Influence of epichlorohydrin content on structure and properties of high-ortho phenolic epoxy fibers

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ABSTRACT: The high-ortho phenolic epoxy fibers (HPEFs) were prepared by the crosslinking of heat-meltable spun filaments derived from melt-spinning of the novolac epoxy resins copolymerized among phenol, formaldehyde, and epichlorohydrin (ECH) in the presence of zinc acetate and sulfuric acid catalyst, and cured in a combined solution of formaldehyde and hydrochloric acid. The resulting fibers were heat-treated in N_2 at elevated temperature. Infrared (IR) spectrometer, thermogravimetric analysis (TGA), scanning electron microscope (SEM), and electrical tensile strength apparatus were employed to characterize the change of functional groups, thermal performance, microstructure of fibers, and mechanical properties. The results show that the addition of ECH in the precursor resin can increase the content of long alkyl ether linkage, and gain the peak of thermal stability and mechanical strength. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43375.

INTRODUCTION

Phenolic fibers are applied widely in flame resistant textiles, composites, friction materials, and precursors for the production of carbon and activated carbon fibers due to high flame resistance, outstanding resistance to corrosive environments, high thermal insulation, and so on.[1–4] But it has kept a low volume of usage compared with that of general fibers, which is primarily due to it being brittle caused by rigid chain, low molecular weight, crosslinking network, and limited thermal stability resulted by the oxidative decomposition of methylene bridge between phenol groups.[5–7] High-ortho phenolic fibers can be prepared by melt-spinning of high-ortho novolac resins,[8] which show more spinnibility and reactivity because of a high molecular weight, regular structure, low viscosity, and high reaction activity of para.[9] However, a high-ortho phenolic novolac resin would generate fibers with a low tensile strength, where a fully dense skin layer formed by the highly active para hinders the diffusion of $^+CH_2OH$ into the core layer of fibers, and causes the formation of an apparent skin-core structure.

Phenolic-epoxy resin combines the properties of phenolic resin (low cost, high impact resistance, high hardness, and high resistance to acid attack), and the properties of epoxy resin (high alkali resistance, flexibility, and low shrinkage). A series of novolac epoxy resins has been synthesized and applied,[10,11] which shows high thermal stability, high mechanical strength. Meanwhile, phenolic fibers modified by epichlorohydrin show an increasing of the elongation and toughness, and also have good heat stability and high carbon yield at the same time.[12] However, the spinning of the high-ortho novolac epoxy resin has not been reported.

In this study, a linear high-ortho phenolic epoxy resin was prepared. Based on the special structure of high-ortho phenolic epoxy resins, the high-ortho phenolic epoxy fibers (HPEFs) were prepared by the melt-spinning, crosslinking of spun filaments in a mixture of formaldehyde and hydrochloric acid, and heating further from room temperature to 240 °C in nitrogen. The resultant HPEFs exhibit excellent thermal and mechanical properties.

EXPERIMENTAL

Synthesis of the High-Ortho Novolac Epoxy Resin
All chemicals were of analytical grade and used without further purification. Phenol, epichlorohydrin (ECH), and zinc acetate were supplied by Tianjin Fengchuan Chemical Reagent Company (China). Formaldehyde (37 wt %) and sulfuric acid (98 wt %) were supplied by Xilong Chemical Co. (China).
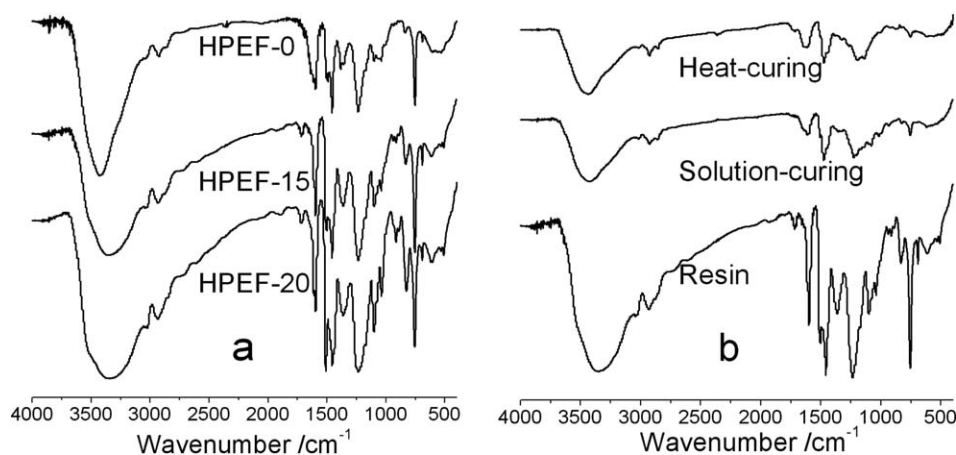
Figure 1. IR spectra of the high-ortho novolac ECH-containing filaments with different ECH contents (a) and the HPEF-15 filaments cured in different conditions (b).

The novolac precursor resins were prepared by the reaction of phenol, formaldehyde, and ECH in the presence of zinc acetate and sulfuric acid catalysts. Phenol (100.0 g), formaldehyde (73.3 g 37% formalin, 0.85 mol per 1 mol phenol), ECH, and zinc acetate (2.0 g, 1 g per 50 g phenol) were added in a three-necked flask, equipped with a reflux condenser, stirrer, and thermometer. The mixture was heated and maintained boiling for 4 h, and then sulfuric acid (0.3 mL, 0.3 mL per 100 g phenol) was added, followed by further heating under reflux for 50 min. The reaction mixture was distilled under vacuum to remove water and unreacted phenol at elevated temperature up to 120 °C for 2 h. A series of novolac precursors was obtained by changing the concentrations of ECH.

Preparation and Curing of the Phenolic Epoxy Fibers

HPEFs were prepared by melt-spinning using the melting phenolic precursor resins at 125 °C with the winder speed of 430 m min^{-1}, where the melt-spinning machine with a single hole spinneret plate customized by our group was applied. The filaments were cured in a combined solution of hydrochloric acid (12 wt %) and formaldehyde (18 wt %) in a bath equipped with a thermometer and stirrer. The solution was heated form room temperature to 95 °C at a heating rate of 15.4 °C h^{-1}. Then, the cured fibers were heated at a rate of 2.5 °C min^{-1} until the temperature reached 240 °C and held for 2 h in nitrogen in oven. Finally, the resultant samples taken out after cooled to room temperature were washed with water and dried at room temperature.

The obtained resins or filaments containing 10.0 g, 12.5 g, 15.0 g, 15.0 g, 17.5 g, and 20.0 g ECH in the reaction flask are denoted HPEF-10, HPEF-12.5, HPEF-15, HPEF-17.5, and HPEF-20, the reference fiber without ECH is denoted HPEF-0. The resultant HPEFs cured in solution and in heating oven are denoted HPEF-C-S1 and HPEF-C-H2, respectively.

Characterization

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Magna-FTIR 750 spectrometer using the KBr disk technique to investigate the change of functional groups of the resins and fibers cured under various curing conditions. The fibers were pulverized and mixed with KBr before being pressed into a disk. The concentration of the samples in KBr was 2.5 wt %, and 0.2 g of KBr was used in the preparation of the sample disks. The relative intensity of infrared (IR) bands was defined as the corrected height of IR peaks divided by the height of 100% transmission in IR spectra.

Thermogravimetric analysis up to 1000 °C with a NETZSCH STA 409 PC/PG thermogravimetric analysis system (Germany) under an inner atmosphere of nitrogen was employed to investigate the high-temperature behavior of the high-ortho ECH-containing phenolic fiber. The heating rate was 20 °C min^{-1}.

The cross-section structure and surface of the fibers were observed with a JEOL JSM-6360LV scanning electron microscopy (Japan).

The tensile performance of HPEFs were measured by a Darong YG(B) 003A electrical tensile strength apparatus (Wenzhou, China), and the diameters of the fibers were observed using microscopy (LWT300LPT, Xian Cewei Optoelectronic Technology Co., China).

RESULTS AND DISCUSSION

FTIR

The chemical structures of the high-ortho novolac epoxy filaments and fibers were confirmed with FTIR. IR spectra [Figure 1(a)] show the characteristic absorptions of a benzene structure for the novolac resins at 1600 cm^{-1} (aromatic C=C stretching), 1230 cm^{-1} and 1103 cm^{-1} (asymmetric and symmetric stretching of C–O–C), 1458 cm^{-1} (methylene bridge –CH_2–), 1041 cm^{-1} (PhCH_2–OH stretching), and 3041 cm^{-1} (stretching of Ph–H). Characteristic absorption bands assigned to the C–Cl appear at 692 cm^{-1}. Additionally, IR absorption band at 914 cm^{-1} was assigned to the groups of epoxy. The peak around 754 cm^{-1} corresponds to 1,3- and 1,2,3-substituted benzene ring. The peak at 825 cm^{-1} is attributable to 1,4- and 1,2,4-substitution.

Quantitative analysis was done according to the literature.[13] The benzene ring absorption at 1600 cm^{-1} was used as the internal

Table I. The Functional Group Values of Samples

Wavenumber/cm^{-1}	HPEF-0	HPEF-10	HPEF-15	HPEF-20	HPEF-15-S1	HPEF-15-H2
1720 (C=O)	0.053	0.139	0.254	0.244	0.496	0.488
1458 (CH$_2$)	0.879	1.551	1.607	1.892	1.520	1.190
1230 (C–O–C)	1.686	1.550	1.656	2.033	1.634	1.063
914 (oxirane ring)	0.097	0.163	0.297	0.370	0.680	0.397
692 (C–Cl)	0.316	0.450	0.479	0.503	0.647	0.514

standard. According to the Beer-Lambert Law, the ratios of X group absorbance (A_X/A_{1600}) were obtained and shown in Table I.

From Figure 1 and Table I, it can be seen that the methylene bridge, oxirane ring, and C–Cl value increase with increasing the content of ECH. The results suggest that ECH reacts with the phenol hydroxyl group in the novolac, leading to an increase of the epoxy value, whereas, partially ECH reacts with active hydrogen via ring-opening of epoxy group.[10,11]

The crosslinking in the curing process could be reflected by changing the functional groups of the fibers.[5] The spun filaments and the solid HPEFs cured in combined solution and cured in heating oven were characterized by FTIR spectroscopy, and the results are presented in Figure 2. In comparison with the spun filaments, the relative intensities of the bands corresponding to the methylene bridge (1458 cm^{-1}), C–O–C stretch-

Figure 2. The reactions between HCHO, ECH, and phenol in synthesis (a) and curings (b).

ing (1230 cm^{-1}) decrease. At the same time the relative intensity of the band corresponding to the C=O (1720 cm^{-1}) converted from the methylene links increases. The unstable methylene ether bridge is transformed into methylene, further into C=O group during curing, which increases the thermal and mechanical properties.

The different wavelengths in the spectra of the different compounds are assigned according to spectroscopic studies of substituted benzene. The changes in the characteristic absorption band intensities are observed between the different ratios of 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene. In all cases, the reference invariant bands of 754 cm^{-1} and 825 cm^{-1} corresponding to the 1,2,3- and 1,2,4-substitution of the aromatic ring are used.[8] The relative intensives (I) of the absorptions at 825 cm^{-1} and 754 cm^{-1} (A_{754}/A_{825}) of the novolac resins are considered a measure of the extent of benzene ring substitution (Table II).[14,15] The effect of the isomeric composition on the novolac resins is evaluated by the study of the substitution of the benzene ring. An approximate evaluation of ortho–ortho ratio of novolac resin can be obtained using the relative intensives.

It is evident that the O/P ratios (substituted ortho and para carbon ratio) of phenolic fibers changes with the curing and ECH-content. As shown in Table II, the O/P values of resin decrease from 6.46 to 1.95 with increasing content of ECH, which implies that more para position of phenol reacts with increasing ECH in the novolac. The O/P value of phenolic fiber cured in solution and heating oven decreases gradually from the highest value of filament. The decreasing value of O/P implies that the para position of phenol easily crosslinks with –OH because of the higher activity than the ortho position during the curing. However, the HPEF-15 fiber shows that the value of O/P increases slightly after the heat-curing, which is more close to ideal structure of crosslinking (O/P=2). During the curing of
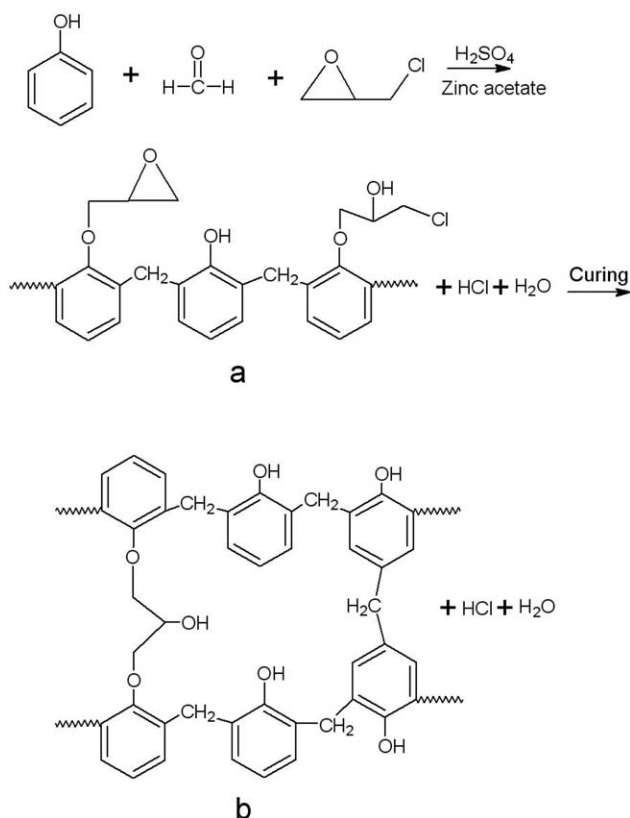
Table II. The Ortho/Para (O/P) Ratios in Different ECH Contents and Curing Processing

Polymer code	O/P ratio of filament	O/P ratio of solution curing	O/P ratio of heat curing
HPEF-0	6.46	2.59	1.66
HPEF-10	3.43	1.51	1.22
HPEF-15	3.27	1.59	1.70
HPEF-20	1.95	1.38	1.26

HPEF-15, the para position of phenolic reacts completely, and then the ortho position has to react continuing. As a result, the HPEF-15 fiber shows satisfying mechanical properties.

Thermogravimetric Analysis (TGA)

The specific advantages of HPEFs, including mechanical properties, heat resistance, and flame retardancy, depend on the change of ECH content, and three-dimensional crosslinking network structure formed during the curings. Their thermal stability and anaerobic char yield increase with enhanced crosslink density. To determine the thermal stability of the polymers, thermogravimetric analysis (TGA) of HPEF was carried out under nitrogen. Figure 3 shows the TGA curves of fibers cured in solution (a) and fibers cured in oven (b).

As shown in Figure 3(a), in the temperature range of 110–300 °C, the total weight loss for all the samples may correspond to the loss of some small, end groups, and weaker bonds in the chains of the PFs, further curing between them.[16,17] Such phenomenon is similar to other experimental results reported elsewhere.[18] With the elevation of the pyrolysis temperatures, especially above 157 °C, the polymeric system is disintegrated gradually, resulting in the continuous weight loss due to the elimination of various volatiles.

From 150 to 320 °C, as shown in Figure 3(a), the initial decomposition temperature decreases from 220 °C to 157 °C with increasing ECH. We believe that it is caused by the bond rupture of the increasing unstable C–Cl, which is obtained by the reaction between the ring-open of ECH with phenol. The addition of ECH increases the cross linkage of phenolic fiber, and the HPEF-10 fiber cured by solution shows a higher thermal stability than HPEF-0 fiber. However, the C–Cl also increases with increasing of the ECH content, and the increasing unstable C–Cl plays an important role in weight loss. On the other hand, the higher loss temperatures of C–Cl induce more chain breaking damaged by HCl. As a result, the weight loss of HPEF-20 is lower than that of HPEF-15 at the first weight loss.

The heat curing was applied from room temperature to 240 °C slowly, and then kept for 2 h. As shown in Figure 3(b), the thermal stability of fiber decreases after the fiber is cured in solution, but it increases after the fiber is cured in oven. The initial decomposition temperature decreases from 207 °C for HPEF-15 to 182 °C for HPEF-15-S1. It may be due to the bond rupture of unstable C–Cl. The heat curing makes the unstable group transformed, and increases the thermal stability of HPEF fiber. The initial decomposition temperature increases to 347 °C for HPEF-15-H2, which is even much higher than the second thermal degradation process of resin and the solution-curing fiber. It suggests that the 2 h heat curing at 240 °C increases the thermal stability of the ECH-containing fibers with increasing the carbonyls converted from the methylene links (analysis in FTIR), leads to lower weight loss [Figure 3(b)]. The final degradation process of the resin, solution-curing fiber, and heat-curing fiber (decomposition temperature higher than 626 °C) are similar with each other, it suggests that the addition of ECH do not change the structure of main chain. Figure 3(b) also shows that the char residues of HPEF-15-H2 resin are 74.1 and 60.7% after being pyrolyzed at 626 °C and 1000 °C, respectively. These values are obviously higher than those of the HPEF-15 resin (60.7 and 52.3%) and HPEF-15-S1 (51.9 and 45.4%).

This is reasonable that the phenolic fibers, derived from the heating curing novolac filament, have a higher degree of crosslinking among epoxy group, PhCH$_2$–OH, Ph–OH, and other reactive groups. HPEFs with the high crosslinking degree have maximum quantity of trisubstituted phenol compounds and less quantity of monosubstituted phenolic rings than the HPEFs cured in solution. In addition, the epoxy group of HPEFs substitutes the labile phenolic hydroxyl group. Therefore, they limit the formation of low molecular weight compounds generated from the unstable terminal groups and inner units during the pyrolysis of the HPEFs. The weight loss of heat-curing fiber is lower than those of the other HPEFs. The results indicate that the increasing of cross linkage can effectively stabilize the terminal benzene rings from scission.

The char yields at 1000 °C were also collected. Char yield is correlated to the polymer's flame retardancy,[19] but it should be pointed out that our experimental char yield of fibers cured in solution show a decreasing when the content of ECH higher than 15%. The increasing thermal stabilities are observed when the fiber is cured in oven, thus the heat-curing processing plays an important role in the char formation. Because char yield has been correlated to flame retardancy, these fibers are expected to have good flame retardant properties.

Mechanical Properties

Figure 4 summarizes the tensile properties of the phenolic epoxy fibers samples after cured in oven. Firstly, the higher
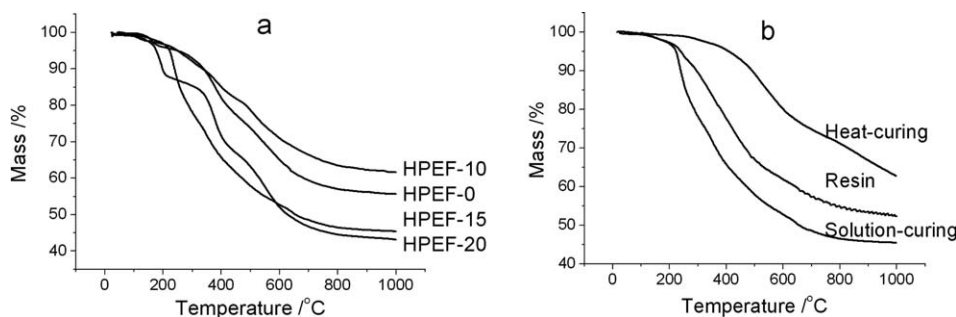

Figure 3. TGA curves of high-ortho ECH-containing phenolic fibers cured in solution (a) and the HPEF-15 filaments cured in different conditions (b).
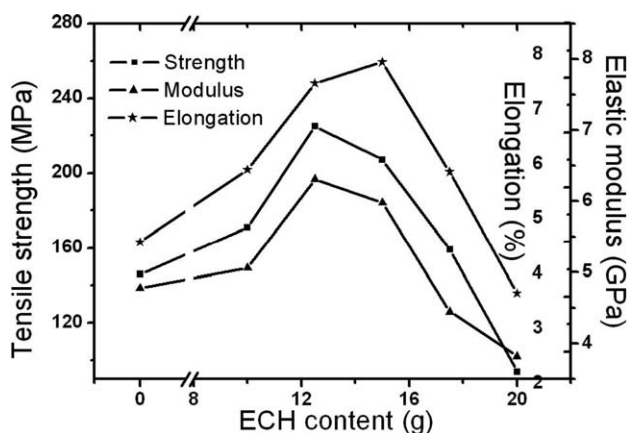
Figure 4. The tensile properties of high-ortho phenolic fibers with different ECH contents.

ECH content results in the higher tensile strength, elastic modulus, and elongation, i.e., from 146 MPa, 4.8 GPa, and 4% for HPEF-0-H2 to 225 MPa, 6307 MPa, and 6.9% for HPEF-12.5, respectively. It is clear that the mechanical properties strongly depend on the content of ECH, where the cross linkage increases with increasing the content of ECH. At the same time, the ring-opening reaction of epoxy increases the molecules chain flexibility because of the longer alkys ethers bridge instead of methylene bridge. However, the tensile strength, elastic modulus decreases to 207 MPa, 5977 MPa for HPEF-15-H2, while the elongation keeps increasing to 7.29%. This is mainly due to the fact that the main chain damaged by escaping HCl results in the tensile strength, elastic modulus decreasing, while the more alkys ethers bridge between phenols increases the elongation. Finally, the mechanical properties begin to entirely decrease when the content of ECH increase to 17.5%.

Scanning Electron Microscope (SEM)

Scanning electron microscopic (SEM) images of the cross-section structure and surface of the filament, and cured fibers are shown in Figure 5. It can be seen that all the fibers have smooth skin. Figure 5(a) shows that the whole cross-section of the filament is uniform and smooth. It suggests that the corresponding novolac resin exhibits a fine and homogeneous spinnability. It can be seen that the filament breaks during the specimen preparation, and the failure of filament shows a brittle manner according with the SEM image.

The as-spun filaments were cured from room temperature to 95 °C in a mixture of hygrochloric acid and formaldehyde solution. Figure 5(b,c) show SEM micrographs of the fiber cured in solution. The smooth skin of fiber is kept after cured in the mixture solution, moreover, the cross-section shows a toughness fracture structure. The inhomogeneous distribution of the rare, linear structure implies that the mechanical properties of fiber increase slightly. The skin-core structures of HPEFs do not appear after curing in solution. It is beneficial to further improve the mechanical and thermal properties through the heat-curing processing.

The fibers were further cured from room temperature to 240 °C in nitrogen. As shown in Figure 5(d), the smooth skin of fiber is kept, and the cross-section structure becomes more roughened than that of fiber cured in solution. The uniform and fine structure formed during the heat curing increases the toughness of fiber further.

CONCLUSIONS

High-ortho novolac epoxy resins have been synthesized by copolymerization among phenol, formaldehyde, and ECH in the presence of zinc acetate and sulfuric acid catalyst. The fibers were prepared by melt-spinning the resin, followed by curing the filaments with
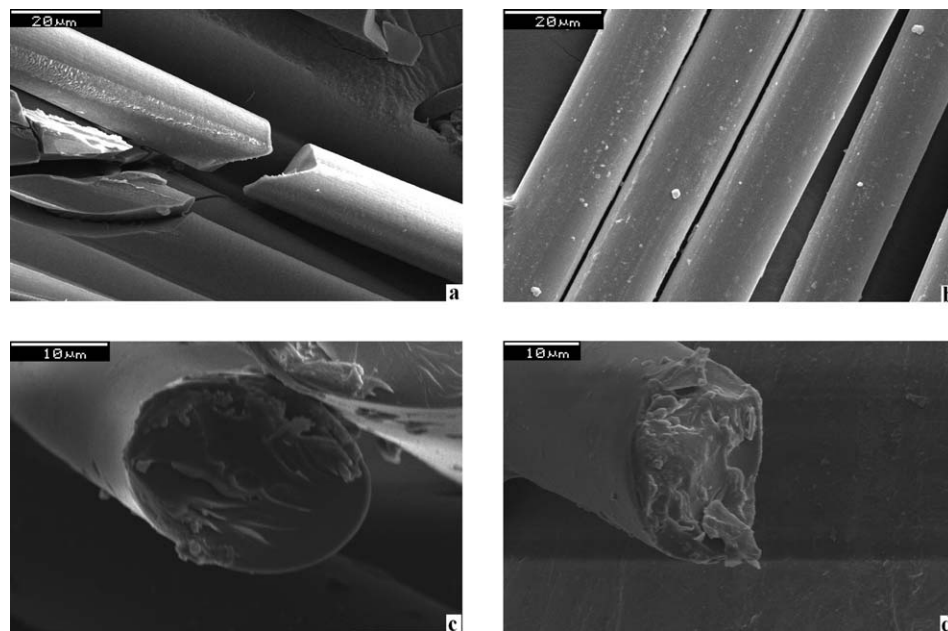

Figure 5. SEM images of HPEF-15 filament (a,b), fibers cured in solution (c), and cured in oven (d).

the mixture of hydrochloric acid and formaldehyde solution, and curing with heat-treated in nitrogen at elevated temperature. The alkyl ether band and carbonyl group formed during the synthesis and curing processing increases the mechanical and thermal properties of fibers. The thermal stability increases further after fibers are cured in nitrogen, and the fibers exhibits the minimum weight loss under 347 °C. The cross-sections of fibers converted from smooth to rough suggest the increasing of the toughness performance. The elongation increase to 7.29% for HPEF-15, however, the tensile strength and elastic modulus begins to reduce from 225 MPa, 6.3 GPa to 207 MPa, and 6.0 GPa when the ECH content increases from 12.5 wt % to 15 wt %.

ACKNOWLEDGMENTS

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