

Preparation Mechanism and Characterization of a Novel, Regulable Hollow Phenolic Fiber

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ABSTRACT: A novel hollow phenolic fiber was successfully prepared by the dissolution of the uncrosslinked core of the partially crosslinking spun filament derived from the melt spinning of the phenolic resin. A series of hollow phenolic fibers with various degrees of hollowness were obtained through different preparation processes. The hollow phenolic fibers were characterized with scanning electron microscopy, infrared spectrometry, and thermogravimetric analysis. The formation of the hollow core in the hollow phenolic fibers

was attributed to partial crosslinking of the filaments during the curing process; the prepared hollow phenolic fibers had high crosslinkage after the second cure, their thermal stability was as excellent as that of the solid phenolic fiber, and their hollowness could be regulated from 5 to 85%. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2108–2112, 2007

Key words: crosslinking; FTIR; fibers; resins; thermal properties

INTRODUCTION

Phenolic fibers (PFs) have been characterized with respect to their high temperature stability and good abrasion resistance,^{1,2} their outstanding resistance to heat and corrosive environments,^{3,4} and their excellent electrical and thermal insulation.⁵ PFs are also the starting materials for the production of carbon fibers and activated carbon fibers.^{6,7} PFs were invented by Economy and Clark in 1968,⁸ and commercial PFs are called Kynol. Kynol fibers are cured phenol–aldehyde fibers made by the acid-catalyzed crosslinking of a melt-spun novolac resin, which forms a fully crosslinked, three-dimensional, amorphous network polymer structure similar to that of a thermosetting phenolic resin.⁹ Kynol products are mainly used for people and for objects as insulation against flames, heat, cold, chemicals, electricity, and noise.⁹

Hollow fibers are tubal fibers that have undergone rapid growth in the past decades. They have higher mechanical properties than round, solid ones because of their hollow structure and the improved molecular orientations created during the process of fiber preparation.¹⁰ Hollow-membrane separation technology has developed quickly with the preparation and modification of many hollow polymer fibers.^{10–12} Hollow carbon fibers based on mesophase pitch and polyacrylonitrile have also been used as reinforcing

materials.^{13,14} However, there are few reports about hollow fibers derived from phenolic resins, except from Masaru and Yoshitaka,¹⁵ who issued PFs with inner holes that were not entirely hollow PFs. If hollow PFs were disclosed, their thermal insulation properties should be elevated in comparison with those of round, solid PFs, whose thermal conductivity is 0.035 kcal/m h C.⁹

In this study, a new hollow PF was prepared by the dissolution of the uncrosslinked core of a partially crosslinking spun filament derived from the melt spinning of a phenolic resin; the hollowness of the hollow fibers could also be regulated through the adjustment of the preparation parameters.

EXPERIMENTAL

Preparation of the hollow PFs

The phenolic novolac precursor resin was prepared by the reaction of phenol with formaldehyde in the presence of an acid catalyst. Phenol (944 g, 10.0 mol), formaldehyde (600 mL of 37% formalin), and oxalic acid (50 g) were added to a three-necked glass reactor equipped with a reflux condenser, a stirrer, and a thermometer, and then the solution was heated and maintained at 90°C for 8 h. The reaction mixture was extracted several times with hot water to remove the unreacted phenol and catalyst. The polymer was fractionated to narrow down the dispersity with a water–methanol mixture and dried *in vacuo* at 115°C for 26 h. A novolac polymer with a relatively narrow molecular weight distribution was

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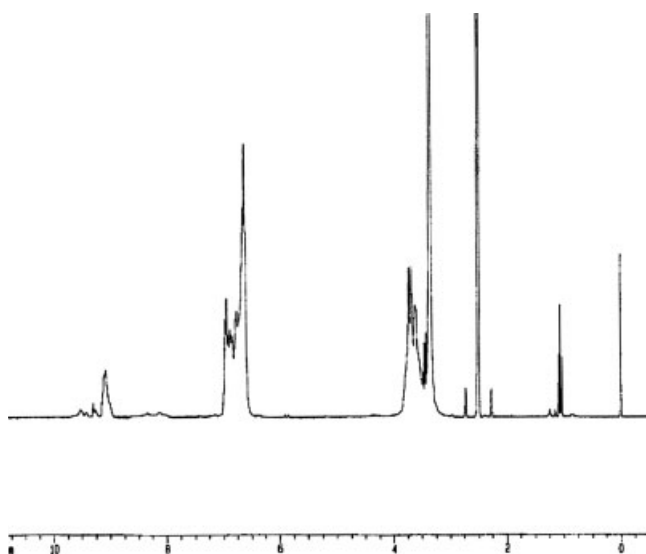


Figure 1 $^1\text{H-NMR}$ spectrum of the phenolic resin.

obtained. The fraction was characterized by $^1\text{H-NMR}$ spectroscopy (Fig. 1). The number-average molecular weight of the fraction was 1800. Melt spinning was carried out at 160°C at a rate of 800 m/min under a pressure of 0.3 MPa; the resin had a viscosity of 19,600 cP at this temperature.

The heat-meltable spun filaments were cut 20 cm from the spool and cured partially in a mixed solution of 15% formaldehyde and 15% hydrochloric acid in a bath equipped with a thermometer, stirrer, and refrigeration column. The solution was heated to a temperature of 65°C at a rate of 20°C/h and kept there for a desired time. Then, the samples were immersed and dissolved in absolute methanol. The hollow PFs were accomplished after they were fully cured again. The processing scheme for the preparation of the hollow PFs is described in Figure 2.

Sample characterization

The $^1\text{H-NMR}$ spectrum of the phenolic resin was measured with a Mercury Plus 4000 NMR (Varian, Inc., California, USA) in deuterated dimethyl sulfoxide as the solvent.

The cross-section structure and surface of the hollow fibers were observed with a Leo 438VP (Cambridge, England) field emission scanning electron

microscope. The hollowness was calculated according to the inner and outer diameters measured on cross-section scanning electron microscopy (SEM) images of hollow PFs.

Infrared (IR) spectra were recorded on a Bio-Rad FTS (Bio-Rad Inc., USA) grating IR spectrometer with the KBr disk technique to investigate the change in the functional groups of the spun filaments and the fibers prepared with various processes.

Heat analysis up to 1000°C with a Netzsch STA 449C (Wittelsbacherstr, Germany) thermogravimetry (TGA)/differential scanning calorimetry (DSC) heat analysis system under an inner atmosphere of argon was employed to investigate the high-temperature behavior of the hollow PFs. The heating rate was 10°C/min .

RESULTS AND DISCUSSION

Formation mechanism of the hollow PFs

The preparation of PFs by the acid-catalyzed crosslinking of a melt-spun novolac resin with formaldehyde was disclosed in 1981.¹⁶ The reaction mechanisms involved in the synthesis of novolacs and the crosslinking of spun filaments were identified as follows.¹⁷ First, because of the electrophilic nature of the reaction between phenol and formaldehyde, a carbonium ion, $^+\text{CH}_2\text{OH}$, reacts with the phenolic ring; the resulting benzylic intermediate reacts rapidly with another phenol to form a methylene bridge between two phenol units. In the following process, enough formaldehyde molecules continue to add onto the free para and ortho positions on the spun filaments, giving rise to the formation of PFs. It has been proposed that heat-meltable spun filaments should be first treated to cure the fibers partially with the sheath layer and then further cured under stronger conditions to form completely cured fibers.¹⁸ In this two-step treatment process, if the filaments are treated only to cure the fibers partially with the sheath layer and stopped after the first step, core-shell-structure fibers with a crosslinking shell and a uncrosslinked core should be formed. When these semifinished fibers are immersed in the solvent, the uncrosslinked core should be dissolved from the crosslinking shell. In this work, hollow PFs were prepared under the direction of this mechanism.

$^+\text{CH}_2\text{OH}$ is first created with the reaction of formaldehyde and hydrochloric acid in the cured solu-

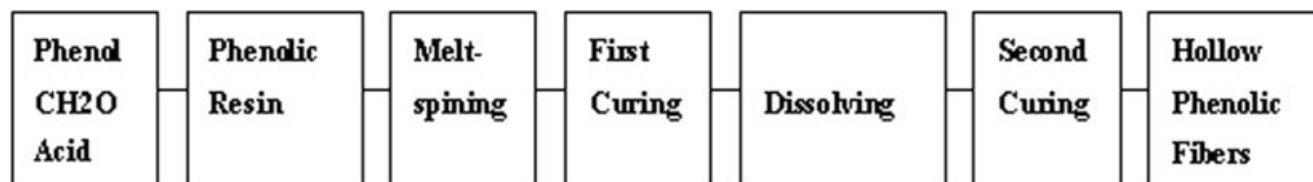


Figure 2 Flow chart for the preparation of hollow PFs.

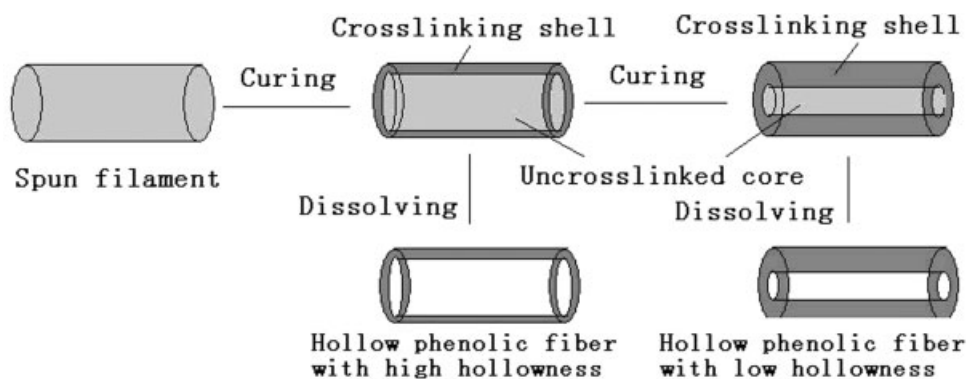


Figure 3 Schematic model of the evolution of hollow PFs.

tion. It reacts with the phenolic rings and diffuses from the skin into the inner layer of the filaments and then reacts at the same time. Therefore, the curing process is the crosslinking reaction, pervading step by step from the filament skin into the core under the appropriate curing conditions. The thickness of the crosslinking skin layer can be controlled through the adjustment of the degree of curing. The same thickness of the hollow-fiber layer remains after the dissolution of the uncrosslinked core in the solvent. As the degree of the cure increases, the crosslinked skin layer becomes thicker, and the hollowness forming in this process decreases accordingly. A schematic model of the evolution of hollow PFs is shown in Figure 3. In this study, the curing degree was controlled by increases in the curing time. The melt-spinning filaments were cured in a

mixed solution of 15% formaldehyde and 15% hydrochloric acid at 65°C for 1, 2, 3, 4, or 5 h. After the uncured core was dissolved in the solvent, a series of hollow PFs with various degrees of hollowness were successfully prepared. The SEM images of the cross-section structure and surface of the hollow fibers are shown in Figure 4. The hollowness of these five hollow fibers [Fig. 4(b–f)] decreased in turn as their curing time and curing degree increased accordingly. The minimum hollowness [Fig. 4(b)] was 4.5%, and the maximum hollowness [Fig. 4(e)] reached 85%, whereas only 40–50% could be obtained in high-hollowness hollow fibers of other polymers prepared with other methods. The thickness of the hollow fibers was symmetrical; the hollow ring was almost concentric circles (see Fig. 4), and the outside [Fig. 4(a)] and inside [Fig. 4(b–e)] surfaces

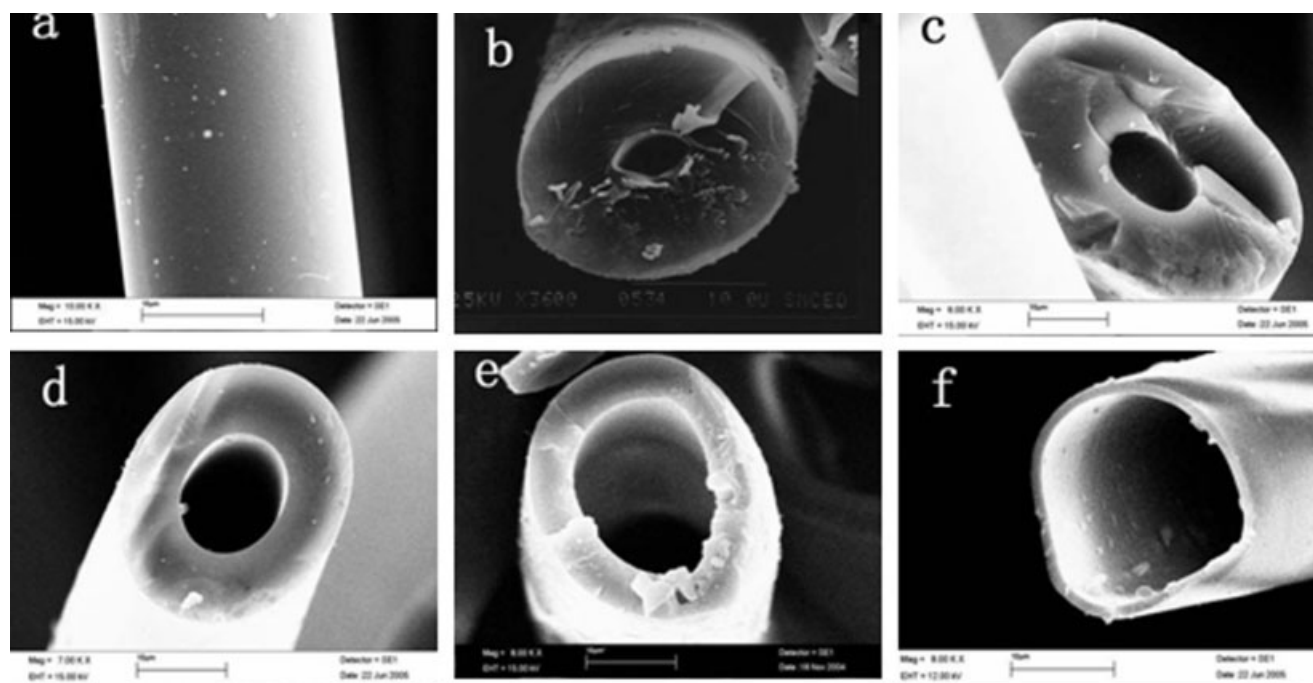


Figure 4 SEM images of (a) the surface of hollow PFs and (b–f) cross-section structures of hollow PFs with various degrees of hollowness: (b) 4.5, (c) 8.0, (d) 25, (e) 45, and (f) 85%.

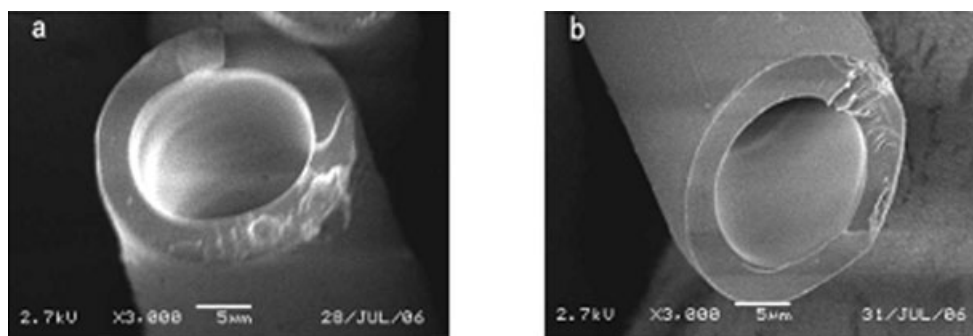


Figure 5 SEM images of cross-section structures taken from different positions of 20-cm hollow PFs: (a) 2 cm to the end and (b) 10 cm to the end.

were flawless and smooth. The structure of these fibers was quite distinct from Masaru's PFs with inner holes,¹³ which were not entirely hollow PFs. The SEM images [Fig. 4(a–e)] also show that the whole cross section of the hollow PFs was uniform and compact, suggesting that the hollow PFs had a high and homogeneous crosslinkage degree after the second curing process.

The filaments were cut to desired lengths of approximately 20 cm before the hollow fibers were prepared. The dissolved solvent was absolute methanol, and the size of the CH₃OH molecule was close to that of the curing ion, ⁺CH₂OH, so CH₃OH could diffuse like ⁺CH₂OH not only from the two ends of the filaments but also from the cured skin to the interior and then dissolve the uncured core. The uncured part could be extracted entirely in this way and leave a round channel through the fibers. Figure 5 presents SEM images of cross-section structures taken from different parts of hollow fibers; the cross-section images were taken not from a single hollow fiber but from a hank of hollow fibers that were prepared under the same conditions. The images confirm that it was a continuous hollow structure extending along the axial direction of the fibers in that length.

IR spectra of the hollow PFs

The degree of crosslinking in the curing process could be reflected by changes in the functional groups of the fibers.¹⁹ The spun filaments and three treated fibers were characterized by FTIR spectroscopy, and the results are presented in Figure 6. In comparison with the spun filaments [Fig. 6(a)], in the IR spectra of the solid PFs cured sufficiently [Fig. 6(d)], the relative intensity of the bands corresponding to the phenolic O–H group stretch (3410 cm⁻¹), aromatic C–H stretch (3005 cm⁻¹), quadrant ring stretch (1608 cm⁻¹), 1,4- and 1,2,4-substituted benzene ring (820 cm⁻¹), and 1,2- and 1,2,6-substituted benzene ring (770 cm⁻¹) decreases; at the same time, the relative intensity of the band corresponding to the methylene bridge

–CH₂– (1475 cm⁻¹) increases. IR spectra of the hollow fibers cured for a second time [Fig. 6(c)] change just the same; this result indicates that after the two-cure treatment, abundant ⁺CH₂OH reacts with the phenolic ring, and enough –CH₂– methylene bridges are created between the free para and ortho positions in the hollow PFs, giving rise to the formation of the same high crosslinkage as that of the solid PFs cured sufficiently.

In the hollow fibers without curing again [Fig. 6(b)], the relative intensity of the aromatic C–H stretch (3305 cm⁻¹), quadrant ring stretch (1608 cm⁻¹), 1,4- and 1,2,4-substituted benzene ring (820 cm⁻¹), and 1,2- and 1,2,6-substituted benzene ring (770 cm⁻¹) is lower, and the relative intensity of the methylene bridge –CH₂– (1475 cm) is higher than that of the spun filaments [Fig. 6(a)]. This is considered to be due to the elementary crosslinking in the preparatory curing process. However, the decreased and increased extent of the functional group bands is lower in comparison with the solid PFs cured sufficiently [Fig. 6(d)] and the hollow PFs cured for a second time [Fig. 6(c)]. This result suggests that the hollow fibers without curing again were not crosslinked sufficiently, although they

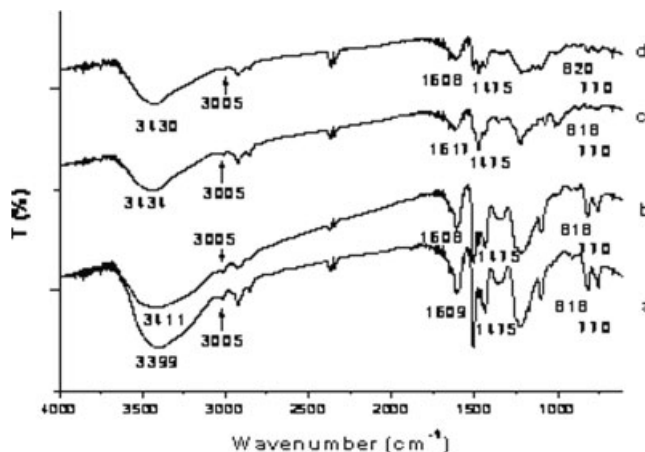


Figure 6 IR spectra of (a) spun filaments, (b) hollow PFs without curing again, (c) hollow PFs cured for a second time, and (d) solid PFs cured sufficiently.

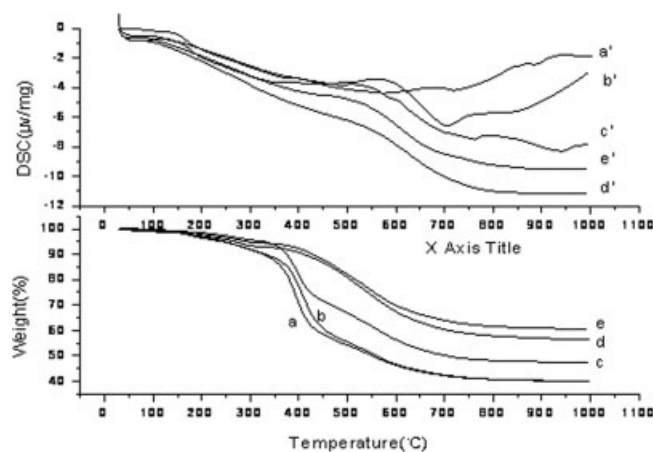


Figure 7 TG–DSC diagrams: (a,a') phenolic resin, (b,b') spun filaments, (c,c') hollow PFs without curing again, (d,d') hollow PFs cured for a second time, and (e,e') solid PFs cured sufficiently.

were crosslinked to some extent in the first preparatory curing process. It also suggests that the second curing process was essential to preparing high-crosslinkage hollow PFs.

Thermal stability of the hollow PFs

The specific advantages, including heat resistance and flame retardancy, of PFs depend on three-dimensional, crosslinking, network structure formation during the curing process. Their thermal stability and anaerobic char yield increase with enhanced crosslink density. The TG–DSC curves of the phenolic resin and four fibers are given in Figure 7. Little change in their thermal stability occurred when the phenolic resin [Fig. 7(a)] turned into spun filaments [Fig. 7(b)]; their DSC curves [Fig. 7(a',b')] differed because the granularity of the phenolic resin differed from the short filaments and the tropism was improved during the melt-spinning process. It is clear from Figure 7 that all three cured fibers possessed better thermal stability than the spun filaments. A significant improvement was made in the solid PFs cured sufficiently [Fig. 7(e)] and the hollow PFs cured for a second time [Fig. 7(d)], and the thermal stabilities of the two fibers were very close. The anaerobic char yield of the hollow fibers [Fig. 7(d)] was lower than that of the solid fibers [Fig. 7(e)] because of their hollow structure, which provided more surface for small molecules to escape in the pyrolysis process; this was also likely to induce the DSC curve [Fig. 7(d',e')] distinctions of these two cured fibers. PFs was carbonized and activated to carbon fibers and high-surface-area activated carbon fibers, so all these hollow PFs were also good precursors of hollow carbon fibers and activated hollow carbon fibers for their high char yields.

As shown in Figure 7, the thermal stability of the hollow fiber without curing again [Fig. 7(c)] was better than that of the spun filaments [Fig. 7(b)] but low compared with that of the two sufficiently cured fibers [Fig. 7(d,e)]. The result confirms that the hollow fibers were cure-graded and not crosslinked sufficiently in the first preparatory curing process.

CONCLUSIONS

Novel hollow PFs were prepared for first time by the dissolution of the uncrosslinked core of a partially crosslinking spun filament derived from the melt spinning of a phenolic resin. The preparation mechanism was depicted in detail, and a series of hollow PFs with various degrees of hollowness were successfully prepared by changes in the preparation parameters under the direction of this mechanism. SEM, FTIR, and TG studies showed that the prepared hollow PFs were highly crosslinked after the second cure, their thermal stability was as excellent as that of solid PFs, and their hollowness could be regulated from 5 to 85%. The hollow PFs behaved excellently with respect to heat resistance and heat insulation in comparison with conventional solid PFs because of their unique hollow structure. All these hollow PFs were good precursors of hollow carbon fibers and activated hollow carbon fibers for their high char yields.

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