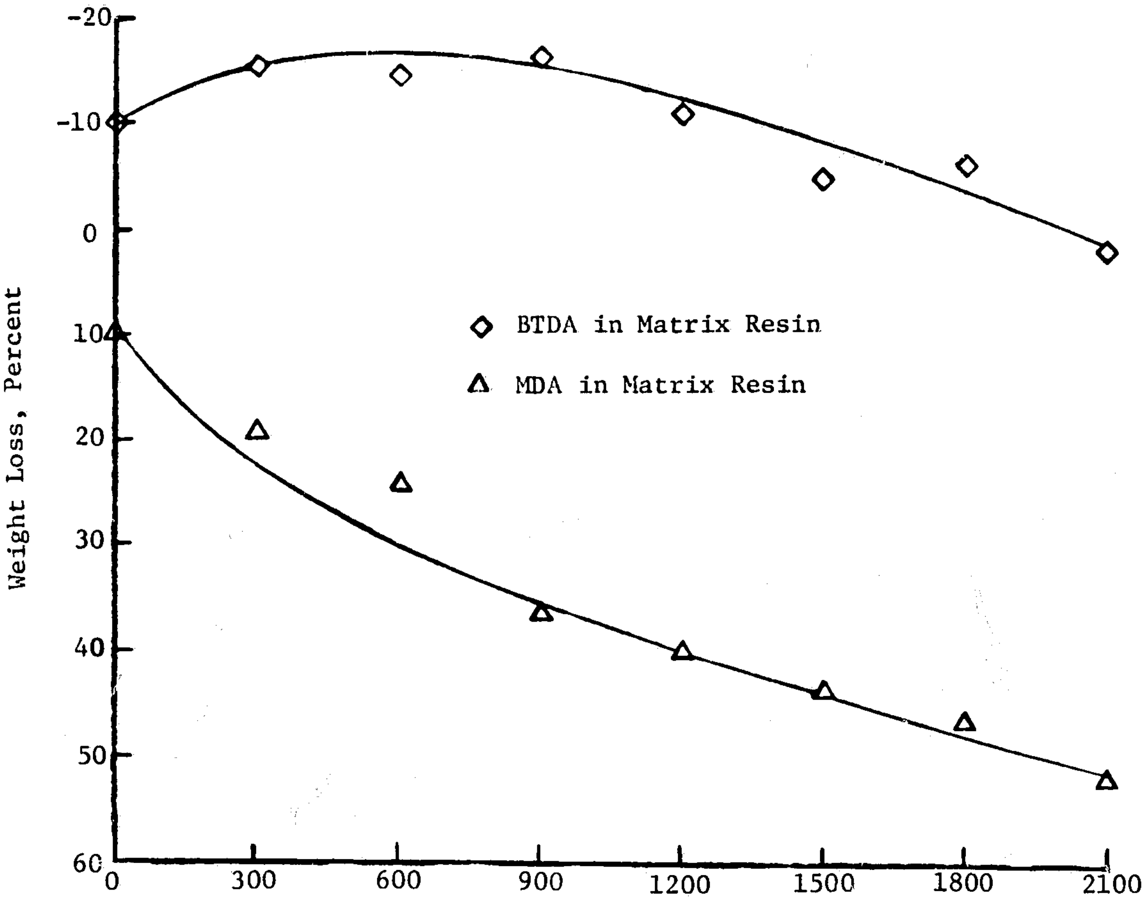

Figure 3. - BTDA and MDA resin component weight loss in Celion 6000/ PMR-15 composite as a function of 600°F air exposure time.

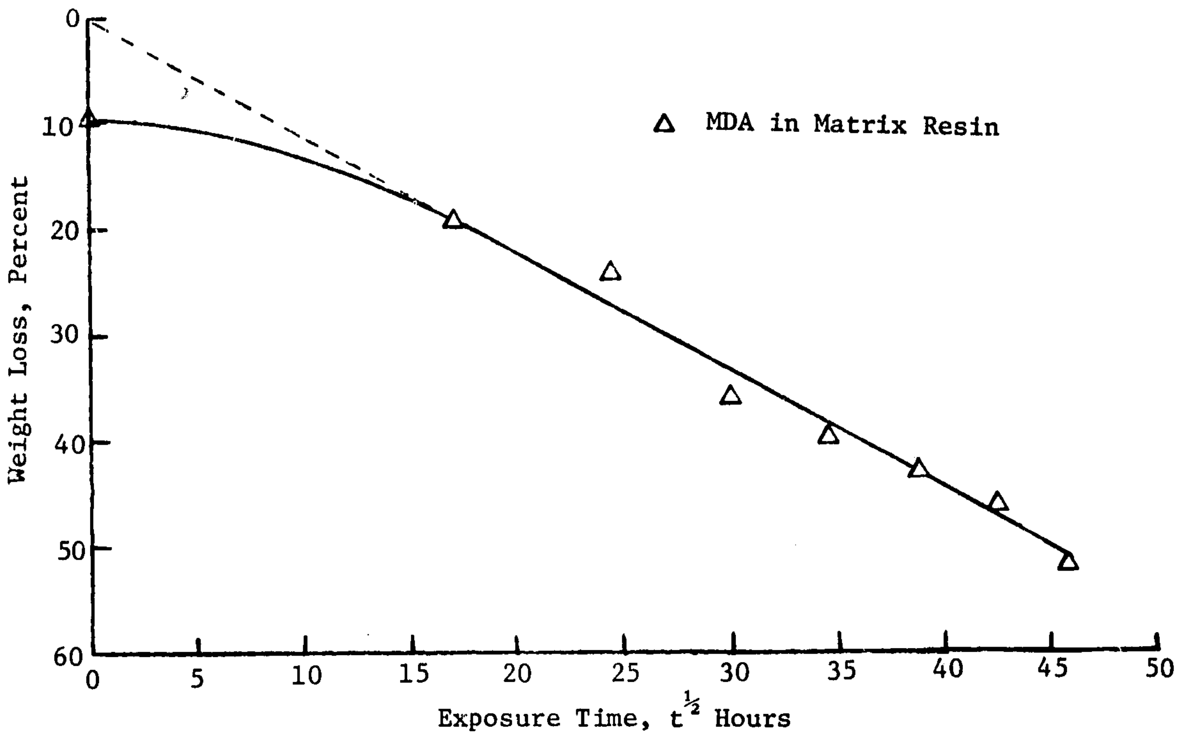

Figure 4. - MDA resin component weight loss in Celion 6000/PMR-15 composite as a function of 600°F air exposure time.

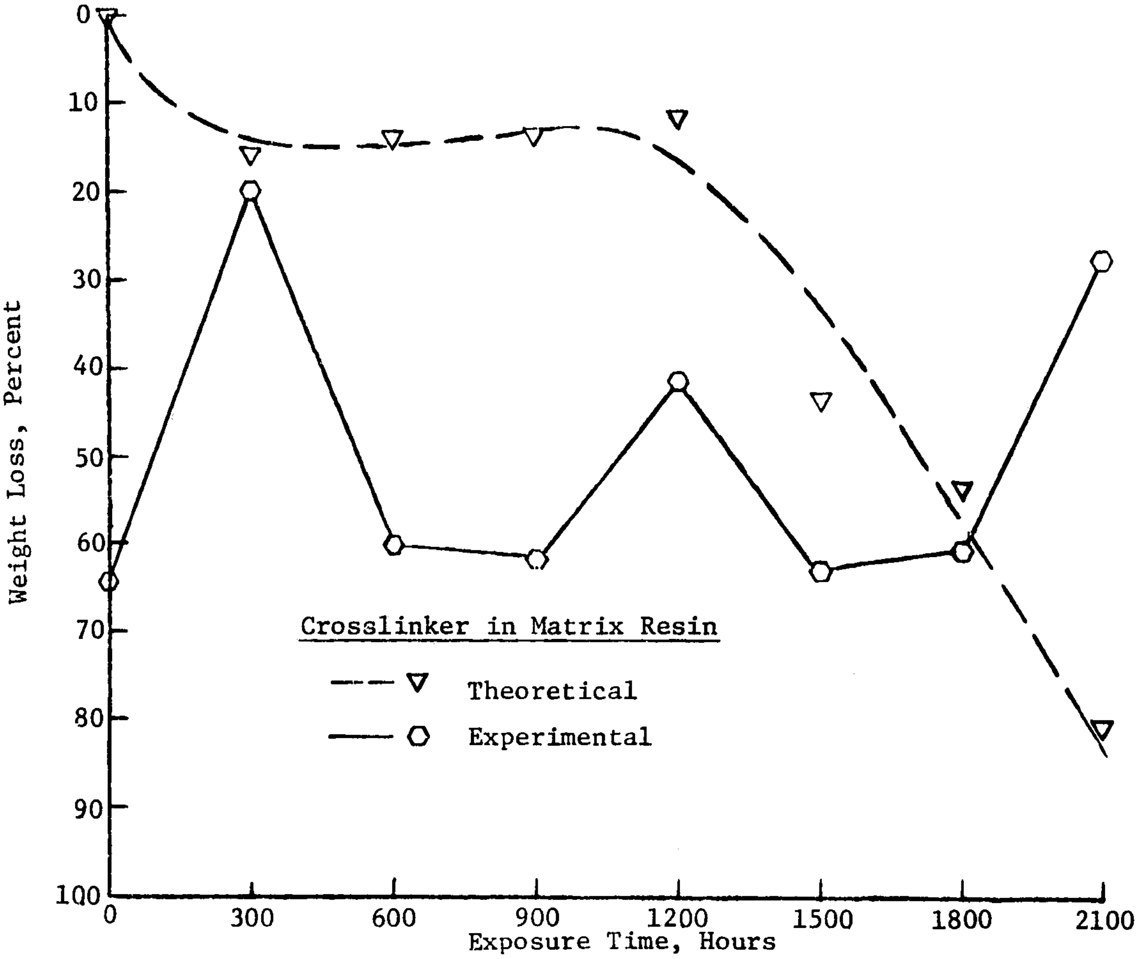

Figure 5. - Theoretical and observed crosslinker component weight loss in Celion 6000/PMR-15 composite as a function of 600°F air exposure time.

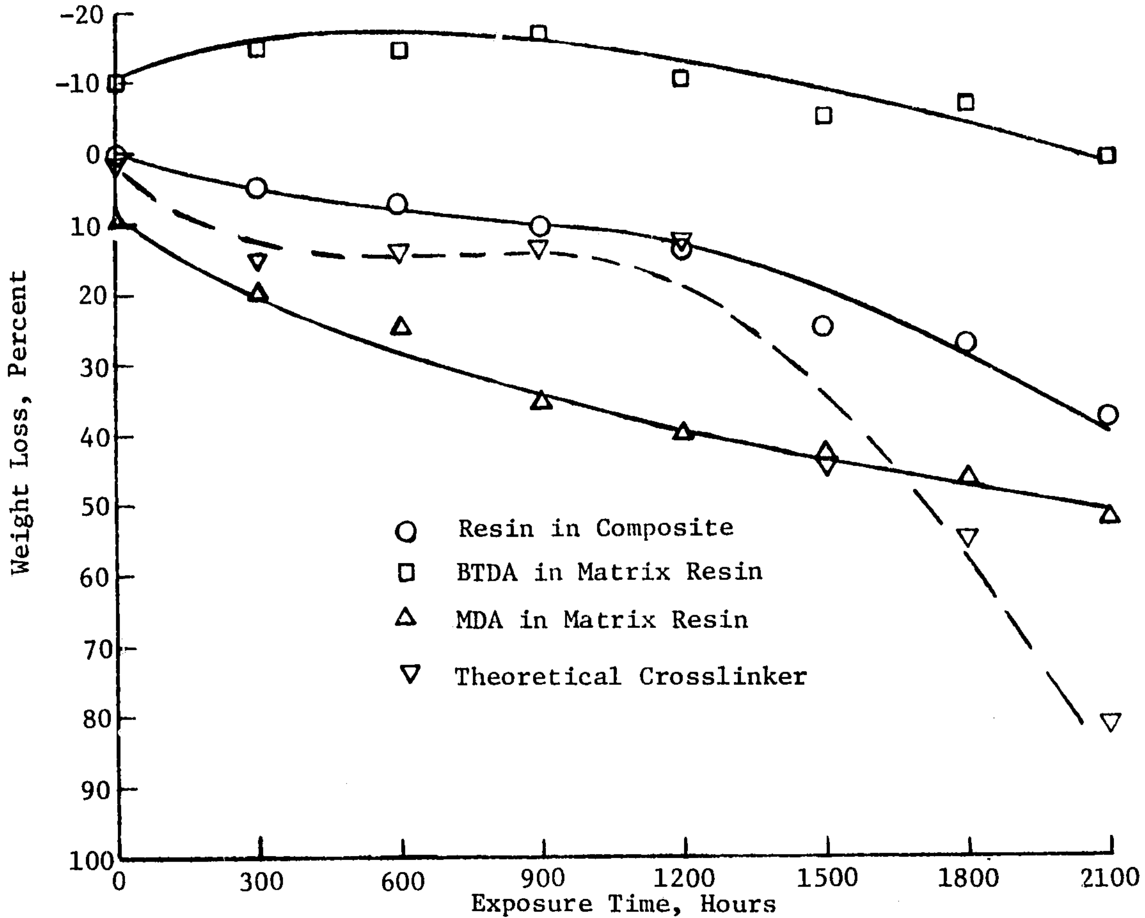

Figure 6.- Resin and resin component weight loss in Celion 6000/PMR-15 composite as a function of 600°F air exposure time.

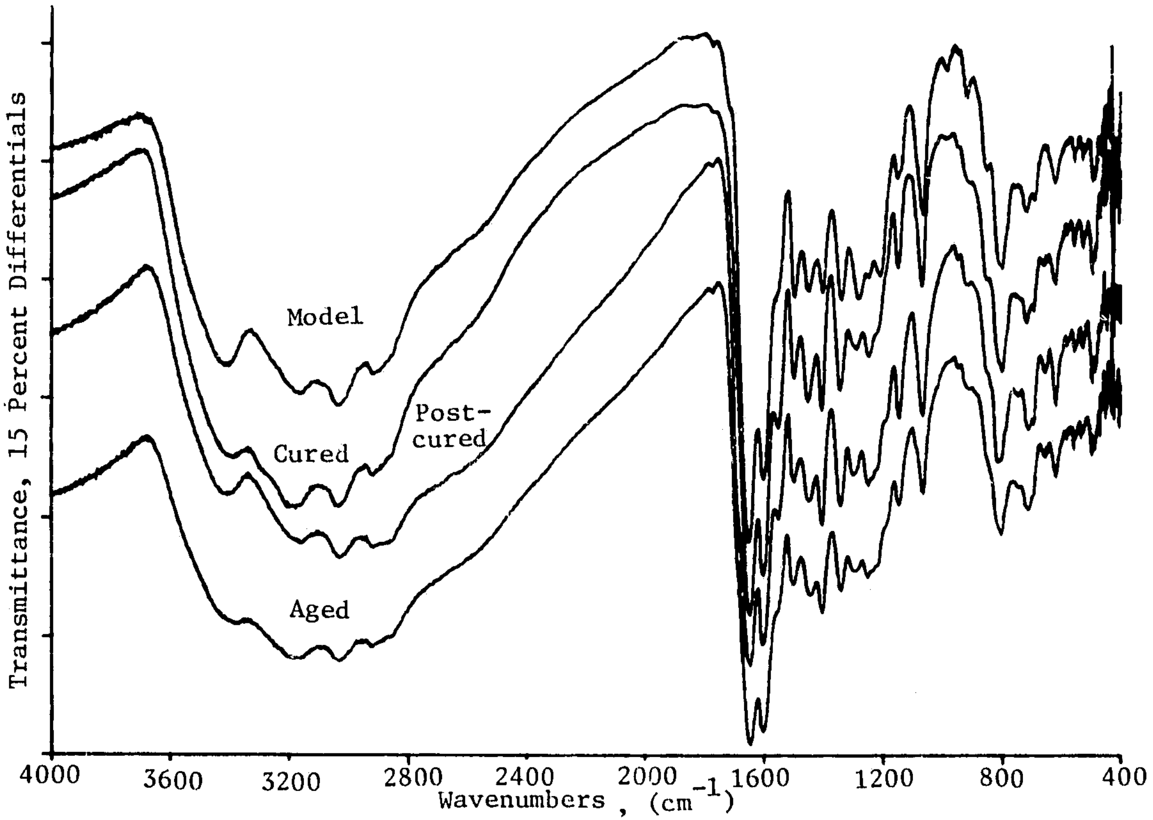

Figure 7. - Infrared spectra of biscyclohydrazide derivatives of BTDA resin component.

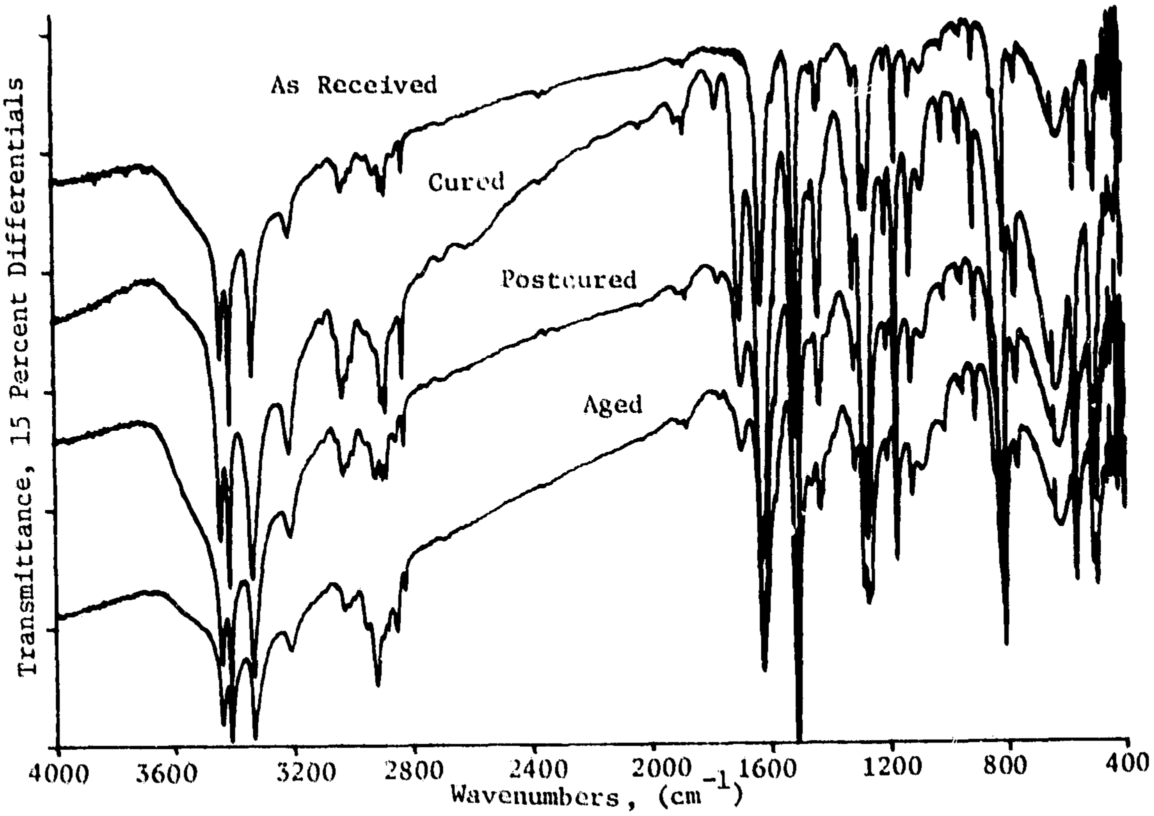

Figure 8.- Infrared spectra of MDA resin component.

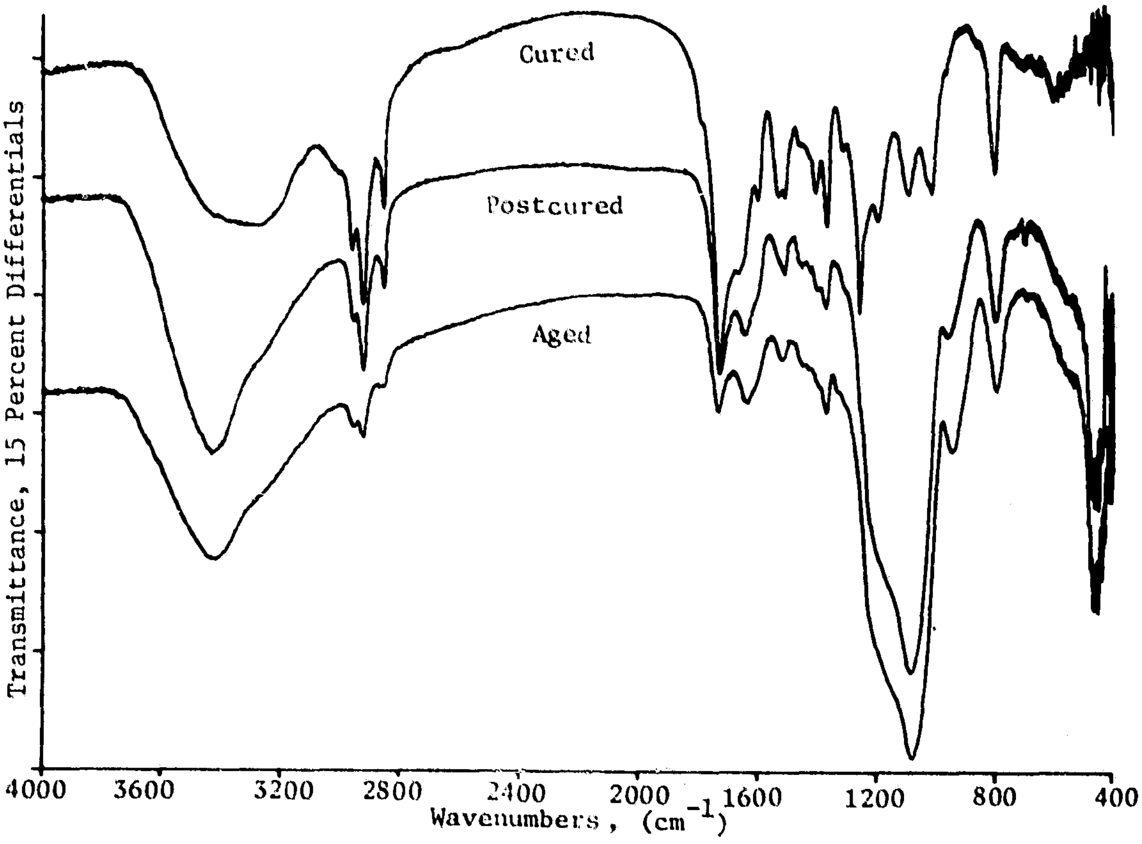

Figure 9.- Infrared spectra of acetylated NA crosslinker component.

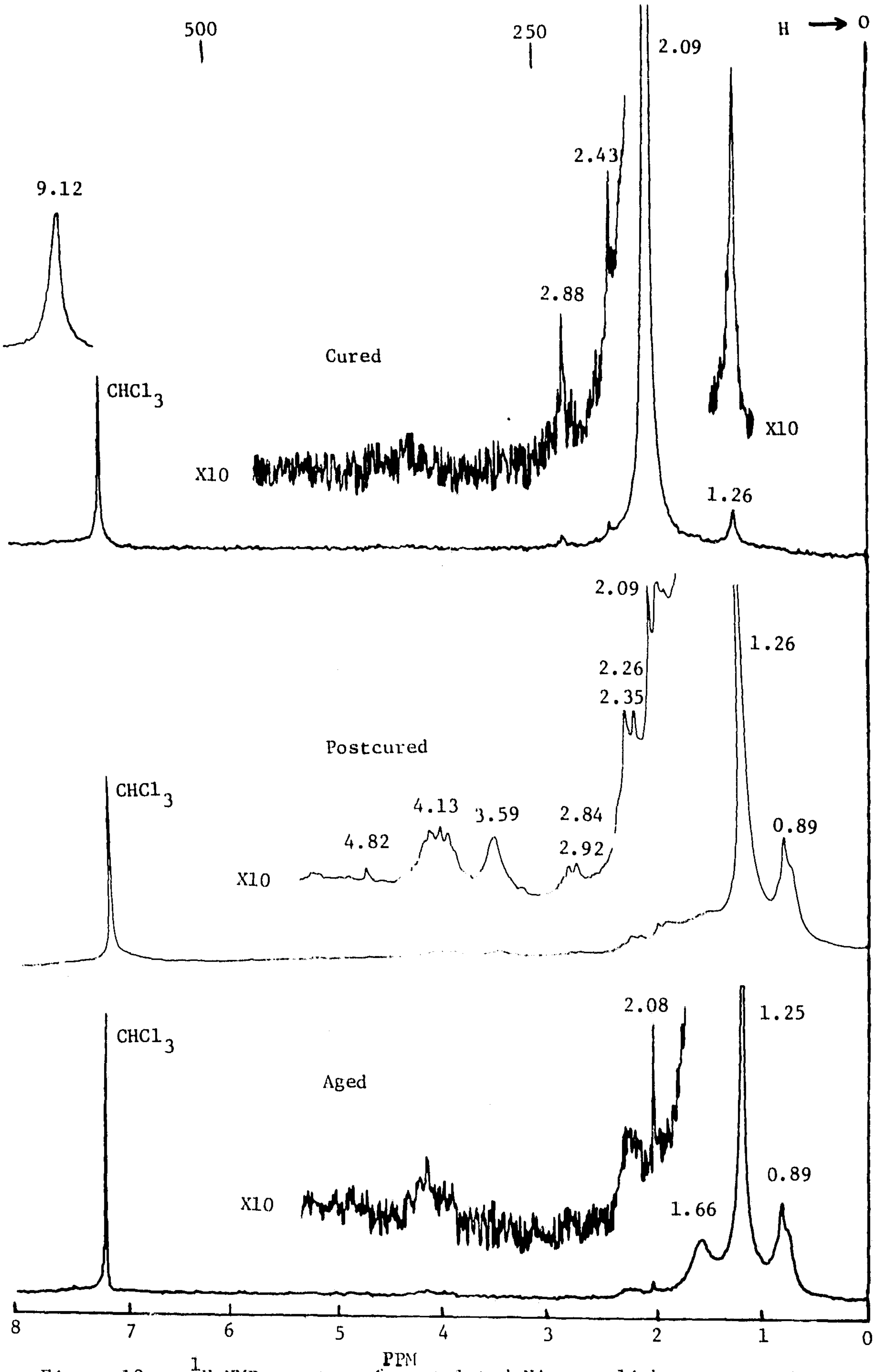

Figure 10. - ^{1}H-NMR spectra of acetylated NA crosslinker component.

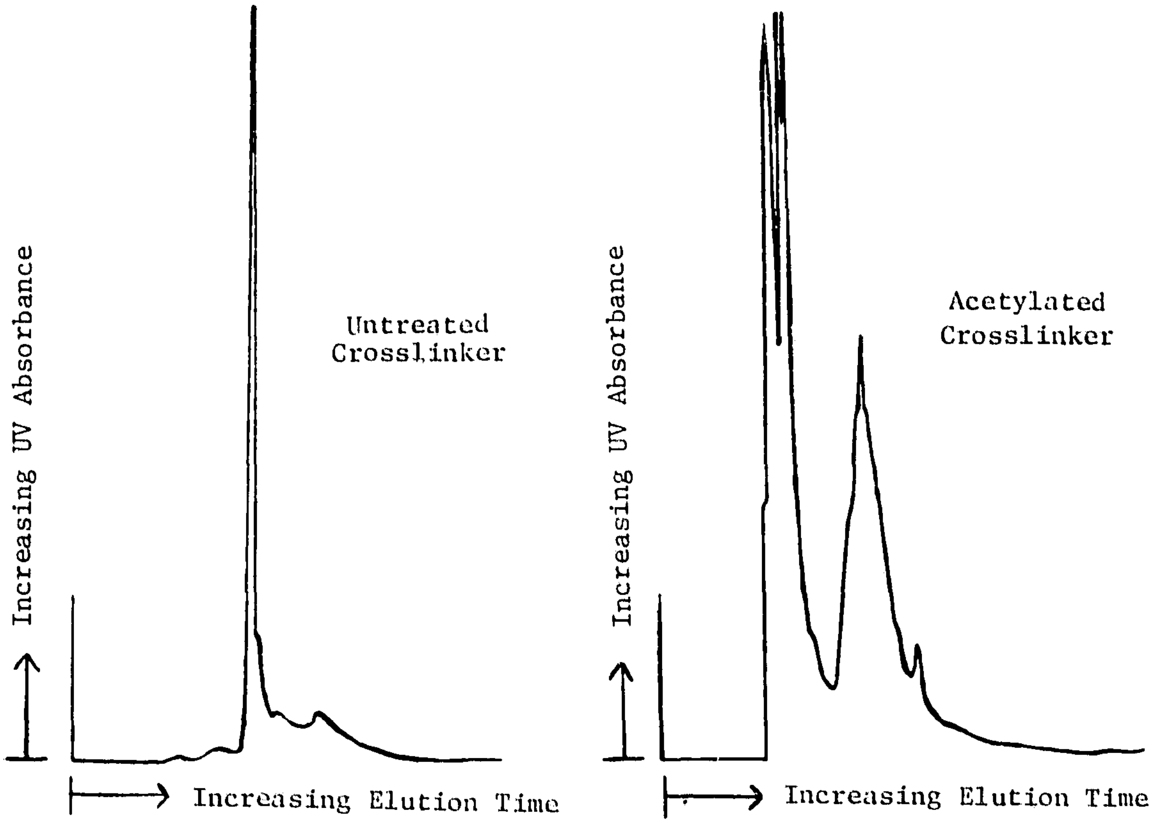

Figure 11.- LC of unacetylated and acetylated cured crosslinker.

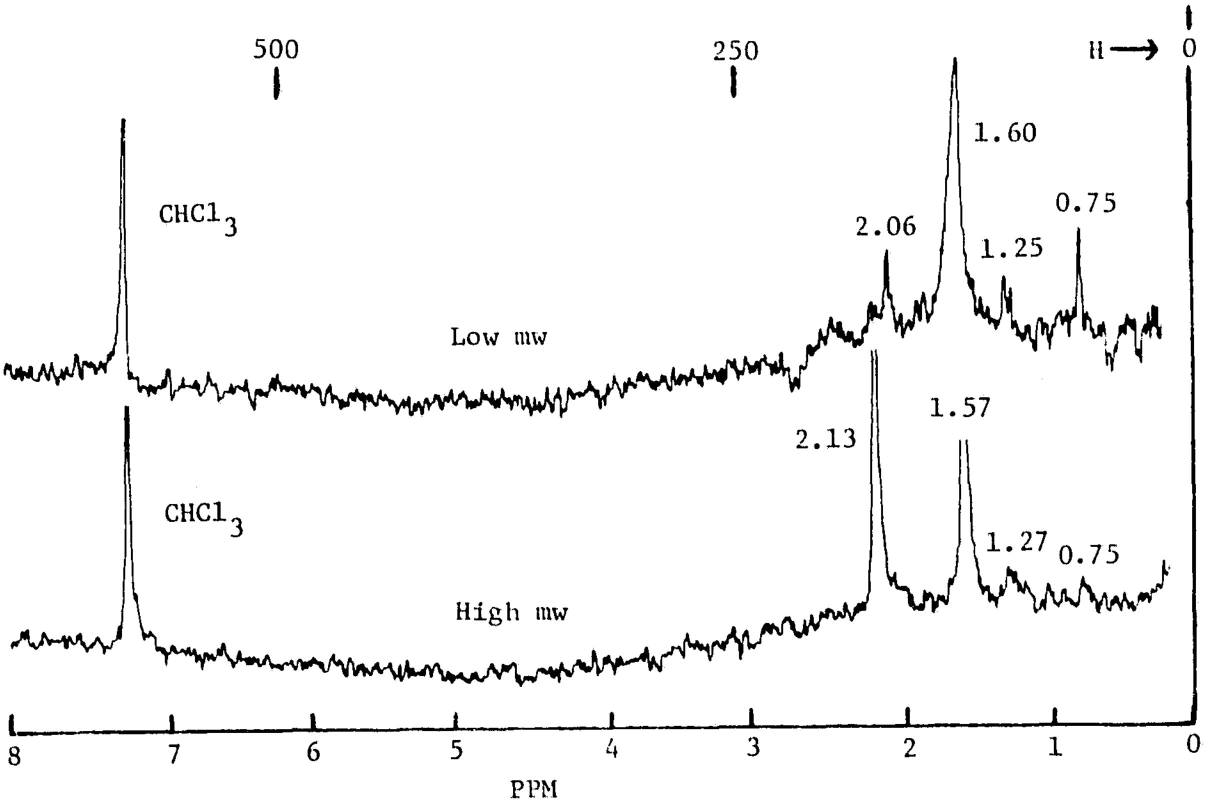

Figure 12. - ^{1}H-NMR spectra of LC acetylated cured crosslinker.