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Synthesis and Characterization of Poly(ether ether ketone) Derivatives Obtained by Carbonyl Reduction

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ABSTRACT: Hydroxylated poly(ether ether ketone) (PEEK-OH) samples, with different degrees of functionalization, have been synthesized by selective carbonyl reduction. The ATR-FTIR and NMR spectra corroborated the reduction success, showing a decrease in the intensity of the peaks related to the ketone group and simultaneously the appearance of new signals associated with the hydroxyl group. TGA curves indicated a reduction in thermal stability with increasing hydroxylation degree (HD), attributed to changes in the spatial organization of the molecules and a less intense resonance effect. DSC experiments showed a progressive diminution in the crystallization and melting temperatures as the number of hydroxyl groups increased due to the restrictions on polymer chain diffusion imposed by the strong hydrogen bonds. Furthermore, the level of crystallinity of the derivatives drastically decreased upon increasing HD, as evidenced from the X-ray diffraction spectra. The random distribution of this functional group inhibits the molecular packing, leading to the formation of smaller and less perfect crystals. DMA studies revealed a decrease in both storage and loss moduli as the extent of modification increased. However, the presence of the hydroxyl group caused a significant improvement in the glass transition temperatures of the polymers, particularly at higher degree of functionalization, where the increment was close to 40 °C. Such enhancement is attributed to a decrease in mobility and flexibility induced by the strong intermolecular interactions between the chains.

Introduction

Poly(ether ether ketone) (PEEK) is a semicrystalline high-performance thermoplastic with a rigid aromatic backbone structure constituted of a hydroquinone and a benzophenone segment. It possess excellent thermal[1] and mechanical[2] properties, broad chemical resistance, oxidation stability,[3] and passive biocompatibility,[4] which combined with its low cost and easy processability make it suitable for a wide range of applications, such as automobile, aerospace, medical, and electronic industries.[5−7] The main disadvantage of this polymer is its insolubility in most of organic solvents, which makes difficult its functionalization and ability to interact with other substances. Chemical modifications of PEEK have emerged as an interesting research field for the development of materials with specific physical-chemical properties that may lead to further new applications. The presence of the aromatic rings in the PEEK structure is important for its functionalization, as they can act as an electron source for electrophilic substitution reactions. Moreover, the carbonyl group in the benzophenone segment is also a versatile reactive handle for selective modifications of this polymer.

In the literature, several methods are reported to prepare PEEK derivates. The most common[8−10] involves the polymerization of previously functionalized monomers, although it can lead to side reactions which result in undesirable byproduct. Other way of PEEK modification is to dissolve the polymer in a strong acid, such as sulphuric, and add a reactant which incorporates the appropriated substituent group; this generally results in amorphous products soluble in polar aprotic solvents. The drawbacks of this procedure are its strong dependence on the reaction conditions (temperature, mechanical stirring, PEEK concentration), the risk of sulfonation, and in some cases degradation of the polymer, which practically limits this method to a sulfonation reaction.[11−14] PEEK functionalization can also be performed in suspension in a single step reaction, as reported by Conceição et al.,[15,16] who prepared different modified polymers by nitration, reduction to the amine group, or carbonyl reduction. Surface reduction of amorphous PEEK samples has been reported by Franchina and McCarthy[17] and Henneuse et al.,[18−20] who developed a series of derivatives through selective reactions on the carbonyl group. Recently, Colquhoun and coworkers[21] reported a different derivatization approach based on the dithioketalization of the ketone groups under strong acid conditions.

Most of the aforementioned studies were aimed at the preparation of soluble derivatives for potential application in biocompatible systems; they focused mainly on the synthesis procedure, but very few of them accomplished an exhaustive characterization of the resulting modified polymers in order to investigate possible changes in its structural and functional properties. Fundamental work in the characterization of PEEK derivatives is required for further practical applications; in particular, the incorporation of nanoscaled carbon fillers into these modified polymers would lead to nanocomposites with unique physical properties such as enhanced tensile strength and exceptionally high electrical and thermal conductivity, suitable for industrial applications, especially for the aircraft industry. To our knowledge, there are no published studies to date related to the integration of carbon nanotubes into PEEK derivatives, although a recent work reported by Baaba et al.[22] deals with functionalization of multiwalled carbon nanotubes surface with sulfonated PEEK, an approach that can be used to facilitate incorporation of nanotubes into polymer matrices.

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In this work, an attempt is made to prepare PEEK derivatives with such an extent of chain modification that enables to maintain the exceptional thermal and mechanical properties of PEEK and simultaneously increases the polymer hydrophilicity and its number of reactive functional groups that can act as potential anchorage points for other molecules. The study has involved two main goals: first, the synthesis of hydroxylated PEEK samples (PEEK-OH) with different degree of functionalization, following the procedure indicated by Henneuse et al.[18] based on selective carbonyl reduction. Second, the study of the resulting modified polymers by different techniques. An extensive characterization has been carried out to obtain information about the degrees of modification attained at different reaction times, their crystalline structure, and thermal and mechanical behavior.

Experimental Section

Materials. Low viscosity grade poly(ether ether ketone), PEEK 150P, was supplied by Victrex plc, UK ($M_w \sim 40\,000$ g/mol, $T_g = 147$ °C, $T_m = 345$ °C). The polymer, provided as a coarse powder, was ground with a ball mill in order to diminish the particle size, vacuum-dried at 120 °C for 4 h, and stored in a dry environment. Dimethyl sulfoxide (DMSO, Aldrich) was distilled in vacuo and then dried for a few days with a Merck 4 Å molecular sieve. Sodium borohydride ($NaBH_4$) supplied by Aldrich was used without further purification.

Preparation of PEEK-OH Derivatives. PEEK (5 g) was added portionwise (ca. 5 min) in a stirred solution of $NaBH_4$ (1.5 g) in DMSO (125 mL), and the suspension was heated at 120 °C using a thermostat with a ethylene glycol heating liquid for different times (4, 8, 17, and 30 h). After cooling at room temperature, the suspension was filtered, and the solid was washed with ethanol, water, and HCl and dried at 80 °C under vacuum. To simplify the nomenclature through the text, the four derivatives will be denominated as PEEK-OH x (x = 1, 2, 3, 4), which correspond to the aforementioned reaction times, respectively.

ATR-FTIR Spectroscopy. The attenuated total reflectance FT-IR spectra were recorded on a Perkin-Elmer Spectrum One spectrometer equipped with a Universal ATR sampling accessory (diamond crystal), a red laser excitation source (632.8 nm), and MIR TGS detector operating at room temperature. Four scans were collected for each sample in the spectral range 4000−600 cm^{-1}. To improve the signal-to-noise ratios, spectra were recorded with an incident laser power of 1 mW and resolution of 4 cm^{-1}.

Nuclear Magnetic Resonance. Solid-state cross-polarization (CP)/magic-angle-spinning (MAS) NMR spectra were recorded on a Bruker Avance 400 spectrometer/imager (Bruker Analytik GmbH, Karlsruhe, Germany) equipped with a Bruker Ultra-Shield 9.4T (^{13}C resonance frequency of 100.5 MHz) and a standard double-resonance probe head. All samples were spun at frequencies of 5 kHz, using ZrO_2 rotors with an outer diameter of 7.5 mm. The 90° pulse lengths were ~4 μs. ^{13}C-CP/MAS spectra were measured with 2 ms contact time, 30 kHz spectral width, and 2K data points. 2128 scans were taken for each slice with a repetition delay of 3 s. During the detection period of the ^{13}C, magnetization dipolar decoupling was used to eliminate the strong $^{13}C-^{1}H$ heteronuclear dipolar coupling. The chemical shifts were referenced to TMS by using the methine carbon of solid adamantine (29.5 ppm) as an external secondary standard.

Thermogravimetric Analysis. The thermal stability of the polymers was analyzed by thermogravimetric analysis (TGA). The measurements were carried out using a TA-Q500 thermobalance coupled to a mass spectrometer, at heating rate of 10 °C/min, under both nitrogen and dry air atmospheres. The analysis was performed on samples with an average mass of 10 mg, under dynamic conditions from room temperature to 900 °C, with a gas purge of 150 mL/min. For each degradation step, two characteristic temperatures were selected: T_i, the initial degradation temperature, and T_{max}, the temperature of maximum rate of degradation.

The hydroxylation degree (HD) of the functionalized polymers was calculated through the thermogravimetric curves under an inert atmosphere considering that the first stage of weight loss after 200 °C of PEEK derivatives is related to the elimination of hydroxyl groups from the polymer backbone.[23]

Differential Scanning Calorimetry. The crystallization and melting behavior of the modified polymers were investigated by DSC using a Mettler TA 400/DSC 30 differential scanning calorimeter, operating under nitrogen flow. Samples of ~10 mg were weighed and sealed in aluminum sample pans. Before the heating and cooling scans, samples were melted at 380 °C and maintained at this temperature for 5 min in order to erase the thermal history of the material. Subsequently, they were cooled from 380 °C to room temperature and then reheated to 380 °C at a rate of 10 °C/min.

The transition temperatures were taken as the peak maxima or minima in the calorimetric curves, and the apparent enthalpies were calculated as normalized integrals of the corresponding peaks. The levels of crystallinity of PEEK derivatives $(1 - \lambda)_m$ were determined from the relation between the apparent melting enthalpy of the functionalized PEEK ΔH_m and the extrapolated value of the enthalpy corresponding to the melting of a 100% crystalline unmodified PEEK, taken as 130 J/g.[24]

X-ray Diffraction. Measurements were performed in a D8 Advanced Bruker Instrument, equipped with a Göbel mirror and a Vantec PSD detector, with a voltage of 40 kV and an intensity of 40 mA, using Cu Kα (λ = 0.154 18 nm) radiation, with an aperture of 0.6 mm. Diffractograms were registered on films or powder, in the angular region of 2θ = 5°−40°, at room temperature, with scan speed of 0.2 s and angular increment of 0.02°.

The degree of crystallinity X_c of the samples was calculated from the diffractograms assuming that the fractions of crystalline and amorphous material are proportional to the corresponding integrals of the intensities of the reflections: $X_c = I_c/(I_c + I_a)$, I_c and I_a being the integrated intensities of the crystalline and amorphous phases, respectively.

Dynamic Mechanical Analysis. The dynamic mechanical performance of the polymers was studied using a Mettler DMA 861 dynamic mechanical analyzer. Rectangular shaped samples of $\sim 19.5 \times 4 \times 0.5$ mm^3 were mounted in a large tension clamp. The measurements were performed in the tensile mode at frequencies of 0.1, 1, and 10 Hz in the temperature range between −130 and 260 °C, at heating rate of 2 °C/min. A dynamic force of 6 N was used oscillating at fixed frequency and amplitude of 30 μm.

Results and Discussion

FTIR Study. The ATR-FTIR spectra of PEEK and the different derivatives were recorded to obtain information about the changes in the chemical structure induced by the functionalization process. The comparison of the spectra at different reaction times (Figure 1) corroborated the conversion from ketone to alcohol, showing a progressive diminution in the intensity of the peak at about 1650 cm^{-1} corresponding to the stretching of the carbonyl group.[19,20] Furthermore, for the derivatives with higher degree of modification, the band seemed to broaden slightly toward higher frequencies, and taking into account the semicrystalline character of these samples, this small change could be related to differences in their level of crystallinity. According to the literature,[25] the IR spectra of semicrystalline polymers containing the benzophenone segment present two carbonyl stretching vibrations: a main feature at 1648 cm^{-1} and a shoulder at 1655 cm^{-1}, which arise from the crystalline and amorphous polymer phases, respectively. The spectra of the

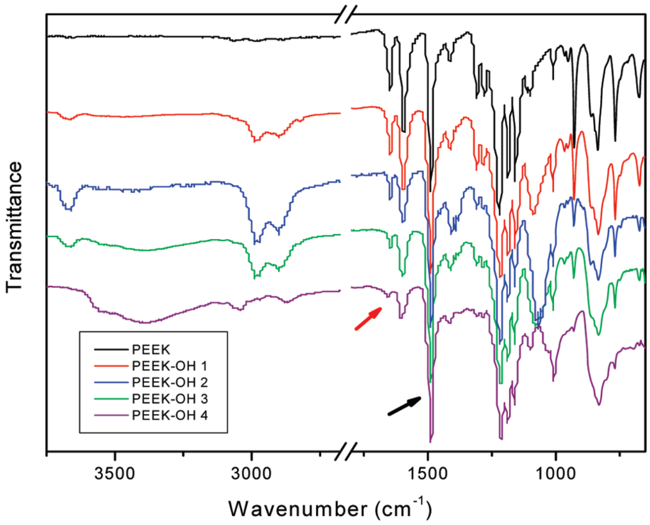

Figure 1. ATR-FTIR spectra of PEEK and the synthesized PEEK-OH derivatives. The arrows show the bands related to the carbonyl stretching at 1650 cm^{-1} and the C−C stretching of the aromatic rings at 1490 cm^{-1}.

parent PEEK and the derivatives with lower degree of modification also evidence an overlapping of the two aforementioned absorptions; however, for PEEK-OH 4 the stretching vibration seems to be mainly related to the amorphous phase. In order to quantitative track the reduction process, the ratio between the area of the carbonyl peak at 1650 cm^{-1} and the area of the reference band (unchanging) at 1490 cm^{-1}, associated with the C−C stretching of the aromatic rings,[16] was calculated for the different polymers. The value decreased from 0.43 for the pure PEEK to 0.39, 0.21, 0.18, and 0.07 for the four derivatives, respectively, which proves that the carbonyl group was gradually reduced with increasing reaction time.

On the other hand, new absorption peaks can be visualized in the spectra of the derivatives, which confirm the success of the reduction process. A weak band appeared at 3670 cm^{-1}, attributed to the stretching vibration of isolated O−H groups. With increasing reaction time, the intensity of this band first increased and then decreased, simultaneously to the growth of a broad band at about 3400 cm^{-1}, referred to the stretching of hydrogen-bonded hydroxyl groups.[26] Furthermore, the latter band shifted to lower wavenumbers as the HD increased; such a result may be caused by the dissociation of hydrogen bonding among hydroxyl groups.[27] The aforementioned features evidence a remarkable growth in the number of hydrogen bonds above a certain degree of hydroxylation. Similar trends were observed for the peaks at about 2900 and 2990 cm^{-1}, related to the C−H stretching of the carbon linked to the functional group.

NMR Study. Solid-state ^{13}C-CP/MAS NMR spectroscopy was used to conveniently monitor the reduction of the ketone group from the benzophenone segment. The evolution of the PEEK-OH NMR spectra upon conversion attained at different reaction times is shown in Figure 2. All derivatives present similar spectrum to that of the parent PEEK polymer, differing mainly in the width and intensity of the peaks. Rotational bands equally separated by 50 ppm can be observed in the spectra, caused by the anisotropic effect of the carbon nuclei and the homonuclear dipole couplings in solid-state samples. The most intense signals appear in the spectral range between 110 and 165 ppm, associated with the carbons of the aromatic rings.[26]

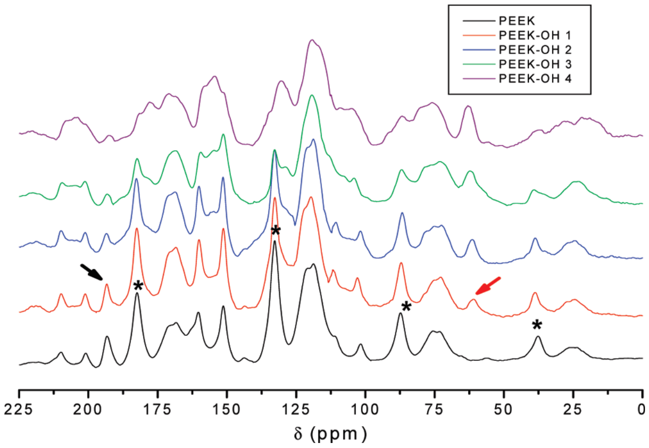

Figure 2. Solid-state ^{13}C-CP/MAS NMR spectra of PEEK and the different PEEK-OH derivatives. The left and right arrows point out the peaks related to the carbon of the carbonyl group and that linked to the hydroxyl group, respectively. The asterisk (∗) indicates the rotational bands.

A close analysis of Figure 2 reveals the gradual diminution of the intensity of the peak at around 193 ppm, associated with the carbon of the carbonyl group[28] and simultaneously the appearance of a new signal at ~62 ppm related to the carbon linked to the hydroxyl group,[29] with increased height as the number of modified groups in the polymer increases. This signal shifts gradually to higher frequencies (up to 2 ppm for PEEK-OH 4) with increasing reaction time due to the formation of intermolecular hydrogen bonds between the neighbor chains. A similar kind of increase in the chemical shift of carbons joined to hydroxyl groups has been reported in the literature for other polymers such as PVA[29] and explained in terms of a deshielded effect of the hydrogen bonds. The progressive modification of the intensity of the aforementioned peaks confirms the partial conversion from ketone to alcohol group and the increase in the degree of modification with the reaction time. NMR analysis reveals that the reduction is completely selective with respect to the carbonyl group and free from undesirable side products as can be deduced from the absence of signals associated with carbons bonded to any functional groups aside from the hydroxyl.

Thermal Stability. It is important to notice at this point that the solubility of PEEK-OH derivatives improves slightly with increasing the extent of modification, although functionalization degrees higher than 65% are required to attain a total dissolution in DMSO. Consequently, the hydroxylation degree (HD) of the modified polymers was calculated through TGA.

The thermal stability of pure PEEK and the four functionalized polymers was characterized under both inert and oxidative conditions, and the degradation thermograms under a nitrogen atmosphere are shown in Figure 3. The plot clearly indicates that the weight loss of the parent polymer is a one-step process, which starts at 520 °C (T_i) and exhibits the maximum rate (T_{max}) at 556 °C. According to the literature,[30] the degradation of its main chain involves decarboxylation, decarbonylation, and dehydration processes, leading to the formation of phenol groups, carbon dioxide, and water. The ether and aromatic structures remain in the residue until very high temperatures, and the residual amount at 650 °C is about 46% of the initial weight. On the contrary, two degradation stages were observed for all the derivatives, in agreement with TGA results reported for sulfonated and nitrated PEEK.[31,32] Furthermore, some

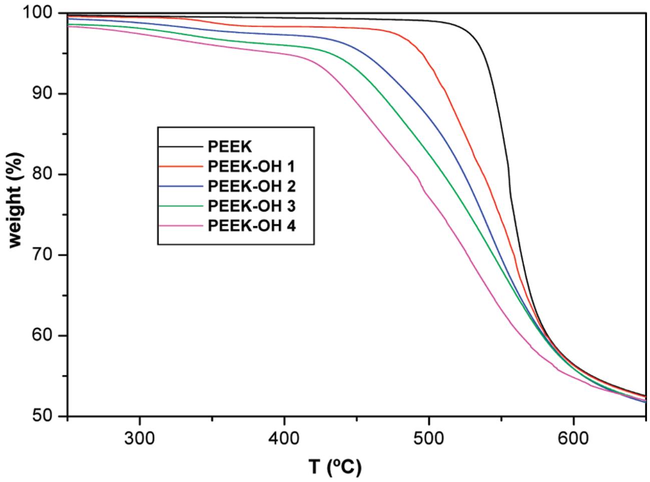

Figure 3. TGA curves for PEEK and PEEK-OH derivatives under nitrogen atmosphere at a heating rate of 10 °C/min. For comparative purposes, only the temperature range between 250 and 650 °C is plotted.

of these polymers present a small weight loss before 250 °C, probably related to water retained during crystallization due to the semicrystalline character of these samples.

Molnár et al.[23] studied the decomposition of different substituted polysulfone (PSU) and PEEK samples and concluded that most compounds presented two steps of mass loss: the first attributed to the splitting-off of the substituted group and the second to the decomposition of the main chain. Therefore, the weight loss in the temperature range between 250 and 400 °C should correspond to the elimination of the hydroxyl group, since this stage did not occur in the unmodified polymer. Nevertheless, to verify this TGA was coupled to a mass spectrometer, which allows the identification of the degradation products: during the former step, a fragment that matches with the OH group ($m/z = 17$) evolved. The initial and maximum degradation rate temperatures of this step decrease while the mass loss rises as the modification degree increases. This can be clearly observed from Table 1, which compares the characteristic degradation temperatures of PEEK and the different derivatives. The weight loss of this step was analyzed to accurately determine the hydroxylation degree (HD) of the modified polymers, and the results are also included in Table 1. A close analysis of this data reveals a low rate of functionalization and a nonlinear growth in the number of carbonyl groups reduced with increasing reaction time: HD increases sharply (up to ~20%) within the first 4 h and then rises slowly, thereby leading to an HD of around 45% after a reaction time of 30 h. This is consistent with previous kinetic studies of PEEK sulfonation,[13] which showed that the sulfonation degree increases with reaction time in an exponential manner even at high temperatures. The slow rate of hydroxylation found should be related with the low solubility of the precursor polymer, since part of PEEK particles are not dissolved even after several hours of reaction.

The degradation of the main chain of all the derivatives takes place at temperatures below that of the pure polymer, although the decrease in thermal stability depends strongly on the degree of modification. Thus, the second degradation stage of PEEK OH-1 begins at 482 °C, about 40 °C lower than PEEK, whereas for the compound with higher degree of functionalization the decrease is considerably stronger, higher than 100 °C (see Table 1). Similar trends are found within the temperatures of maximum degradation rate of this step, where the difference between PEEK and PEEK-OH 4 was about 60 °C. These observations correlate well with the thermal behavior reported for other PEEK derivatives,[16,31,32] where the stability was also influenced to a great extent by the substitution degree. However, for similar functionalization degrees, improved thermal stability was found for our PEEK-OH derivatives in comparison to those incorporating nitro[16] or sulfonic[33] groups.

Table 1. Characteristic Degradation Temperatures and Hydroxylation Degree (HD) of the PEEK-OH Derivatives Obtained from TGA Measurements under a Nitrogen Atmosphere at a Heating Rate of 10 °C/min[a]

sample	$T_{i,1}$ (°C)	$T_{max,1}$ (°C)	$T_{i,2}$ (°C)	$T_{max,2}$ (°C)	HD (%)
PEEK			520	556	
PEEK-OH 1	329	348	482	539	18.8
PEEK-OH 2	281	324	441	526	25.8
PEEK-OH 3	278	318	429	513	34.6
PEEK-OH 4	263	309	412	497	45.2

[a] The displayed temperatures are T_i = initial degradation temperature and T_{max} = temperature of maximum rate of degradation. The subscripts 1 and 2 refer to the first and second degradation stages, respectively.

It is noteworthy that the compounds with higher degree of functionalization exhibit a bigger range of weight loss (Figure 3), which could be explained by an enhanced asymmetry in the polymer structure due to the introduction of the OH group that renders it less stable. This reduction in thermal stability may be related to changes in the spatial organization of the molecular groups caused by the reduction process. As known,[34] the efficiency of chain packing drastically decreases by randomly distributed end groups along the polymer backbone, resulting in a reduction of the degradation temperatures. Experimental results[35] also demonstrated improved thermal stability for polymers with greater chain symmetry, which is responsible for a closer packing. In PEEK all carbons are sp^2, which favors the packing of the molecules, whereas in PEEK-OH the presence of sp^3 carbons inhibits the molecular packing and therefore favors the diffusion of the degradation products from the bulk of the polymer to the gas phase. Furthermore, the resonance effect is less pronounced in PEEK-OH, which also leads to lower thermal stability.

The aforementioned destabilization effect is qualitatively similar to that observed under dry air atmosphere (data not shown); the thermogravimetric curves of all derivatives display two stages, which initiate around 50 °C lower than in nitrogen atmosphere. The major weight loss (about 62−65% for all samples) occurs in the second step, which leads to the total decomposition of the material. Despite the indicated destabilization, it is proven that these derivatives are thermally stable enough for potential aircraft applications.

Crystallization and Melting Behavior. The influence of the reduction process on the crystallization and melting behavior of these modified polymers has been investigated by means of DSC analysis. The crystallization exotherms and heating endotherms of pure PEEK and the different derivatives are compared in Figure 4, and the calorimetric data derived from DSC curves are presented in Table 2.

In the case of the melting process (see Figure 4a), pure PEEK shows an intense endothermic peak at 344.2 °C, which corresponds to the melting temperature T_m. It is clear that the reduction process leads to a progressive shift of the melting peak toward lower temperatures (see Table 2), and hence for PEEK-OH 4 T_m decreases by ~10 °C. Furthermore, the apparent melting enthalpy ΔH_m (about 58 J/g for pure PEEK) and consequently the degree of crystallinity considerably decrease as the modification degree increases and seem to approach zero for substitution degrees higher

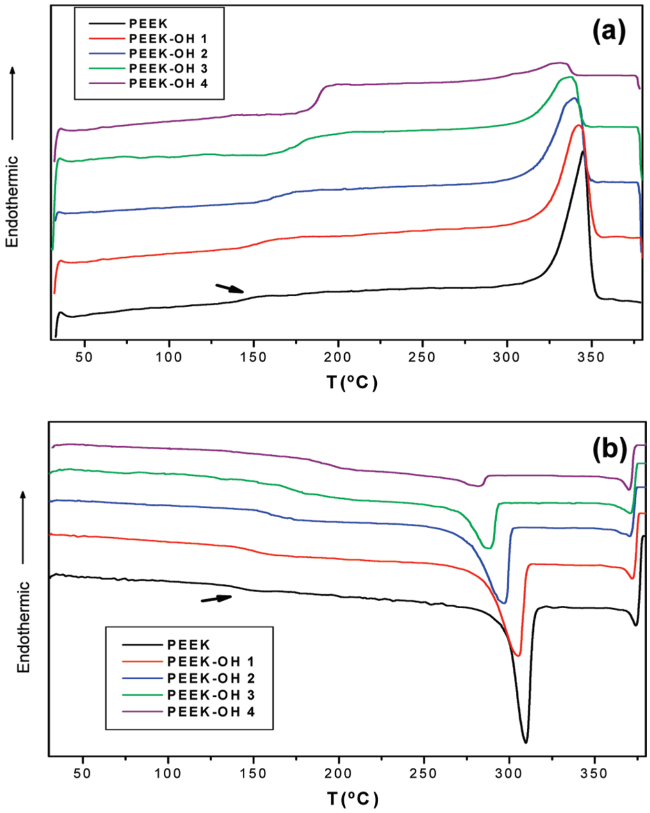

Figure 4. Nonisothermal DSC curves for PEEK and PEEK-OH derivatives at rates of 10 °C/min: (a) heating scans; (b) cooling scans. The arrows indicate the position of the glass transition in the parent polymer.

Table 2. Crystallization and Melting Temperatures and Degree of Crystallinity of the PEEK-OH Derivatives, Obtained from DSC and X-ray Measurements[a]

sample	T_c (°C)	$(1-\lambda)_c$ (%)	T_m (°C)	$(1-\lambda)_m$ (%)	X_c (%)
PEEK	309.1	42.5	344.2	44.8	40.4
PEEK-OH 1	304.8	35.8	342.8	37.7	35.6
PEEK-OH 2	297.3	29.1	340.6	31.9	28.7
PEEK-OH 3	288.6	14.5	338.3	15.3	16.9
PEEK-OH 4	282.1	4.4	334.7	4.7	7.3

[a] The displayed data are T_c = crystallization temperature, T_m = melting temperature, $(1-\lambda)_c$ and $(1-\lambda)_m$ = crystallization and melting crystallinities derived from the peak areas of DSC thermograms, and X_c = degree of crystallinity obtained from WAXS diffractograms.

than 45%. Similar observations were reported for other semicrystalline poly(aryl ether ketone) derivatives,[36] where the rise in the substituent content reduced gradually their crystallinity. Oh et al.[37] also found a decrease in T_m and ΔH_m of carboxylic acid PEK derivatives, which magnitude depended strongly on the position of the substituent. As mentioned earlier, the incorporation of the OH group disrupts the structural regularity and inhibits the molecular packing. In addition, the reduction of the spatial order results in the formation of smaller and less perfect crystals, which present lower T_m. Thereby, as the functionalization degree increases, T_m and the extent of crystallinity of the sample are reduced. The latter fact is consistent with the observations made from the IR spectra of the derivatives with higher degree of functionalization, where the remaining carbonyl stretching vibration was mostly associated with the amorphous polymer phase. It is worthy to notice that, despite the above-mentioned spatial order decrease, these PEEK-OH derivatives still retain a certain level of crystallinity, whereas nitrated or sulfonated products with similar substitution degree are generally amorphous.[16,26]

Table 3. Storage Modulus E' and Loss Modulus E'' at 25 °C, Glass Transition T_g, and β Relaxation Temperatures for the Different PEEK-OH Derivatives, Obtained from Dynamic Mechanical Analysis Measurements at the Frequency of 1 Hz

sample	E' (GPa)	E'' (MPa)	T_g (°C)	$T_g{}^a$ (°C)	β (°C)
PEEK	3.83	37.2	148.3	147.8	−95.1
PEEK-OH 1	3.75	34.6	153.4	151.9	−90.3
PEEK-OH 2	3.58	29.9	163.3	162.2	−79.5
PEEK-OH 3	3.40	22.7	172.1	169.5	−64.7
PEEK-OH 4	3.19	19.8	185.6	184.3	−49.6

[a] Glass transition temperatures obtained as the midpoint of the baseline of DSC heating thermograms.

Focusing on the cooling thermograms (Figure 4b), it can be observed that the reduction of the carbonyl group results in a significant decrease of the crystallization temperature: T_c is about 309 °C for pure PEEK and around 25 °C lower in the case of PEEK-OH 4. Moreover, the crystallization enthalpy ΔH_c and consequently the level of crystallinity of these polymers become smaller with increasing degree of modification. The increase in the number of sp^3 carbons linked to hydroxyl group leads to the formation of strong inter- and intramolecular hydrogen bonds; this imposes important restrictions on polymer chain diffusion and thus slows down the overall crystallization process, leading to lower extent of crystallinity and T_c values for the derivatives. In all cases, crystallinity data derived from the melting curves are slightly higher than those derived from the cooling thermograms (see Table 2). This fact may be due to a recrystallization from defective to higher perfection crystals, which takes place during the heating.[1]

On the other hand, the thermograms show a small variation of the heat capacity (located around 148 °C for pure PEEK) related to the glass transition process. This transition temperature (T_g) and the associated change in the specific heat rise as the extent of modification increases (in the case of PEEK-OH 4 the increment is about 40 °C; see Table 3), which is consistent with the restriction in mobility imposed by the incorporation of OH groups, the formation of hydrogen bonds, and the decrease in crystallinity observed for these derivatives. Small differences are found in the determination of this transition temperature from the heating and cooling scans. Nevertheless, T_g values of the different polymers have been more accurately determined from DMA measurements and will be discussed in a following section.

Crystalline Structure. The crystalline structure of PEEK and the different derivatives was also characterized using wide-angle X-ray diffraction, and the corresponding diffractograms at 25 °C are compared in Figure 5. In the case of the parent polymer, four main peaks can be observed at 2θ of 18.8°, 20.7°, 22.9°, and 28.9°, which correspond to the diffraction of the (110), (111), (200), and (211) crystalline planes,[38] respectively, of the orthorhombic unit cell. The derivatives exhibit qualitatively similar diffractogram to that of the pure PEEK, differing mainly in the width and intensity of the peaks. With increasing hydroxylation degree, peaks became wider and less intense, probably caused by the asymmetry induced by the random distribution of the hydroxyl groups. However, no progressive shift in the position of the crystalline reflections is observed with increasing HD, hinting that the OH groups are not included in the crystal unit cell of the modified polymers.

The degree of crystallinity X_c of the samples was calculated from the WAXS diffractograms, and the values obtained are in very good agreement with those derived from DSC

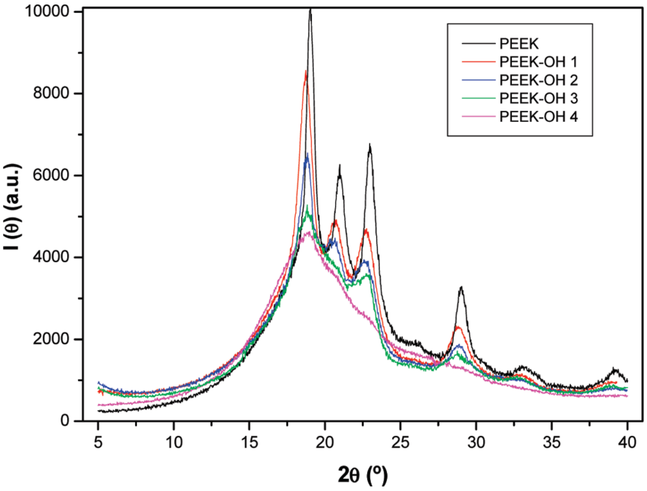

Figure 5. Wide-angle X-ray powder diffraction patterns of PEEK and PEEK-OH derivatives at room temperature.

thermograms (see Table 2). It is confirmed once again that the incorporation of the hydroxyl group leads to a progressive reduction in the level of crystallinity of the modified polymers. The functional group inhibits polymer chain packing, and the changes in bond angle make more difficult for the chains of the derivatives to adopt the "zigzag" conformation that allows the parent PEEK to crystallize so readily. In the case of PEEK-OH 1 X_c decrease is only about 5%, whereas for PEEK-OH 4 the degree of crystallinity attained is lower than 10%, quite close to an amorphous character. Similar crystallinity decrease was reported by Francis et al.[39] working with functionally terminated PEEK with tertiary butyl groups. The presence of bulky groups modifies the ordered structure of the base polymer and consequently reduces drastically its crystallinity, which could lead to a potential improvement in their processability and blending with other materials.

Dynamic Mechanical Properties. DMA was employed to evaluate the influence of the functionalization process on the mechanical behavior of the synthesized polymers as well as to obtain information about the molecular relaxations and interactions taking place in these materials. Figure 6 shows the temperature dependence of the storage modulus (E') and loss modulus (E'') of PEEK and the different derivatives at the frequency of 1 Hz. The storage modulus of pure PEEK decreases progressively with increasing temperature, showing a sharp drop (higher than 85%) in the temperature range between 138 and 170 °C, attributed to changes in Poisson's ratio of the polymer when going through the glass transition.[40] The loss modulus curve presents a broad peak around −95 °C, named β relaxation,[2] associated with local motions of the ketone groups, and an intense peak at 148.3 °C, α relaxation, which corresponds to the glass transition of the polymer.

In the whole temperature range, the magnitude of both moduli progressively decreases with the incorporation of hydroxyl groups, being the reduction considerably stronger for the derivatives with higher functionalization degree. Thus, at room temperature, E' of PEEK-OH 1 is only about 2% lower than that of the parent polymer, whereas for PEEK-OH 4 the decrease approaches to 17% (see Table 3). This behavior is probably related with the drastic reduction in the level of crystallinity observed for these derivatives, since the crystalline regions are known to enhance the modulus of the semicrystalline polymers.[41] Furthermore, the strength decay could also arise from the changes in the polymer structure and morphology induced by the presence of the functional group. Analogous behavior of the tensile strength drop has been reported for sulfonated PEEK derivatives.[14]

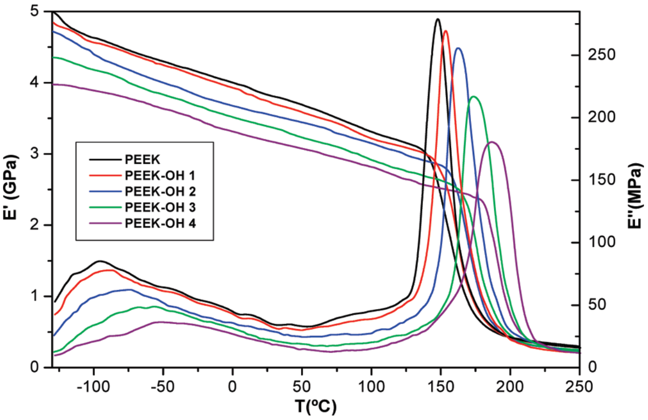

Figure 6. Temperature dependence of the storage modulus E' and loss modulus E'' of PEEK and PEEK-OH derivatives, obtained from DMA measurements at the frequency of 1 Hz.

Regarding the loss modulus data, which provide information about the overall flexibility of the material, it is evident that the increase in number of hydroxyl groups results in a significant reduction of E'' magnitude at temperatures below T_g (see Table 3) and therefore enhances the stiffness of these polymers. In addition, β relaxation was broadened, smoothed, and shifted to higher temperatures with increasing HD; this suggests that the presence of this functional group acts as a barrier for the local movements of the ketone groups. It can be clearly observed from the figure that the position of the α peak (T_g) shifts gradually to the higher temperature region as the degree of modification increases, which indicates again an improvement in the stiffness of the polymers. Since the glass transition is associated with the mobility of chain segments in the amorphous regions, a likely explanation is the increment in the energy between adjacent chains produced by intermolecular interactions between the polar groups, mainly hydrogen bonds. The formation of a strong supramolecular arrangement of the chains decreases the mobility and flexibility of the ether groups and hence increased their barriers of bond rotations, leading to a noticeable increment in T_g. Such behavior has also been reported for sulfonated PEEK derivatives, explained in terms of interactions between the sulfonic groups via the ionomer effect.[12] Moreover, Colquhoun and co-workers,[21] dealing with poly(ether dithioketal) derivatives with high conversion degrees, reported analogous T_g enhancement, ascribed to the steric bulk of the cyclic dithioketal group. In contrast, very small improvements in T_g have been reported for nitrated PEEK samples, since the rotational restrictions imposed by the nitro groups in the hydroquinone ring only become effective for nitration degrees close to 100%.[16]

The values of T_g for the PEEK derivatives obtained from both DSC and DMA experiments are compared in Table 3. Both data series agree fairly well and reveal the strong influence of the hydroxylation degree on T_g. Thus, for PEEK-OH 1 T_g was only about 5 °C higher than that of PEEK, whereas for PEEK-OH 4 the increment was significantly larger, close to 40 °C. Such magnitude of enhancement is consistent with the observations made from the IR spectra of these polymers, which revealed a drastic rise in the number of hydrogen bonds with increasing HD. Thereby, T_g values rise with an exponential manner with the functionalization degree. Conceição et al.[16] and Jaafar et al.[33] illustrated similar effects for sulfonated PEEK, where the change in T_g increased up to 50 °C for the derivatives with greater extent of modification.

On the other hand, HD also seems to influence the height and width of the glass transition peak, which becomes broader and less intense with increasing the modification. The reduction in height could be interpreted as progressive immobilization of the polymer chains as increasing the number of hydrogen bonds, and the broadening might be related to the random distribution of the hydroxyl groups. The aforementioned effects of the functionalization process on the DMA behavior of PEEK derivatives were reproduced at the other frequencies tested, with an increase in the storage modulus and in the temperature of the relaxation peaks as frequency is shifted to higher values. Thereby, the tests confirm that the overall mechanical performance of these derivatives is well enough suitable for engineering applications.

Conclusions

With the intentions to increase the reactivity of PEEK polymer, hydroxylated derivatives with different degrees of functionalization have been synthesized by carbonyl reduction. The evolution of the ATR-FTIR and NMR spectra upon conversion attained at different reaction times confirmed the functionalization success, showing a progressive diminution in the intensity of the peaks related to the carbonyl group and the appearance of signals referring to OH ends. The reduction from ketone to hydroxyl group produces a small loss in the thermal stability of the compounds. This destabilization could be attributed to a decrease in the resonance effect due to the presence of sp^3 carbons and changes in the spatial organization of the molecules. The degrees of hydroxylation were accurately determined from TGA curves considering that the first stage of weight loss of the modified polymers is related to the elimination of the hydroxyl group. The calculated values show an exponential growth with increasing reaction time. DSC experiments revealed a decrease in the crystallization and melting temperatures of the derivatives due to the restrictions on polymer chain diffusion imposed by the strong hydrogen bonds. Both DSC and X-ray diffraction experiments indicated a drastic decrease in the level of crystallinity of the modified polymers upon increasing HD, since the random distribution of the functional group inhibits the molecular packing. DMA studies showed a decrease in both the storage and loss moduli of the derivatives as the degree of modification increased. The former probably arises from the reduction in the level of crystallinity, and the latter should be related to the stiffness enhancement caused by the strong hydrogen bonds. These interactions also lead to a significant improvement in the glass transition temperatures of the polymers, particularly for the derivatives with higher extent of modification, where the increment was about 40 °C.

Our results reveal that the degree of functionalization and thereby the hydrophilicity of these materials can be controlled by the reaction time and confirm that small changes in the chemical structure of the polymer result in drastic reduction of its level of crystallinity, and consequently slight decrease in the macroscopic properties, in particular the thermal and mechanical. Considering all the tests performed, we can conclude that the overall performance of these PEEK-OH derivatives is above the required for technological applications and is expected to improve considerably when the modified polymer interacts with other substances (e.g., polymers, nanocharges, or nanoparticles) through covalent bonding or other interactions like van der Waals forces or H-bonds. Based on the promising results observed here, other works related to the integration of carbon nanotubes in PEEK derivatives for aircraft applications are currently in progress.

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