

A Novel Method for Crosslinking Polyetheretherketone

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Synopsis

A novel method for crosslinking polyetheretherketone via imine formation at carbonyl groups is presented. In polyetheretherketone these Schiff bases form short, stiff crosslink junctions which are stable up to 630°C. Dynamic mechanical and thermal properties of polyetheretherketone and imine crosslinked polyetheretherketone are reviewed. A large reduction in the temperature sensitivity of the material stiffness has been achieved. Increases in the glass transition temperature from 143°C to greater than 280°C have been obtained.

INTRODUCTION

The demand for tough high-temperature, low-density materials has greatly increased in recent years.¹ These materials are sought as replacements for metals in structural applications where specific strength and specific stiffness are of great importance.² Areas of high demand include the aerospace and transportation industries, where cost is often a secondary concern. Many polymeric materials have been developed that have achieved substantial improvement over metals. One such polymer is the polyaryletherketone based upon hydroquinone and 4,4'-difluorobenzophenone produced by ICI Inc.³ This semicrystalline material is of great commercial importance as a result of its excellent mechanical properties. Hydroquinone polyetheretherketone (HDQPEEK) exhibits excellent toughness, stiffness, and resistance to most solvents.⁴⁻⁸ While this material boasts a melting point of 335°C, there is a substantial loss in stiffness at the glass transition temperature of 143°C along with an increased tendency to creep.^{5,6} This drop in modulus is of grave concern to those seeking a material for higher temperature applications. In an effort to reduce the temperature effect upon the mechanical properties, a novel synthetic technique has been developed to provide sites for short, stiff crosslink formation along the HDQPEEK molecular backbone. The approach taken here is novel in that it is the first to use the carbonyl functionality of the polymer backbone in the formation of short-chain di-imine crosslinks via an aromatic diamine. Other methods for crosslinking HDQPEEK have been developed. In fact, it has been observed that HDQPEEK crosslinks upon heating above 400°C, however the rate of this crosslinking reaction is too slow to be economically viable. Lyle et al.⁹ have reported crosslinking in aromatic amine-terminated bisphenol A polyaryletherketone when processed above 220°C. Crosslinking occurs via attack of the amine ends at the ketone groups along the polymer backbone to form a lightly crosslinked network. Sasuga and

Hagiwara have investigated the potential for electron beam irradiation crosslinking.¹⁰ Their data suggest that chain scission accompanies the crosslinking reactions. An increase in the glass transition and a decrease in the melt temperature are observed. Small increases in the shear storage modulus above the glass transition temperature were detected. Researchers at Raychem have developed a method for crosslinking HDQPEEK using elemental sulfur.^{11,12} Again, chain scission is observed along with crosslinking. Increased modulus and strain at break at 200°C are reported as well as improved high temperature creep resistance.

EXPERIMENTAL

Reagents

1,4-Phenylenediamine and phenylsulfone were used as received from Aldrich Chemical Co. HDQPEEK of approximately 16,000 number-average molecular weight and a polydispersity of 2 was used as received from ICI Inc.

Synthesis

A 4 neck 250 mL round-bottom flask was equipped with a stirrer, thermometer, nitrogen inlet and outlet, and a heating mantle. HDQPEEK (5 g), 1,4-phenylenediamine (20 g), and phenylsulfone (80 g) were weighed into the flask. The diamine is at a ten times excess with respect to carbonyl and end groups to minimize crosslinking in solution. The flask was continuously purged with dry nitrogen. The system was heated to 270°C to effect a complete solution then cooled to 230°C ± 10°C. This temperature was maintained for 3 h. The system was then cooled to 125°C, at which point the contents of the flask were transferred to a crystallization dish. After cooling to room temperature, the now solid reaction mixture was broken into small pieces and dispersed into 500 mL of acetone. The phenylsulfone and excess 1,4-phenylenediamine dissolve leaving a rubbery precipitate. This precipitate was further washed with acetone. A thin film (0.08 mm) was pressed from this acetone swollen rubbery precipitate. The film was heated at 200°C for 1 h under pressure to remove residual acetone and give the film sufficient mechanical integrity for handling.

Mechanical Properties

Tensile samples were cut from the amine-functionalized HDQPEEK (AFHDQPEEK). Dynamic mechanical properties of these film samples were characterized as a function of temperature and time using a Dynastat dynamic mechanical tester from IMASS Inc. For comparison, samples of HDQPEEK were also characterized. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were also made on these films at a heating rate of 20°C/min on Perkin Elmer DSC II units.

RESULTS AND DISCUSSION

The reaction of the diamine with the HDQPEEK occurs at the carbonyl linkages along the polymer backbone leading to the formation of hemiaminals

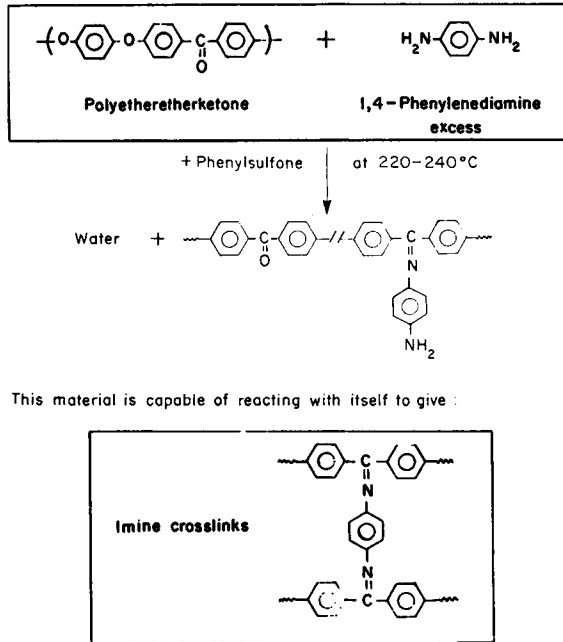


Fig. 1. Chemical modification of commercially available polyetheretherketone.

that eliminate water to form imine linkages¹³ as shown in Figure 1. Upon further heating of this material unreacted amine reacts with unreacted carbonyl to give imine crosslinks with the elimination of a second molecule of water. In Figures 2 through 4, the dynamic tensile storage modulus is plotted against temperature for commercial HDQPEEK, uncured AFHDQPEEK, and

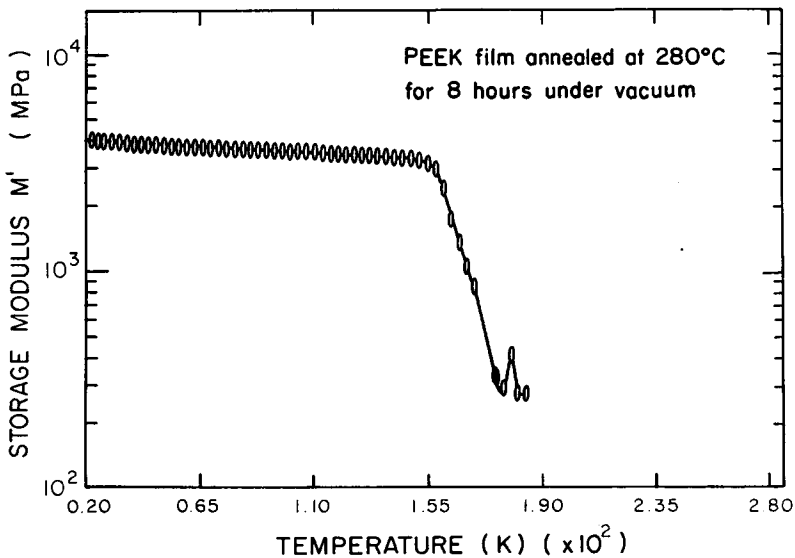


Fig. 2. Commercial PEEK with maximum crystallinity.

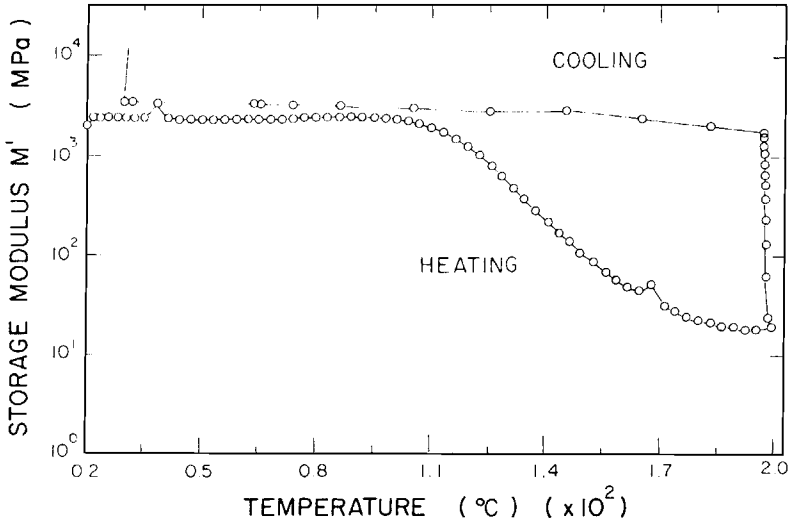


Fig. 3. Modified PEEK during cure.

cured AFHDQPEEK. In Figure 2, commercial HDQPEEK is represented. This sample was annealed to obtain maximum crystallinity prior to the temperature sweep. Even with the high level of crystallinity a sharp drop in M' is observed at 150°C to a level of 200 MPa. In Figure 3, the uncured AFHDQPEEK shows an even larger drop in M' 30°C below that of the starting material to a level of 10 MPa. This figure also shows a large increase in M' at 200°C during isothermal cure in the Dynastat temperature chamber at 200°C . The actual time at 200°C is 3 h, during which M' climbs from 10 MPa to 2 GPa. Upon isothermal heating of commercial HDQPEEK, no such

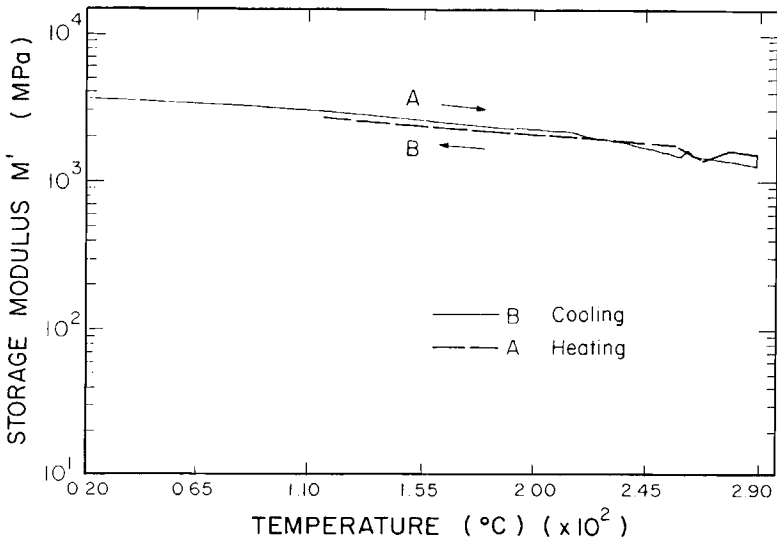


Fig. 4. Cured modified PEEK.

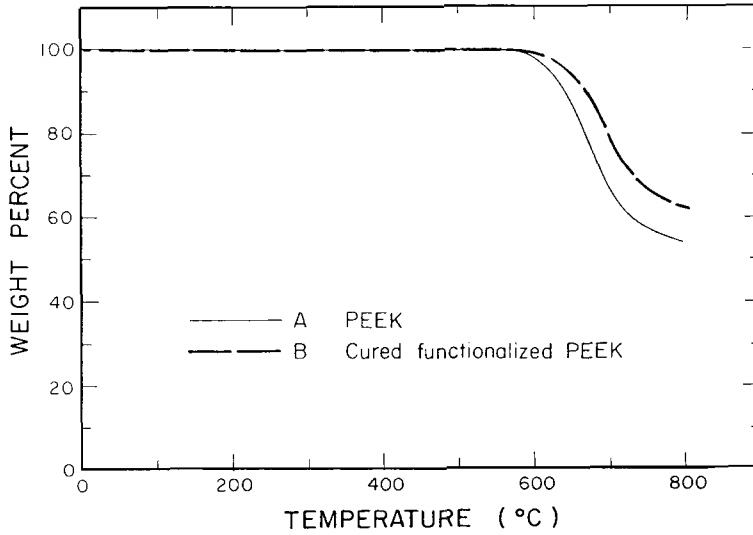


Fig. 5. Thermogravimetric analysis.

increase is observed. Figure 4 is a plot of M' versus temperature up to 280°C for the film used in Figure 3. This figure shows no drop in M' that can be associated with a glass transition temperature below 280°C. Therefore a material that was originally a soft rubber at 280°C is now a stiff glass at this temperature. A large dependence of cure time on film thickness was observed in this AFHDQPEEK as a result of the dependence of the crosslinking reaction on water removal.

TGA data for commercial HDQPEEK and cured AFHDQPEEK is shown in Figure 5. The two materials behave quite similarly with no weight loss until

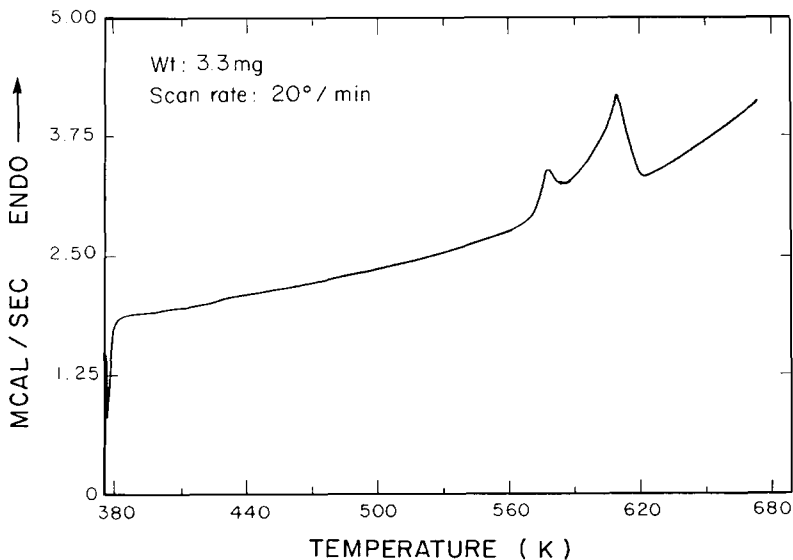


Fig. 6. DSC scan of commercial PEEK.

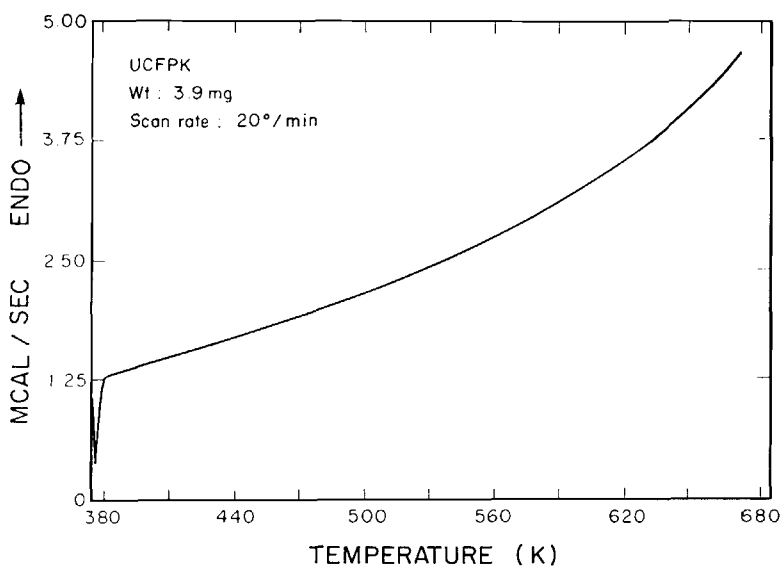


Fig. 7. DSC scan of uncured modified PEEK.

600°C and 630°C, respectively. The thermal degradation curves parallel each other, with the cured AFHDQPEEK losing 10% less than commercial PEEK at 800°C. TGA of uncured AFHDQPEEK shows significant weight loss at the cure temperature of 200°C due to the evolution of water of reaction.

DSC data for commercial HDQPEEK, uncured AFHDQPEEK, and cured AFHDQPEEK is shown in Figures 6 through 8. The scan for HDQPEEK shows the double melting peaks typical of this material.^{14,15} The DSC scan for the uncured AFHDQPEEK shows no melt transition, however, there may be

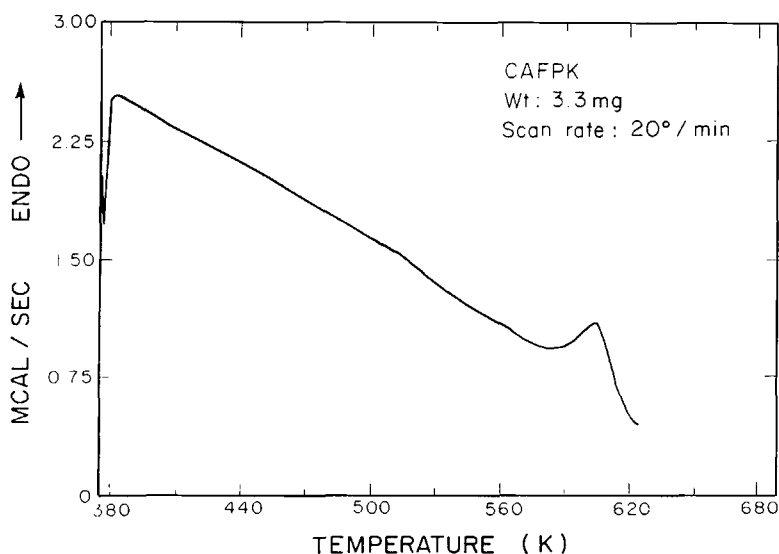


Fig. 8. DSC scan of cured modified PEEK.

one large endotherm due to volatilization of water of reaction. The data on the cured AFHDQPEEK shows a single melting peak at the same temperature as the higher melting peak in the HDQPEEK doublet.

Solubility studies have revealed that cured AFHDQPEEK is swollen by, but insoluble in methane sulfonic acid despite the solubility of HDQPEEK.

Elemental analysis of the uncured AFHDQPEEK shows an increase in the nitrogen content over HDQPEEK of 6.6%. Nucleophilic aromatic substitution of the diamine for the fluorine end groups accounts for 0.1%, with the remaining 6.5% suggesting replacement of 2/3 of the carbonyl groups with imine groups.

Carbon 13 nuclear magnetic resonance data for the cured AFHDQPEEK shows the absence of the carbonyl absorbance at 192 ppm and the presence of the imine absorbance at 156 ppm.

CONCLUSIONS

From the data it can be concluded that the observed increase in M' upon curing at 200°C and the lack of solubility of the cured AFHDQPEEK strongly support crosslink formation but alone do not confirm it. The dependence of cure time upon film thickness, elemental analysis data, weight loss of the uncured film at the cure temperature and the endotherm above 100°C in the DSC scan of the uncured AFHDQPEEK also support the imine formation mechanism. Carbon 13 nuclear magnetic resonance has shown conclusively that the AFHDQPEEK crosslinks via an imine formation reaction with the evolution of water.

Since crosslinking is occurring through reaction at the carbonyl groups this technique could be used on many ketone-containing polymers. Polymers containing benzophenone linkages are the most likely candidates as a result of the inherent stability of the Schiff bases formed. Polymers with aliphatic ketones would be less sterically hindered, however the imines formed would be much more sensitive to hydrolysis. The crosslink densities of these materials could be modulated simply by regulation of the amount of functionalization of the polymer backbone. Through the regulation of the crosslink density a wide spectrum of mechanical properties will become available. Preliminary work has suggested potential uses for AFHDQPEEK as a molecular composite matrix with poly-*p*-phenylenebenzobisthiazole as well as use as an adhesive repair material for ketone-containing thermoplastic composites.

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