Amino Derivatives of PEEK-WC

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ABSTRACT: The synthetic procedure and the characterization of the new amino derivatives of poly(oxa-*p*-phenylene-3,3-phtalido-*p*-phenylene-oxa-*p*-phenilene-oxy-phenylene) (PEEK-WC) with various average degrees of substitution, is reported. The amino PEEK-WC was extensively characterised by using Fourier transform infrared (FTIR) spectroscopy, thermogravimetric analysis, differential scanning calorimeter, scanning electron microscopy, Elemental analyses, NMR, and viscosity measurements. The amino PEEK-WC shows different solubility in some solvents in comparison with the parent polymer, good thermal stability and is able to form membrane by means of the phase inversion technique. Amino PEEK-WC results to be quite reactive and can lead to further modification. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 117: 2258–2264, 2010

Key words: poly(ether ketones); membranes; synthesis

INTRODUCTION

Poly(ether ether ketones) (PEEK)[1] are highly crystalline polymers, which have exceptional chemical, thermal, and mechanical characteristics. Due to the high strength and toughness properties exhibited by the PEEK, this material has raised great deal of interest in the technological and industrial research devoted principally to tribological application.[2–5] Moreover, as these properties are integrated by stiffness and high biocompatibility, PEEK is also under investigation for manufacturing medical instruments and orthopedic implants.[6]

In addition to these peculiarities, its high thermal stability makes it a good applicant to wire and cable insulation.[7]

As they are characterized by a high degree of crystallinity they result insoluble in almost all the organic solvents; for these reasons, the introduction of functional groups on the polymeric chain are rather difficult. Moreover, they are not able to form membranes by means of the phase inversion technique,[8,9] the simplest method to produce both symmetric and asymmetric membranes.

In the last few years, it was patented the synthesis of a new kind of polyeteheretherketone named PEEK-WC, that is poly(oxa-*p*-phenylene-3,3-phtalido-*p*-phenylene-oxa-*p*-phenilene-oxy-phenylene)[10] (Fig. 1).

It is characterized by the presence of the cumbersome lattonic group that confers it a lower degree of cristallinity. As a consequence, it results soluble in some hydrochlorocarbon solvents and also in DMF and DMSO. Thus, PEEK-WC is able to form membranes that show interesting peculiarities that have attracted great interest for their potential applications in several areas. Actually the technology of membranes is currently in a phase of remarkable development and many potential applications grow every day. The development of innovative chemical processes, with high performances and low environmental impact, is crucial for a sustainable growth. In this perspective, membrane technology can offer important new opportunities in the design, rationalization, and optimization of processes and products.

Separation membrane have become essential parts of the human life because of their growing industrial applications in hitech areas, such as membrane for selective transport,[11] high surface area support for bio catalysts,[12] optical apparatus,[13] and ultrafiltration.[14]
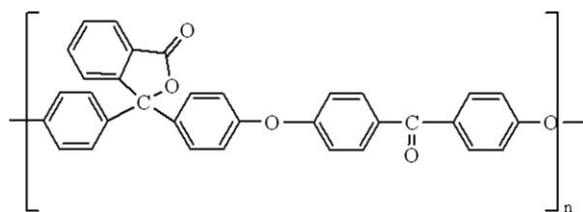
Figure 1 Molecular structure of PEEK-WC.

To extent the properties and the applications of such membranes, in the last years the syntheses of some PEEK-WC derivatives were already reported. In particular nitro derivative[15] was described and also sulfonated derivatives were obtained as well.[16] Noticeably, sulfonated PEEK-WC shows good proton conductivity and low methanol cross-over, and therefore it is under investigation for possible PEM fuel cells applications.[17] Sulfonated PEEK-WC also increases the selectivity towards CO_2/CH_4 gas separation.[18] On the other hand, also nitro derivatives show interesting properties, for instance nitro PEEK-WC has greater contact angle in comparison with the parent PEEK-WC,[15] very close to PVDF value. This property is of interest in membrane contactors devices used to improve mass transfer coefficients in respect to the traditional extraction or absorption processes.

However, nitro group is rather stable and it can not easily undergo further reactions with other reactive molecules. It is well known, however, that the nitro group could be reduced to the more reactive amino group by some reducing agents.

It is of great interest to have available polymers containing reactive groups to facilitate the syntheses of polymer composites; this is particularly important for composite materials where the layers are not fully compatible.

In this article, the synthesis and characterization of the new amino derivatives of PEEK-WC by using $NaBH_4$ in presence of $BiCl_3$ and few examples of further modification on the polymer chain is reported.

EXPERIMENTAL

PEEK-WC was received from Chan-Chung Institute (Academia Sinica–Shangai–China). Before use the PEEK-WC was purified by Soxhlet extraction with methanol to remove low molecular weight by-products.

The Chemicals used, chloroform, methanol, anhydrous sodium sulfate, bismuth chloride, and potassium borohydride were of reagent grade (ACS), purchased from Fluka (Switzerland) and were used as arrived. Anhydrous tetrahydrofuran (THF) was prepared by distillation over CaH_2.

The Fourier transform infrared (FTIR) spectra of all samples were recorded in the frequency range 4000–400 cm^{-1} on a PerkinElmer FTIR model 2000 spectrometer. The spectrum was recorded at the scanning speed of 0.2 cm^{-1} and at the average of 32 scans making a film of the polymer on a KBr pellet.

The thermal behavior was followed by thermogravimetric analyses (TGA). The TGA apparatus was a TA Instrument TGA 2050 operating in air atmosphere with alumina crucibles containing 15–20 mg of polymer. The runs were carried out at a constant heating rate of 10°C min^{-1} under air flow from 50 to 700°C. The simultaneous thermogravimetric analysis–differential thermal analysis (TGA–DTA) determinations were carried out on a TGA/SDTA 851 apparatus (Mettler- Toledo), using a stream of air. The analytical crucibles were made in alumina and the runs were carried out at a heating rate of 10°C min^{-1} from 25 to 800°C. Data were acquired every 0.8 s and samples weighed between 30 and 40 mg.

Differential Scanning Calorimetry (DSC) analysis were performed on a TA Instrument DSC 2010 apparatus by a warming ramp with a speed of 10°C/min under nitrogen flow. Scanning electron micrographs (SEM) have been realized using a Stereoscan 360 electron microscope set at 20 kV. NMR spectra were recorded with a Bruker 300 Avance (300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively) at 25°C; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: The data were elaborated with Mestre-C software.

Elemental analyses were carried out on Thermo Electron elemental analyser model Flash EA 1112. Viscometry measurements of the synthesized polymer were carried out at 25°C using an Ubbelohde-type viscometer, immersed in a temperature-controlled water bath DC 30 (Thermo Electron Corporation), in a dimethylformamide solution.

The membrane thickness has been measured by using a micrometer Mitutoyo Mod IDC-112B. Membranes were prepared following the process of traditional phase inversion technique (evaporation or precipitation method), which permits the production of membranes with both symmetric or asymmetric pore structure, respectively. The solvent used was DMF and the nonsolvent was distilled water.

In particular, symmetric membranes were obtained by dissolving the polymer in DMF (15 wt %) and magnetically stirring overnight to allow the complete dissolution at room temperature. The solution was centrifuged to remove possible macroscopic impurities and then was cast with a knife on to a glass plate. The knife was supplied from Brane Instruments. The knife height was set at 300 μm and the evaporation occurred at room temperature.

Asymmetric membranes were obtained from the same aforementioned solution of the polymer in
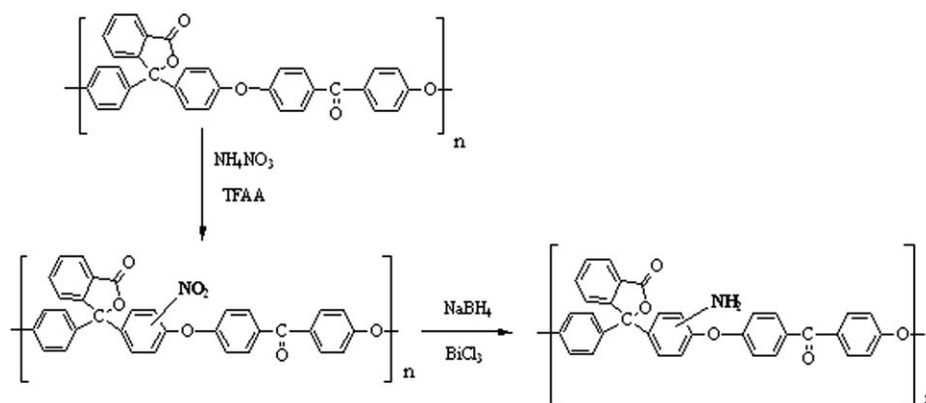
Figure 2 Scheme of the synthetic pathway to PEEK-WC-NH$_2$.

DMF and cast with a knife on a glass plate at the same thickness (300 μm) and after an initial evaporation time of 45 s at room temperature, it was immersed in a coagulation bath containing distilled water. The cast film was kept in water for 10 min and then transferred to fresh distilled water and dried at room temperature for at least 1 day.

Solubility tests were performed at room temperature by weighing 10 mg of the polymer and then adding 1 mL of the selected solvent at room temperature. Nitro PEEK-WC derivative (PEEK-WC NO$_2$) was synthetised according to the previous reported procedure with minor modification.[15]

The synthesis of amino derivative of PEEK-WC was carried out in a three necked round bottom flask equipped with a condenser and nitrogen inlet. To a solution of nitro PEEK-WC (2.0 g) in 50 mL of anhydrous tetrahydrofuran (THF) was added bismuth chloride (1.3 g) and potassium borohydride (0.15 g) of NaBH$_4$ and the reaction mixture was vigorously stirred at reflux temperature under inert atmosphere. After stirring for 2 h further 0.15 grams of NaBH$_4$ was added to the resulting solution and the reaction was allowed to react for additional 3 h and 30 min. Once the reaction was over, upon cooling down, the resulting mixture was filtered under vacuum and the organic solution recovered. Aminated PEEK-WC was isolated by precipitation in petroleum ether and recovered by filtration. A 90% yield of a pale yellow amino PEEK-WC was obtained after drying it under vacuum at 80°C for 10 h.

RESULTS AND DISCUSSION

Reduction of aromatic nitro compounds to the corresponding amines is an important functional group transformation in organic chemistry and it is carried out with a large set of reducing agents and methods.[19] Among the hydrides, sodium borohydride alone is a weak reductive reagent for the aromatic nitro groups; however, it increases its reactivity in presence of some transition metal halides such as CoCl$_2$, TiCl$_2$, FeCl$_3$, and NiCl$_2$ that allows also the reduction of the nitro compounds. It was reported that bismuth chloride was an effective catalyst for selective reduction of aromatic nitro compounds by means of sodium borohydride under relative mild reaction conditions.[20] As nitro PEEK-WC has a good solubility in many organic solvents, the latter method was also effective for the reduction of the parent nitro PEEK-WC to the corresponding amino derivative.

The synthetic pathway to amino PEEK-WC is reported in Figure 2.

The FTIR spectrum of PEEK-WC is showed in Figure 3 together with those of its derivatives. The parent PEEK-WC polymer is characterized by absorption related either to the PEEK or cardo (WC) skeletons. PEEK structure is characterized by conspicuous band at 1653 cm^{-1} due to carboxyl group (C=O stretching), strong to very strong ring vibrations at 1590 and 1498 cm^{-1}, ν_{as} (C—O—C) at 1240 cm^{-1}, and two medium-strong bands in the 928–754 cm^{-1} region, probably g vibration of p-disubstituted ring; the cardo structure is characterized by the strong absorption at 1770 cm^{-1} of the lactone. The nitro derivative presents in addition to the previous bands new absorption at 1537 and 1347 cm^{-1} (ν_{as} and ν_{sym} NO$_2$) and 734 cm^{-1} (ringing Ar-NO). The reaction of reduction of NO$_2$ to NH$_2$ is easily followed by FTIR analyses detecting the signals at 1537, 1347, and 735 cm^{-1} that progressively disappear during the course of the reaction up to a complete disappearance once the reaction was complete. Contemporary, new absorptions appear in the amino derivatives: absorption associated with NH deformation mode appears near 1620 cm^{-1} but this is greatly masked by other strong absorptions in the same region. In addition, the two characteristic bands of symmetric and asymmetric stretch of primary amine at 3460 and 3350 cm^{-1} are present (Fig. 3). Moreover, elemental analyses confirm the retention of
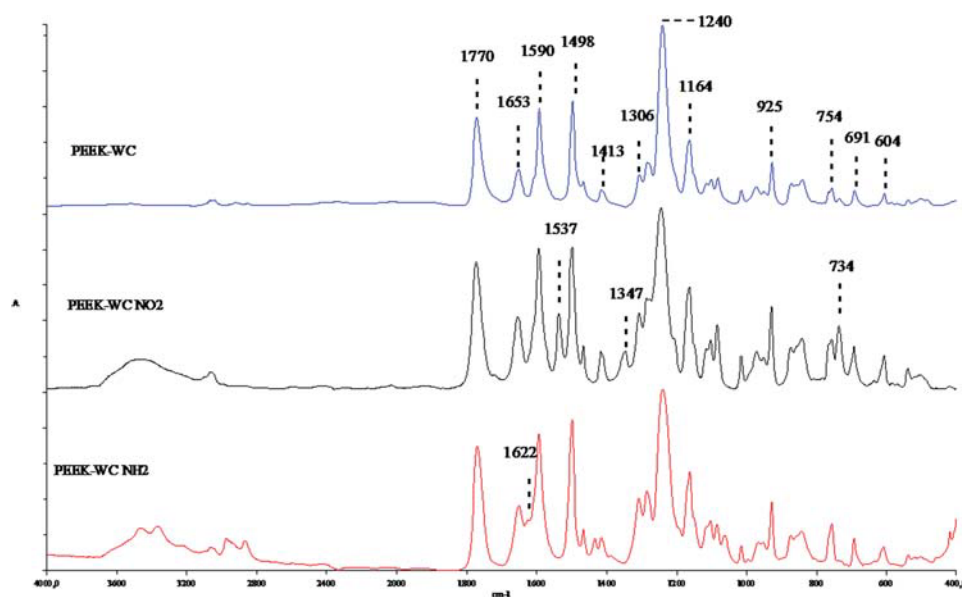
Figure 3 FTIR spectra of PEEK-WC derivatives. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

nitrogen after the reduction reaction in almost the same amount presents in the parent nitro PEEK-WC thus proving the complete reductions of the substrate.

The reaction is quite selective. In fact, no modification of carbonyl signals were observed thus suggest that the reducing mixture $BiCl_3/NaBH_4$ does not effect on carbonyl group.

This is in accordance with previous article, in which the reduction of p-nitrobenzoic acid to p-aminobenzoic acid was achieved with the same reducing agent without affecting carbonyl group.[21]

In addition, classical colorimetric reaction of amino group i.e. nynidrine test reaction was also positive for the amino PEEK-WC.

The insertion of the amino functional group onto the polymeric chain, makes a change on the solubility of the polymer. Table I reports the solubility of amino PEEK-WC in some common solvents; in particular, the amino derivative of PEEK-WC is still soluble in DMSO, DMF and to a lower extent also in THF, but remains insoluble in chloroform and dichloromethane that were, on the contrary, good solvents for the parent PEEK-WC and also for PEEK-WC NO_2. The decrease of solubility of the amino PEEK-WC in nonpolar solvents denotes an improvement of the polar character in comparison with both parent PEEK-WC and its nitro derivative.

The hydrophilic behavior exhibited by the amino derivative of PEEK-WC is proved by its aptitude to absorb air moisture and to retain the water at high temperature as proved comparing its DSC thermogram with those of both the pristine PEEK-WC and the nitro derivative one (Fig. 4).
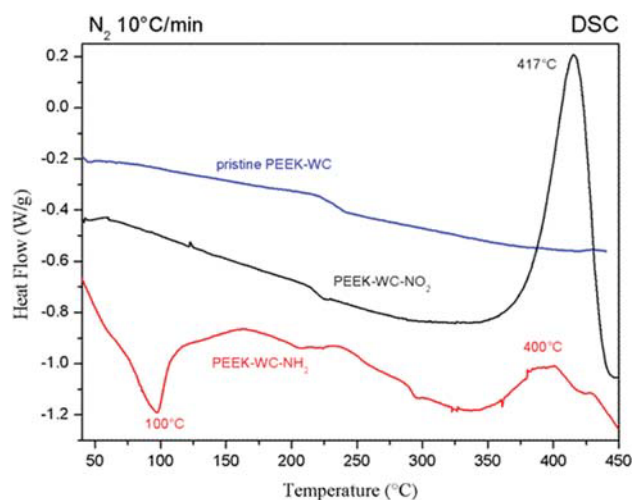
TABLE I
Solubility of PEEK-WC and its Derivatives in Several Solvents

	PEEK-WC-NH$_2$	PEEK-WC-NO$_2$	PEEK-WC
Water	−	−	−
Et-OH	−	−	−
Me-OH	−	−	−
DMSO	+	+	+
DMF	+	+	+
THF	+/−	+	+
CHCl$_3$	−	+	+
CH$_2$Cl$_2$	−	+	+

Room temperature. [10 mg/ml]. (+ soluble within 1 h; +/−, swelling; − insoluble)

Figure 4 DSC analysis of pristine, nitro derivative, and amino derivative PEEK-WC under nitrogen flow. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
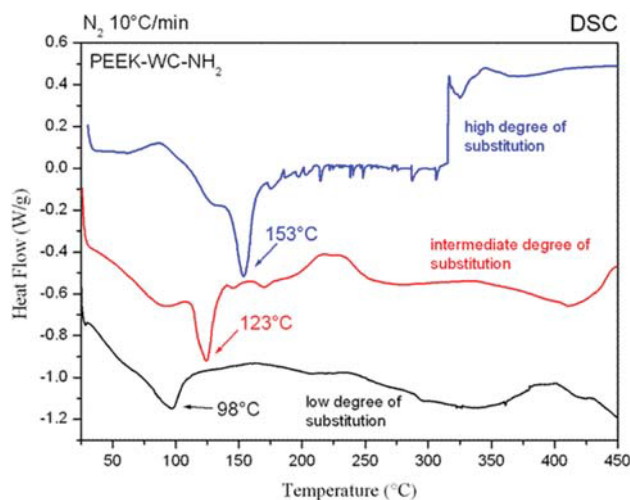
Figure 5 DSC analysis comparison of several PEEK-WC NH$_2$ with different degree of amination under nitrogen flow. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In fact, only the amino PEEK-WC curve shows a broad endothermic peak at approximately 100°C due to the loss of water previously absorbed on the hydrophilic surface. However, both amino and nitro derivative samples denounce an exothermic processes at higher temperatures (400°C) that could be ascribed to a possible cyclization reaction not exhibited by the pristine PEEK-WC.

Moreover, as reported in Figure 5, increasing the degree of amination, water release is shifted to higher temperature as confirmed by comparing several amino derivatives. This phenomenon can be attributed to the stronger interaction between water and NH$_2$ groups in polymer chains.

The presence of absorbed water in amino derivatives was also confirmed by TGA; although the polymer was carefully dehydrated in vacuum before the characterization, a weight loss corresponding to water evaporation can be detected.

The thermal stability of the PEEK-WC derivatives was determined by using TGA under air atmosphere, as reported in Figure 6. In a general way, the functionalization of PEEK introduces some weak points in the polymer chain leading to its cracking, the major weight loss stage occurs at higher temperature of degradation (450°C), which corresponds to the decomposition of the polymer chain.

An oxidation of the residue progressively formed takes places at 500–570°C and leaves, in the case of PEEK-WC NH$_2$ a considerable amount of no further oxidizable residue (27%). This can be attributes to a different reactivity of NH$_2$ and NO$_2$ in charring reactions.

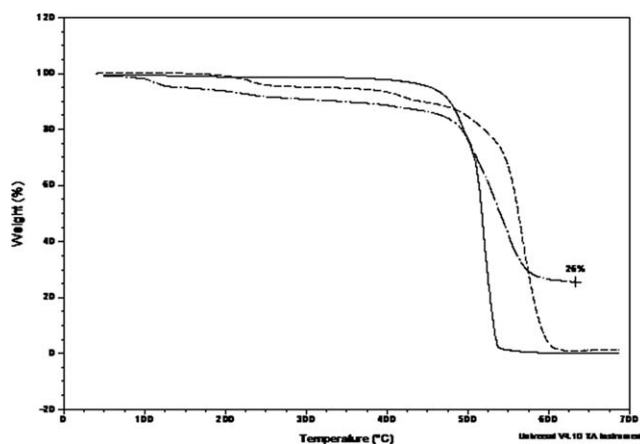In comparison to the thermal behavior of the parent PEEK-WC, it is anyway possible to see a marked

Figure 6 TGA under nitrogen flow of PEEK-WC (———) and PEEK-WC derivatives: PEEK-WC NO$_2$ (- - - -) and PEEK-WC-NH$_2$ (—· —· —).

influence of the nitro group on the thermal stability of the polymer that is seen to be higher than the parent PEEK-WC above 500°C (Fig. 6). As polyether ether ketones find applications in many fields thanks to their exceptional thermal stability, this behavior is a relevant point.

The thermal stability was further determined by using a simultaneous TGA-DTA apparatus.

In Figure 7 is reported a thermogram recorded under air. Two curvs are illustrated:

- TG, thermogravimetric plot of amino and nitro PEEK-WC (weight loss)
- DTA, differential thermal plot of amino and nitro PEEK-WC (heat flow)

The differential curve is complex, it shows that there is an endothermic peak at 125°C due to evaporation of water and it confirms that PEEK-WC NH$_2$ is more hydrophilic than parent PEEK-WC NO$_2$,
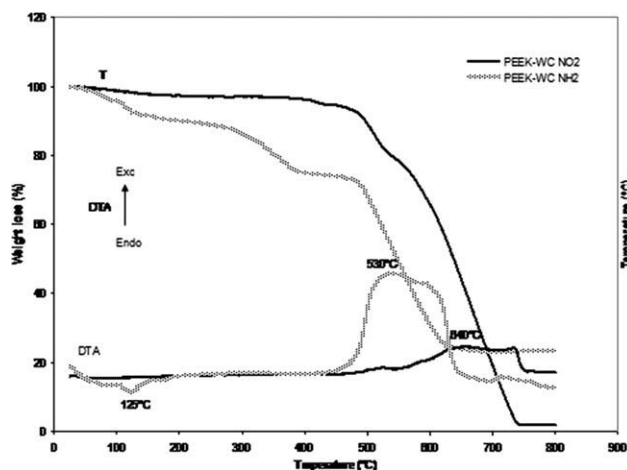

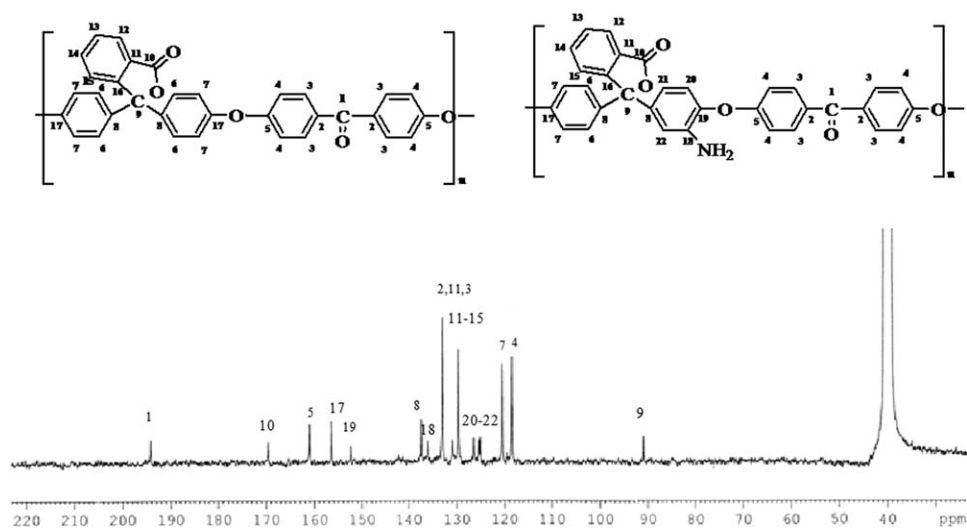**Figure 7** TGA/DTA under air flow of PEEK-WC-NH$_2$ and PEEK-WC NO$_2$.

Figure 8 ^{13}C-NMR spectrum of PEEK-WC-NH$_2$.

which does not show any endothermic peak, followed by a little endothermic peak could be ascribed to the evaporation of solvent. An exothermic peak is presented at about 530°C followed by an other exothermic peak, both peaks combine to become one peak so it is difficult to suggest a tentative degradation mechanism, due a significant weight loss has happened in this range of temperature, probably the peaks correspond to a degradation of polymer chain it occurred before correspondent exothermic peak of nitro derivative.

The viscosity measurements clearly show that the obtained material is still a polymer, because it has an intrinsic viscosity of about 0.24 dm^3/g. Although this latter is significantly different from nitro PEEK-WC viscosity (0.3124 dm^3/g). Nevertheless, the decrease could be ascribed to a different aggregation of the polymer coils, due to the higher polarity of amino group rather than to possible minor degradationo of the polymer chain. In any case amino PEEK-WC was still able to form membrane by means of the phase inversion technique.

PEEK-NH$_2$ was also analyzed by ^{1}H-NMR dissolved in DMSO-d_6. The interpretation of the ^{1}H-NMR spectrum was limited by line broadening effect, however, a peak 6.52 ppm confirmed the presence of the amino group (it disappeared when 10 µl of D$_2$O were added to the sample because of the proton exchange). ^{13}C-NMR was performed so to confirm the structure of the polymer. As depicted in the Figure 8, a peak at 152 ppm referred to the C$_{19}$ and a peak at 138 ppm to the C$_{18}$ of the amino phenyl moiety, between 125 and 128 ppm are evidenced the C$_{20,21,22}$.

Morphology of the membranes (both the surface and the cross section), was investigated using a scanning electron microscope (SEM) (See Fig. 9).

SEM photomicrograph of cross section of the dried amino PEEK-WC membrane prepared by phase inversion method, is reported in Figure 8. It is evident the presence of a typical asymmetric structure composed of a dense thin skin on the upper surface exposed to the air during the casting, and a porous homogeneous substructure.

As predictable aminated PEEK-WC is quite reactive and leads further modification by reacting with suitable reagents. For instance, amino PEEK-WC reacts at room temperature with acetyl chloride to give the corresponding esters and also with cyclic anhydride such as succinic anhydride and maleic anhydride to give the corresponding carboxylic acid.
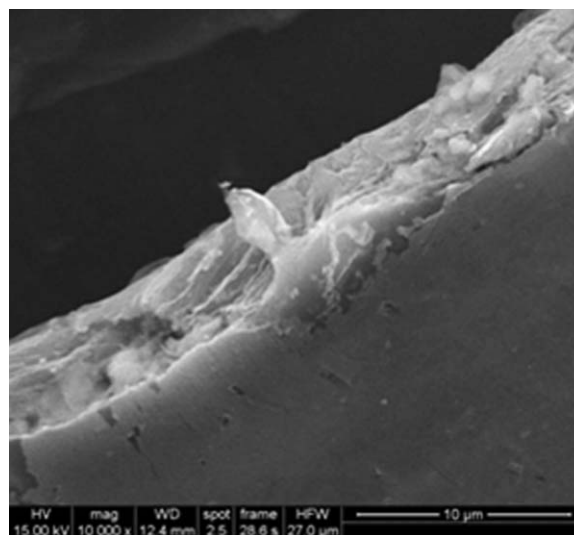

Figure 9 SEM photomicrograph of a membrane made of amino derivative PEEK-WC. Magnification 10,000x.

CONCLUSION

It was reported the synthesis of the new amino derivative of PEEK-WC.

The novel polymer was characterized by ^{1}H and ^{13}C-NMR, FTIR spectra, thermal analyses it shows a good solubility in several solvents and is able to form membrane by means of the phase inversion technique. Moreover, amino group could easily react with many organic compounds thus allowing the introduction of different organic group on the polymeric chain.

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