Thermal Cure Behavior and Pyrolysis of Methyl-Tri(phenylethynyl)silane Resin

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ABSTRACT: A polyfunctional organic–inorganic hybrid monomer, methyl-tri(phenylethynyl)silane (MTPES) could be thermally polymerized by a free radical mechanism to a highly crosslinked structure of interest as a high temperature composite matrix resin. The structural changes during thermal cure process were characterized by fourier transform infrared spectrum and ^{13}C-CP-MAS-NMR spectrum. The disappearance of secondary acetylene stretching band at 2166 cm^{-1} was used successfully to monitor cure reaction accompanied with the formation of *cis*-polyene structure at 1600 and 754 cm^{-1}. The possible cure mechanism of MTPES was also proposed. The pyrolysis of cured MTPES under a stream of argon to 1450°C gave a ceramic in high yield (81%). Thermal conversion of polymer to ceramic was studied by means of X-ray diffraction, Raman spectrum, and energy dispersive spectrometer analysis. The results showed that pyrolytic products were made up of β-SiC, graphite, and glassy carbon. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 10–16, 2009

Key words: curing of polymers; high temperature materials; organic–inorganic hybird; pyrolysis

INTRODUCTION

Fiber reinforced polymer matrix composites can offer significant advantages over other materials because of their high temperature resistance, processability, low density, and high specific strength. These composites are in great demand by the aerospace, electronic industries, military, and so on. Typically they are stable to 300–400°C in air, however, decompose rapidly and completely at temperature higher than 400°C.[1,2] Current researches have indicated a trend toward enhanced mechanical property, high thermal stability, and flame retarding when inorganic moieties are incorporated into organic based polymers to form nanocomposites.[3–5] Many studies of silicon-containing organic–inorganic hybrid polymers composed of [—SiR$_2$—C≡C—](R = alkyl or phenyl) units have been reported because of their excellent thermal and oxidative properties.[6–11] Itoh reported that poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [—Si(ph)H—C≡C—C$_6$H$_4$—C≡C—] (abbreviated MSP), which was prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the presence of magnesium oxide, had extremely high thermal stability.[12–14] In our previous article,[15–17] synthesis, characterization, and thermal cure kinetics of methyl-tri(phenylethynyl)silane (MTPES) had been reported and thermoset possessed excellent thermal and oxidative properties. The temperature of 5% weight loss (Td$_5$) in nitrogen was 695°C and total weight loss at 800°C was 7.1% as shown thermo gravimetric analysis. The structure of MTPES was as shown in Figure 1. In this article, we have investigated the structure changes of MTPES during thermal cure process on the basis of DSC, fourier transform infrared spectrum (FTIR), and ^{13}C-CP-MAS-NMR, and possible crosslinking reaction mechanism was proposed. In addition, the composition and structure of the pyrolytic products were characterized by energy dispersive spectrometer (EDS), X-ray diffraction (XRD), and Raman spectrum (RAM).

EXPERIMENTAL

Synthesis of MTPES

MTPES was prepared according to the literatures.[15,16]

Thermal cure

To remove any volatile material, the sample was preheated at 150°C. MTPES resin was cured by heating in oven with argon as the following cure
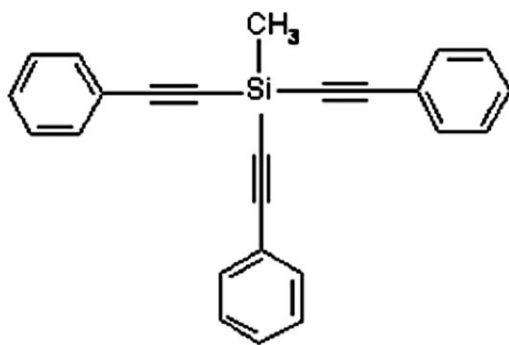
Figure 1 Structure of MTPES.

schedule: 250°C/2 h → 300°C/2 h → 350°C/2 h → 400°C/2 h.

Pyrolysis of cured MTPES

The cured MTPES was sintered under argon as the following schedule: 400°C/0.5 h → 800°C/0.5 h → 1200°C/0.5 h → 1450°C/12 h.

Characterizations

Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurement was performed with a Perkin–Elmer DSC-7. The DSC was calibrated with high purity indium. Sample (8–10 mg) was weighed into small DSC aluminum pans, sealed with holed aluminum lid, and experiment was conducted under a nitrogen flow of 20 cm^3/min. In the dynamic analysis, the sample was scanned at 10°C/min. The enthalpy of curing, ΔH, was determined from the area under the exothermic peak and the sample mass.

Fourier transform infrared spectrum

FTIR spectroscopic characterization was carried out by Nicolet Magna-IR550 with following conditions: spectral bandwidth 4000–400 cm^{-1}, 32 accumulations, resolution 2 cm^{-1}. All solid samples were examined as potassium bromide (KBr) pellets.

^{13}C-Cross polarization MAS NMR measurement (^{13}C-CP-MAS-NMR)

^{13}C-CP-MAS-NMR spectra were recorded on a Bruker Avance 500 spectrometer. Solid samples (powder) were placed in boron nitride sample holder. The observation frequency was 125.77 MHz. $H_0 = 11.7T$, the recycle delay time was 7 s. The contact time was 2.5 ms and the MAS speed was set to 5.625 KHz.

X-ray diffraction

The XRD measurements were carried out at room temperature on a Digaku (Japan) D/max 2550 VB/ PC diffractometer with Cu K_α radiation ($\lambda = 0.1542$ nm). Specimens were scanned from 3 to 80° with a scan speed of 4°/min.

Raman spectrum

The RAM measurement was conducted on a Renishaw RM-2000. He-Ne laser (633 nm) was used as an excitation source. Wavelength range: 500–2000 cm^{-1}.

Energy dispersive spectrometer

To analyze composition of the pyrolytic MTPES, EDS was recorded on a NewQuiz 14 Elements.

RESULTS AND DISCUSSION

Structure changes of MTPES during thermal cure reaction

FTIR spectral analysis

Figure 2 showed the FTIR absorption variations of MTPES during the cure reaction. MTPES showed a strong absorption around 2166 cm^{-1} indicating the presence of acetylenic functionality. The absence of primary acetylenes was ascertained by the lack of an absorption in the 3295 cm^{-1} (C≡C—H). Other functionalities were identified by absorption at 3045 cm^{-1} (Ph—H), 2970 cm^{-1} (CH$_2$—H), 1594–1485 cm^{-1} (aromatic, C=C), 1256 and 840 cm^{-1} (Si—CH$_3$).[15] In the initial stage of cure, no obvious change of absorptions was observed which indicated secondary acetylenic group still remained dormant until 250°C. With the reaction proceeding, the absorption of acetylenic group was apparently decreased due to the occurrence of cure reaction. Meanwhile, the appearance of absorption bands at 1600 cm^{-1} ($\gamma_{=C=C}$) and 754 cm^{-1} (cis, $\gamma_{=C—H}$) indicated the formation of cis double bond structure. Consequently, the change of acetylenic group at 2166 cm^{-1} can be successfully used to supervise the cure reaction. Absorption frequency of C=C decreased from 1660 to 1600 cm^{-1} which was attributed to the average of density of electron cloud resulting from obtaining cis-polyene structure. When cure temperature reaches to 400°C, the absorption of C≡C totally disappeared accompanying by the increasing of intensity of absorption bands at 1600 and 754 cm^{-1}. Comparison of Figure 2(a) and (f), it can be seem clearly that Si—C in thermoset still remained dormant because of the existence of absorption at 1256 and 840 cm^{-1}. Although the overlaps of absorptions lead to complications in analysis, the appearance of absorptions between 700 and 800 cm^{-1} after curing at 400°C gave an indication of characteristic of cis-polyene structure. The trans structure was absent
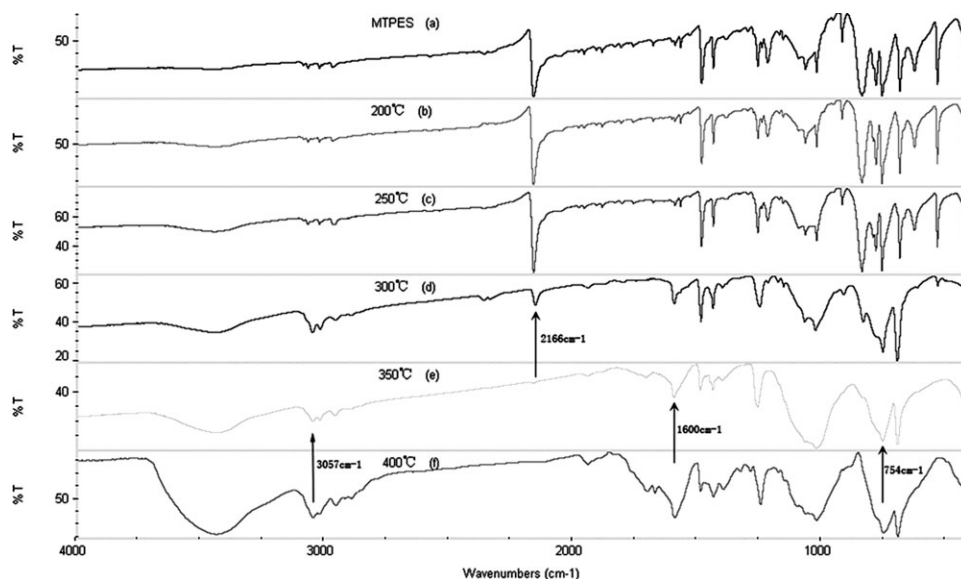
Figure 2 Variations of FTIR of MTPES during cure.

associated with the range of 900–1000 cm^{-1} attributing to stereo hindrance in the thermoset.

^{13}C-CP-MAS-NMR spectral analysis

^{13}C-CP-MAS-NMR study of polymers is very important for structural analysis of these materials which are insoluble and amorphous after curing, because the NMR observations of individual nuclei lead to unique and different information about structures. To confirm that the acetylenic group played an important role in thermosetting reactions of MTPES, the structure changes were characterized by ^{13}C CP-MAS-NMR. Figure 3 showed ^{13}C-CP-MAS-NMR spectrums of MTPES, in which (a) MTPES monomer,

(b) cured at 250°C, (c) cured at 300°C, and (d) cured at 400°C. The spectrum of MTPES before curing had very resolved and narrow peaks, but the spectrum became very broad with an increase in curing temperature. From these experimental results, it was found that thermal curing lead to structure changes. In Figure 3(a), the peak assignment was made as follows: the methyl substituent attached to the silicon had resonance with chemical shift of 2.2 ppm (Si—CH$_3$). The second aromatic acetylenic carbons appeared as a pair of resonances at 88.6 ppm(Si—C≡C) and 107.1 ppm (Ph—C≡C) when bonded to the silicon-phenyl unit. The aromatic carbons were symmetrical and had resonances between 122.9 and 133.0 ppm. Next, we were concerned with
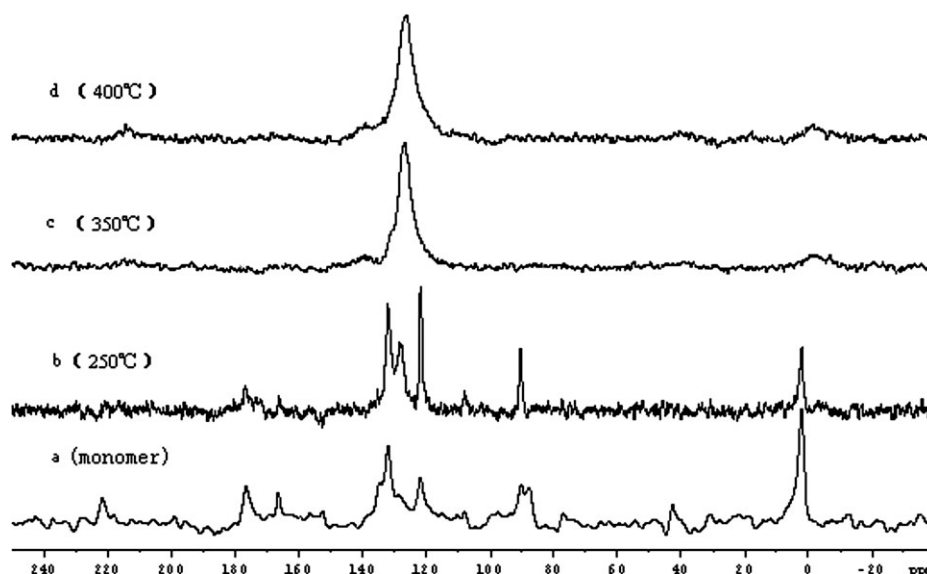

Figure 3 Variations of ^{13}C CP-MAS-NMR of MTPES during cure (a: monomer; b: 250°C; c: 350°C; d: 400°C).
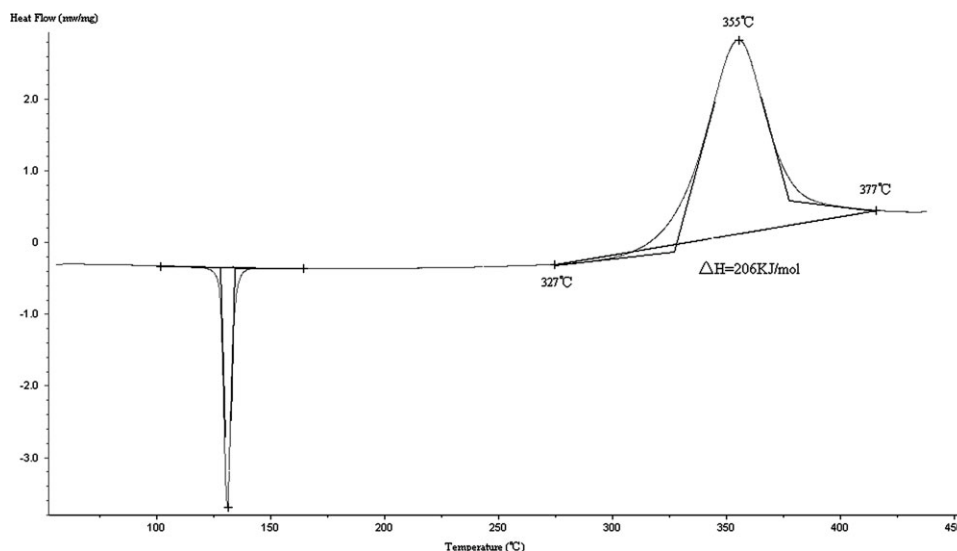
Figure 4 DSC curve of MTPES at heating rate of 10°C/min.

^{13}C CP-MAS-NMR spectra of thermally cured polymers. ^{13}C CP-MA-NMR spectra of MTPES cured at 250°C was very similar to that of uncured MTPES. It can be said that the structural changes were very small at curing temperature below 250°C. As curing temperature was further increased, the intensity of the peak largely decreased. The intensities of peaks from the C≡C carbons ($\delta = 88.62$ ppm) and the phenyl carbons bonded to the C≡C($\delta = 107.1$ ppm) decreased with the increase of curing temperature, and the peaks completely disappeared until curing at 350°C. At the same time, a broad shoulder which comes from the C=C carbons appeared at 140 ppm. From these results, it can be said that the C≡C group changed to C=C by free radical addition reaction at temperatures from 250 to 400°C and three-dimensional network may be formed. These spectra changes were agreed with the FTIR results.

Proposed cured structure

Since it is difficult to obtain evidences directly by insoluble cured resins, the cure mechanism of secondary acetylenic resin is not clearly known by now. Kovar et al.[18] and Admur et al.[19] have discussed the mechanism of the thermal polymerization of phenylacetylenes with and without radical initiators. In the absence of initiators, in general, the observed polymerizations were predominantly initiated by the thermal homolysis of impurities, including peroxides or hydroperoxides formed due to oxygen, present in the monomer. Once initiated, a number of reaction routes were possible during thermal polymerization of acetylenic compounds. For instance, cyclotrimerization to form trisubstituted benzene, Diels–Alder coupling with aromatic backbone, free radical polymerization with the formation of linear and branched conjugated products were the main ways by which chain propagation could occur. Generally, as the molecular chain of a thermally cured resin changes from high entropy to a network structure with low entropy during thermal cure, an exothermic reaction occurs. Figure 4 shows dynamic DSC spectrum of MTPES from room temperature to 400°C. MTPES started curing at 327°C with a maximum at 355°C, the cure ending at 377°C. The strong exothermic signal was typical of a crosslinking reaction between the secondary acetylenic groups. In reference to cyclotrimerization of acetylenic groups as a possible pathway of polymerization in these resins, the theoretically predicted ΔH value based on bond energy calculations, for the cyclization of each acetylenic group is 189 ± 10 KJ/mol. According to Figure 4, the heat of polymerization, ΔH, calculated from the area under the cure exotherm of MTPES was 206 KJ/mol or 68.7 KJ/mol of each acetylenic group. The fact that the heat of polymerization of MTPES was less than the enthalpy of cyclotrimerization suggested that cyclotrimerization was not the major reaction pathway during initial polymerization. Furthermore, Diels–Alder reaction with backbone to form aromatic structure appeared to be a sterically unfavorable process. The bulk phenyl moieties linked to the acetylenic groups would probably precluded achievement of the necessary orientation for the Diels–Alder reaction. In the present study, based on FTIR and ^{13}C-CP-MAS-NMR studies, combined with above thermodynamics and stereo hindrance effect, the possible cure mechanism was proposed. Because of the existence of oxygen in the atmosphere, the cure reaction was predominantly initiated by the thermal homolysis of peroxides or hydroperoxides. The thermal curing of MTPES with phenylethynyl groups most likely proceeded predominantly
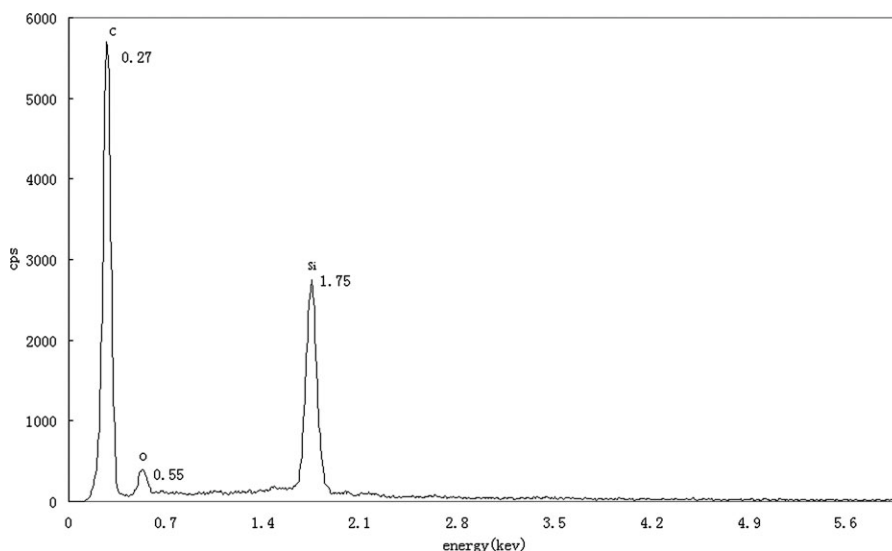
Figure 5 EDS pattern of pyrolysis product.

by a free radical process. The likely product formed in the initial stage of cure was a branched *cis*-polyene structure, which could further undergo a variety of addition reactions to yield a crosslinked polymer.

Thermal conversion of cured MTPES to ceramic

As previously reported,[20–22] organometallic or inorganic polymers, even of high molecular weight, with a linear structure do not lead to high amounts of ceramic residue by pryolysis. The polymeric chain is progressively broken into short fragments. In contrast, a polymer that undergoes crosslinking reactions in preference to skeletal cleavage will form a stabilized network system. On further pyrolysis, such a material will lead to ceramic residue in good yield. Thus, the presence of appropriate reactive functionalities whose reactivity will result in substantial crosslinking during the thermal cure is one of the factors that determine the ceramic yields. In this respect, the presence of the secondary acetylenic group organic–inorganic hybrid polymers should be of interest. In this article, we describe the pyrolysis of MTPES under an argon atmosphere and attempt to understand the components of ceramic.

EDS analysis

In a typical experiment, cured of MTEPS was heated to 1450°C under a stream of argon. It was maintained at 1450°C for 12 h, and a black ceramic type residue was obtained in high yield (81%). Figure 5 shows the compositions of ceramic by EDS. The Figure 5 suggested that the ceramic contained total three kinds of elementary, including carbon, silicon, and trace of oxygen which was introduced by oxygen.

RAM analysis

Raman spectrum is a powerful technology to provide compound identification and structural information such as free carbon and crystalline carbon. Raman spectra of sample was as shown in Figure 6. Two Raman bands were observed at 1586 cm^{-1} which was assigned to a doubly degenerate deformation vibration of the hexagonal ring attributing to the E$_{2g}$ mode of graphite with D$^4_{6h}$ crystal symmetry and 1344 cm^{-1} which was corresponding to stretch band of glassy carbon. The relative intensity of the 1344 cm^{-1} band to the1586 cm^{-1} band was 1.5 : 1, which was large than those of graphite prepared from an organic compound such as phenol resin. A material of a peculiar structure, which was difficult to change into crystal graphite, would be formed from MTPES.

XRD analysis

XRD was performed in an attempt to characterize the inorganic phases formed after curing and pyrolysis of MTPES. XRD spectra of cured and pyrolysis MTPES was as shown in Figure 7. Cured MTPES had only two broad peaks at 2θ = 8.0° and 18.8° which excluded the possibility that the material had small scale crystallinity or grain structure. After pyrolysis 12 h at 1450°C, obvious transformations were observed which indicated original disordered structure was destroyed accompanying with the formation of new ordered material. Two broad peaks at 2θ = 14–30° and 40–50° were attributed to amorphous carbon corresponding to diffraction peak of glassy carbon at {002}, {10}, and {11}. Meanwhile, two new peaks were observed at 2θ = 26.6° and 43.4° corresponding to diffraction peak of graphite at {002} and
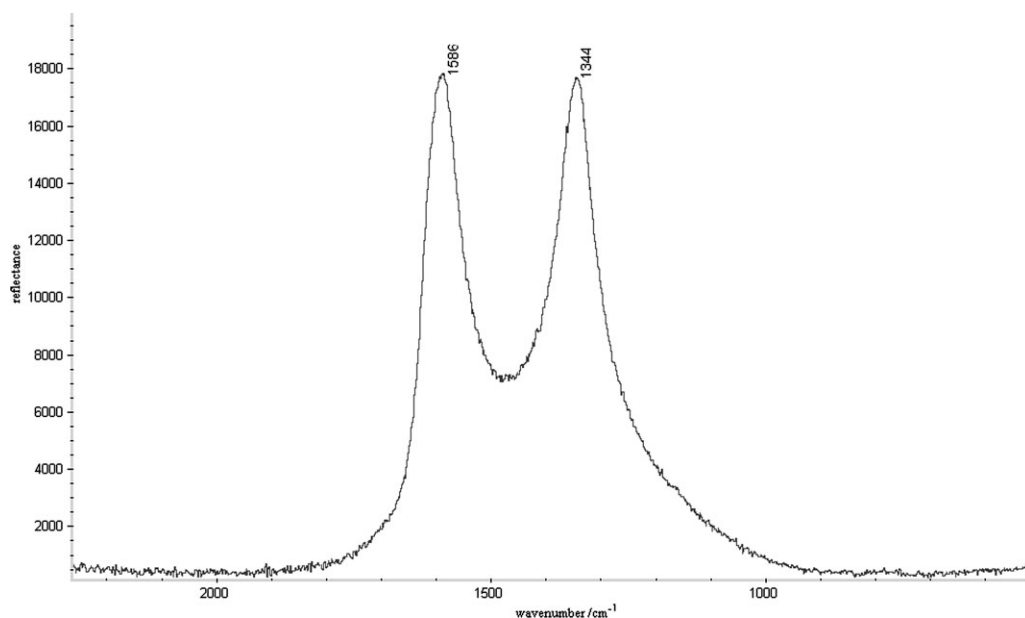
Figure 6 RAM pattern of pyrolysis product of MTPES.

{101}. In addition, XRD pattern of pyrolysis of MTPES was indicative of the formation of β-SiC. Three peaks were observed at $2\theta = 35.6°$, $60.0°$, and $71.8°$ which were attributed to β-SiC at {111}, {220}, and {311}. As discussed above, the formation of β-SiC and graphite will take place inside an amorphous carbon matrix after pyrolysis under a stream of argon.

CONCLUSIONS

In this study, thermal cure reaction of MTPES was studied using FTIR and ^{13}C-CP-MAS-NMR. Initiated by the thermal homolysis of peroxides, MTPES most likely proceeded by a free radical process. During the cure reaction, we found that acetylenic groups gradually disappeared accompanied with the formation of *cis*-polyene structure, which could further
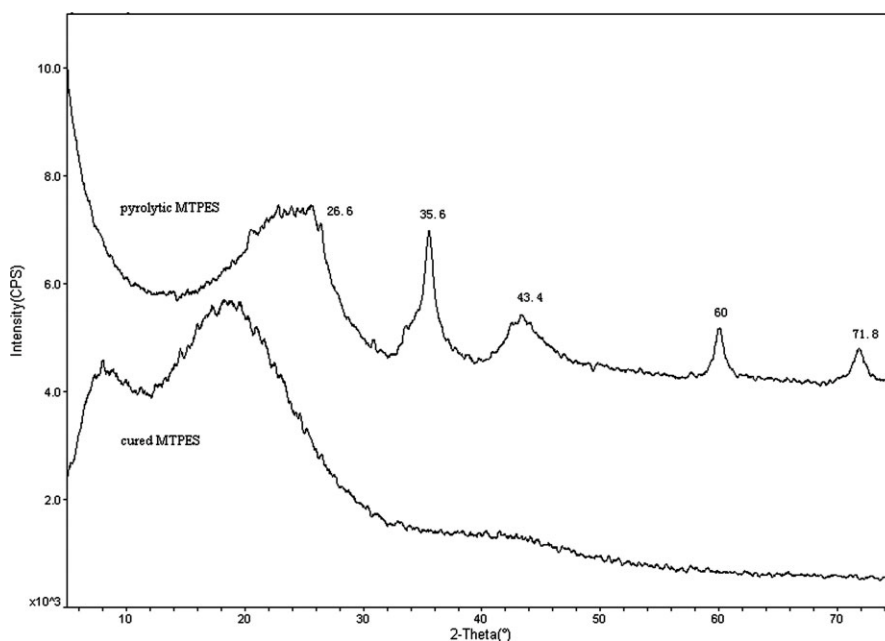

Figure 7 XRD pattern of cured and pyrolysis MTPES.

undergo a variety of addition reactions to yield a crosslinked polymer. Thermal conversion of polymer to ceramic was studied by means of XRD, RAM, and EDS analysis. The results showed that pyrolytic products were made up of β-SiC, graphite, and glassy carbon.

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