

Poly(ether ether ketone) Solutions Suitable for Microfiltration Membrane Preparation

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ABSTRACT: Poly(ether ether ketone) shows high stability against chemical and physical agents but is poorly soluble in most common solvents. We tested new solvents to obtain concentrated solutions that we used to prepare microfiltration membranes by the phase-inversion technique. The prepared membranes were tested by the filtration of oily emulsions, and their structure was studied with scanning electron microscopy. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2550–2555, 2001

Key words: poly(ether ether ketone) (PEEK); solutions; membranes; microfiltration

INTRODUCTION

Poly(ether ether ketone) (PEEK) is a polymer characterized by outstanding physical and chemical properties. Such characteristics make it a potential basic material for preparing membranes resistant to etching. Unfortunately, among its chemical properties, PEEK also shows a relevant resistance to solvents. When we began our research, it was reported that only sulfuric acid and *p*-chlorophenol could dissolve it to a reasonable extent.^{1,2}

Such behavior is a drawback when concentrated solutions must be obtained to prepare membranes by the phase-inversion technique.³ Sulfuric acid affects the chemical structure of PEEK by introducing sulfur atoms to the polymer chain, and *p*-chlorophenol is a very toxic substance.⁴ It is, therefore, necessary to look for other possibilities to obtain concentrated PEEK solutions and to find out new solvents that must be, moreover, water-soluble. Our work has been devoted to the search for such new PEEK solvents and to the use of the obtained PEEK solutions for

casting microfiltration (MF) membranes. The membrane structure was studied with scanning electron microscopy (SEM), and their performances were checked with oily emulsions.

EXPERIMENTAL

Materials and Methods

PEEK was produced by ICI (Wilmington, DE). The trade name was Victrex 450G, and it was kindly supplied by LATI Industria Termoplastici S.p.A. (Milan, Italy). The polymer had a density of 1.32 g/cm³ and a melting point of 334°C

All of the chemicals used as solvent candidates were reagent-grade and obtained from Aldrich Chemicals (Milan, Italy). We performed the solution tests by heating a 10% (w/w) solution of PEEK in the chemical under study until dissolution symptoms were noticed. The homogeneous liquid or paste, when obtained, was cooled at room temperature to check its behavior (only fluid mixtures can be properly cast to prepare membranes) and was, thereafter, tested for the phase-inversion step by immersion in cold water. To prepare the membranes, we spread the solution on a glass plate with a hand-driven doctor blade, and the plate was then slowly immersed in water.

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The MF tests were performed with a flat cell apparatus equipped with temperature, pressure and flow controls, as described elsewhere.⁵ A cutting oil emulsion was used as a feed and was continuously recycled on the membrane surface. Permeate flux (L/hm²) and rejection (percentage decrease of oil in the permeate) were recorded. Oil concentrations were evaluated with total organic carbon measurements via an ASTRO 2001 instrument. A Leica Stereoscan 440 electron microscope was used for studying the membrane surfaces and sections. The specimens were carbon-coated before observation.

RESULTS AND DISCUSSION

Solubility Tests

These tests were performed for the purpose of screening a large number of possible solvents on a qualitative rather than quantitative basis: 1 g of PEEK was thoroughly mixed with 9 g of the candidate solvent, and the temperature was raised to 100°C or just above the melting point of the tested chemical, if solid. The mixtures were then kept at a constant temperature under slow stirring for 30 min. The tendency of each chemical to dissolve the polymer was expressed by fictional numbers ranging between 0 and 2; no true solubility data were considered in this step of the search. The chemicals reported in Table I were tested. The results enabled us to make the following selection:

1. Benzoic acid, perfluorooctanoic acid, benzene-sulfonic acid, monochloroacetic acid, naphthionic acid, phenylacetic acid, sulfamic acid, maleic anhydride, sulfanilic acid, and thymol had no valuable effect and were discarded.
2. *p*-Chlorophenol was discarded because of its noxious characteristics.
3. Cinnamic acid, tetrachlorophthalic anhydride, 4-hydroxybenzoic acid, sulfo-salicylic acid, phthalic anhydride, and 2-naphtol were discarded because of their low water affinity and their melting temperature, which was too high to keep the solutions in the liquid state at room temperature.

The best compromise was then represented by trichloroacetic acid (TCA; solid at room temperature and melting at 56.3°C) and dichloroacetic acid

Table I Results of Solubility Tests

Chemical	Melting Point (°C)	Result
<i>p</i> -Chlorophenol	43.0	2
Cinnamic acid	42.0	2
Benzoic acid	122.4	0
4-Hydroxybenzoic acid	214.5	1
Perfluorooctanoic acid	58.0	0
Benzene-sulfonic acid	52.5	0
Trichloroacetic acid	56.3	2
Dichloroacetic acid	13.4	1–2
Monochloroacetic acid	63.0	0
Tetrachlorophthalic anhydride	255.0	1
Sulfo-salicylic acid	98.0	1
Naphthionic acid	d	0
Phenylacetic acid	76.0	0
Sulfamic acid	209.0 (d)	0
Phthalic anhydride	130.8	2
Maleic anhydride	56.0	0
Sulfanilic acid	288.0	0
2-Naphtol	122.0	2
Thymol	51.0	0

0, insoluble; 1, turbid solution; 2, clear solution; d, decomposes.

(DCA), which is less effective but liquid at only 13.4°C.

Solutions Used for the Membrane Preparation

TCA Solutions

TCA is a strong organic acid that is water-soluble. It behaves like a strong corrosive, but its toxicological characteristics are acceptable (LD 50 oral rat 400 mg/kg).⁶ When used for preparing membranes, the solutions in TCA were prepared by TCA being mixed thoroughly with PEEK and then slowly heated to melting temperature. As the temperature reached 170°C, the mix was further stirred for 15 min. This solution was liquid and clear until it was cooled below 60°C. During this procedure, a yellow-brown coloration appeared. This was considered a symptom of structural and chemical changes in PEEK. For this reason, accurate Fourier transform infrared (FTIR) spectrograms were run on the polymer feed from TCA, and we report on them later.

TCA/DCA Mixture

DCA is a less acidic compound, has reasonable toxicological properties, and is liquid at room temperature. Unfortunately, it can dissolve PEEK at

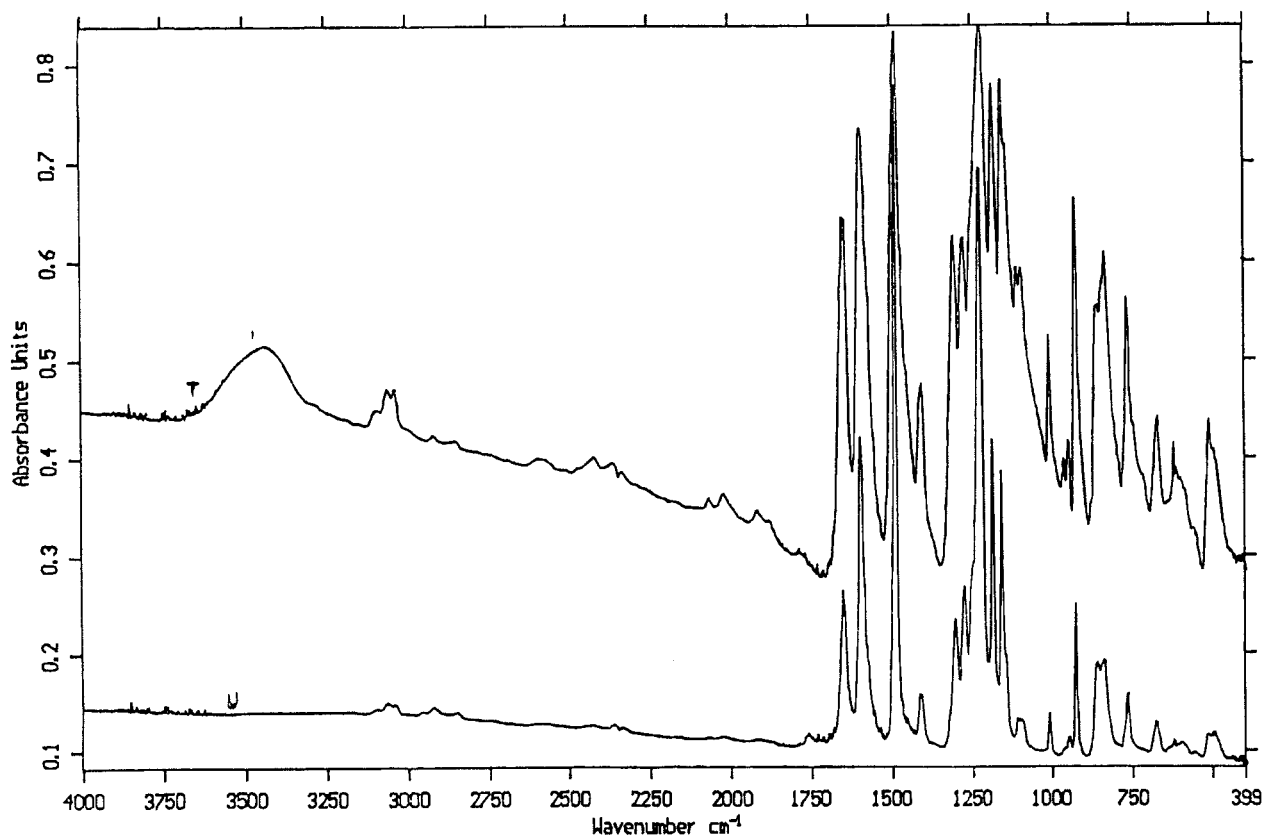


Figure 1 FTIR spectra of PEEK 450 (U) untreated and (T) after dissolution in TCA and precipitation in water.

170°C but cannot keep it in solution if it is cooled down. For this reason, we tried to add DCA to TCA to obtain the right compromise between solubility and solution viscosity at room temperature.

After prolonged testing, we found that a mixture with a TCA/DCA composition ratio of 50% (w/v) is the most suitable to keep liquid at room temperature solutions of PEEK up to 20% (w/v). The dissolution procedure was the same as that described previously. Also, in this case discoloration occurred, and it was attributed to chemical changes in the polymer. FTIR spectrometry, nevertheless, demonstrated that such changes, if present, are quite negligible, as no substantial difference between untreated PEEK and dissolved PEEK was noticed. The wide band at 3400 cm^{-1} was attributed to residual humidity (Fig. 1).

Membrane Preparation

Membranes from TCA

PEEK solutions were cast according to the procedure already described. The solution had to be

kept at 60°C to avoid PEEK precipitation, and the glass plate also was heated at this temperature. Once spread, the solution covered the plate with a 0.4-mm-thick layer; after a few minutes of immersion in the precipitating agent (distilled water at 12°C), a white PEEK film detached from the glass support. This film had a structure typical of asymmetrical MF membranes, as demonstrated by SEM (not reported). Unfortunately, the film was unstable when dried and had to be stored in a 20% (v/v) glycerin/water solution. The membranes so obtained were highly defective and could not be tested.

Membranes from TCA/DCA Mixtures

These membranes were prepared with cool water (12°C) and a glass plate at room temperature. The films prepared in this way were smooth and asymmetrical in structure and could be easily handled. Also, these membranes could not be stored in a dry form, and some of them were supported on nonwoven tissue to improve their mechanical characteristics. After immersion in

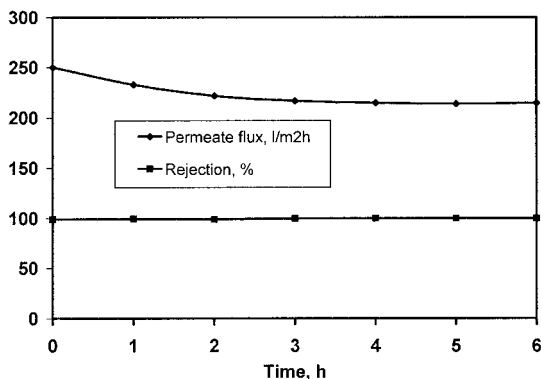


Figure 2 Permeate flux versus time for a membrane prepared from a 10% (w/v) solution of PEEK in a 50% (w/w) TCA/DCA mixture. MF pressure = 100 kPa; recycle speed = 4.4 m/s.

the water bath and separation from the glass plate, the membranes were left for 2 days in running water to remove any residual acids; finally, the membrane surface pH was checked. The membranes were then spread on filter paper or tissue and placed in the MF flat module.

The membrane pieces to be submitted to SEM were carefully dried.

MF Tests

Effect of the Run Time, Tangential Velocity, and Polymer Concentration

With the device mentioned previously, MF tests were run with a 3% cutting oil emulsion at 40°C and a 5 m/s recirculation rate over the membrane surface. The permeate flux and separation factor (rejection) were recorded. In Figure 2, data concerning a membrane prepared from a 10% (w/v) solution of PEEK in a 50/50 acidic mixture are reported. The behavior of this membrane was encouraging, as high permeate fluxes and more than 99.99% oil removal were measured after 6 h of running; moreover, the flux decline, typical of several membranes, was reduced to the first 3 h of running. The influence of tangential velocity on the flux and separation factor is shown in Figure 3. The trends of plots reported in Figure 3 are typical of coarse-pore ultrafiltration and MF membranes.⁷ They suggest a strong effect of turbulence on the membrane skin structure, which overcomes the customary boundary layer reduction. In particular, it appears that even at the maximum recycling speed, a steady permeate flux cannot be obtained, whereas a decrease in the

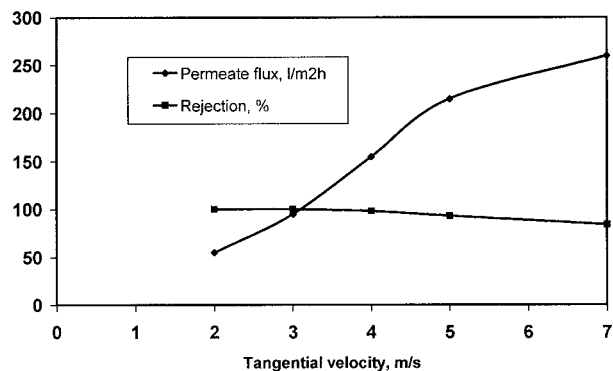


Figure 3 Influence of the recirculation speed on the membrane performances.

separation factor can be observed. This behavior could be interpreted as pore-size enlargement due to mechanical stress. Such membrane skin instability can be due to both an excessive pressure gradient during higher speed tests and the roughness of the membrane surface (as can be seen in the SEM photographs). Experimental checks nevertheless demonstrate that the pore-size deformation is not persistent

The effect of the PEEK concentration in the solutions used for membranes is reported in Figure 4. The trend is customary for membranes prepared by the phase-inversion technique. The decaying plot demonstrates that the concentration of the polymer in solution affects the thin-layer porosity in addition to the supporting layer.

Membrane Support

As already highlighted, the membranes prepared by the technique previously described were rather fragile and difficult to handle. The simplest way

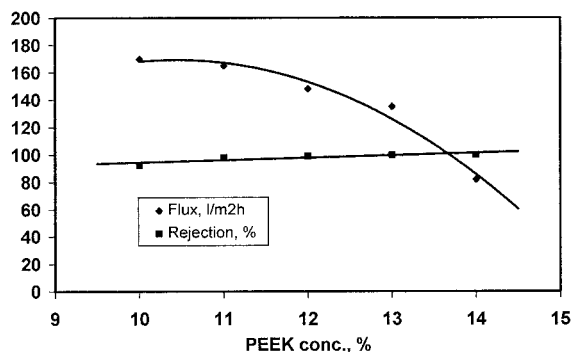


Figure 4 Effect of the polymer concentration on the permeate flux.

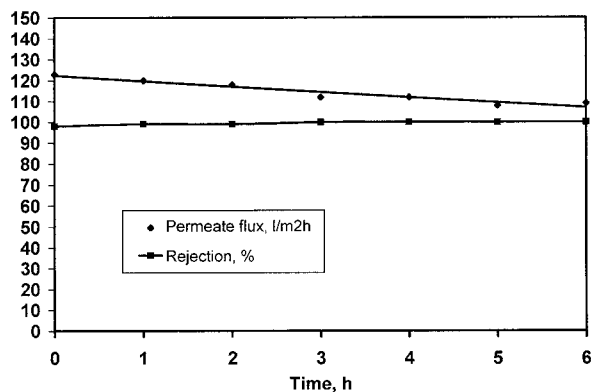


Figure 5 Permeate flux versus time for a 12% PEEK-supported membrane. Pressure = 100 kPa; oil = 6%; t . speed = 4.4 m/s; temperature = 40°C.

to get more resistant membranes is to cast them onto a support. We used a polyester tissue supplied by Karl Freudenberg. The support was closely stretched on a glass plate, and a PEEK solution was cast onto it. To avoid excessive penetration of the solution into the support fabric and subsequent surface dishomogeneity due to small peels, we used calendered-type tissue. In this way, the roots of the membranes were anchored to the support, whereas the upper surface floated far from support defects. The resulting composite membrane showed good mechanical and MF performances characteristics, as shown in Figure 5, where permeate flux as a function of time is reported.

The same flux decline ratio of unsupported membranes (see Fig. 2) was observed with time, although the initial value was lower than expected from the plot of Figure 4. Indeed, the support itself can introduce additional resistance to water flow through the membrane. The rejection was more than 99%.

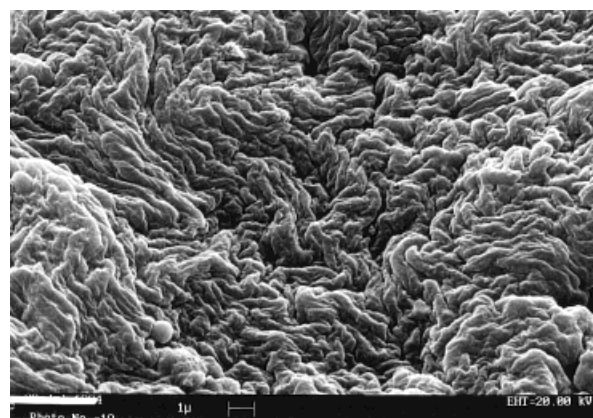
The same result was obtained with another kind of support, a polypropylene (PP)-calendered tissue supplied by Viledon (Milan, Italy).

Among SEM photographs of sections of both types of supported membranes (Figs. 6–8), the section of a polyester-supported membrane shows a change in the thickness of the dense layer.

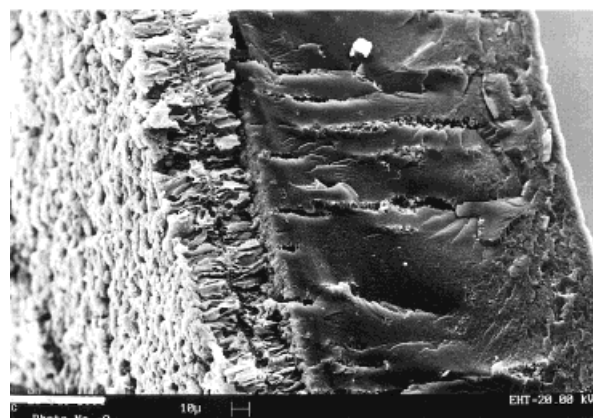
Morphological Investigation

An SEM investigation on the structure was performed to obtain more information on the potential features of such membranes. In Figures 6 and 7, photographs of both the surface and a section of an unsupported membrane are provided. By up-

per surface, we mean the one facing water during casting. The photograph shows the roughness of the membrane surface in accordance with the MF behavior reported in Figure 3. This surface shows fairly large pores, demonstrating that such a membrane is indeed suitable only for MF. The section shows an asymmetrical structure quite similar to those of most membranes prepared by the phase-inversion technique. In our case, the compact layer just under the upper surface is sharply defined but looks thicker than usual ($\sim 30 \mu\text{m}$). We attributed this to the difficulties of our solvent system to diffuse into water at room temperature, and for this reason we decided to use a 1% sodium hydroxide solution instead of pure water as precipitating agent; the accomplishment of a chemical reaction should indeed facilitate the extraction of the solvent.



(a)

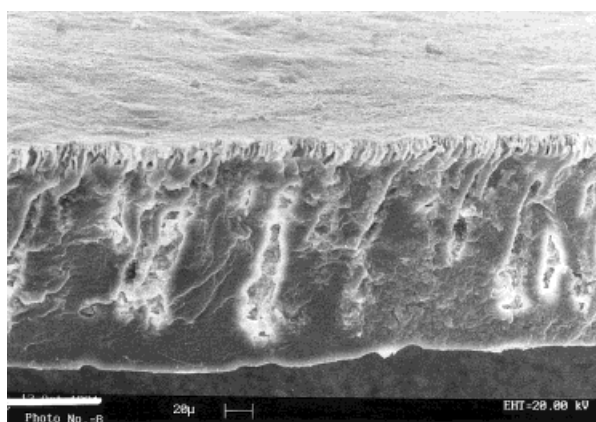


(b)

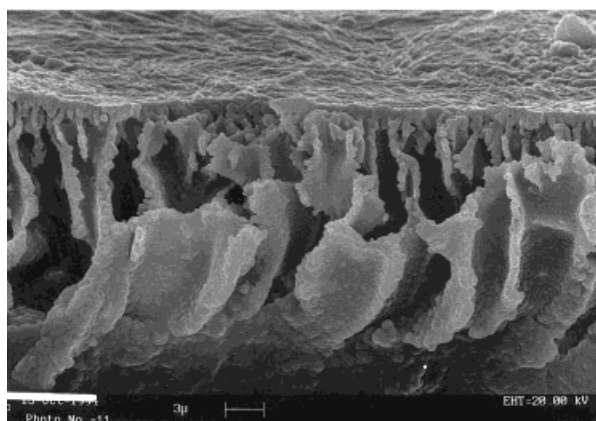
Figure 6 SEM micrographs of a PEEK-TCA/DCA mixture membrane: (a) the upper surface (original magnification of 2500 \times) and (b) a section (original magnification of 400 \times).

SEM photographs of sections of both kinds of supported membranes are provided in Figures 7 and 8. Figure 7 shows a section of polyester-supported membrane obtained by fracturing under liquid nitrogen; the supporting fibers are not clearly shown, but the section does show interesting details of the membrane structure. The asymmetry appears more pronounced here than for the unsupported membranes, as can be better seen in Figure 7(b) with a higher magnification.

The support fibers are clearly shown in Figure 8; we obtained the section by cutting the membrane with a microtome instead of using liquid nitrogen fracturing. In this way, the porous structure was damaged, but it was possible to outline the fibers from the elliptical traces of their sections and better understand how the support was placed in the membrane.



(a)



(b)

Figure 7 SEM photograph of a polyester-supported membrane: (a) original magnification of 500 \times and (b) original magnification of 2700 \times .

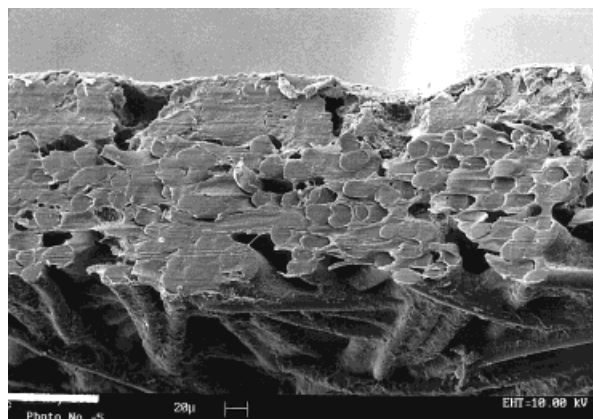


Figure 8 SEM photograph illustrating the role of the support embedded in the bottom part of the membrane.

CONCLUSIONS

We have demonstrated that PEEK has many solvents other than those reported in the technical report supplied with the polymer. Some of these solvents are useless for preparing membranes because of the aforementioned problems (mainly low solubility at room temperature). We have also shown that other solvents, or mixtures of solvents, can be used to prepare membranes from PEEK. The membranes so prepared must be kept wet, for example, with a mixture of water and glycerol, but they have outstanding properties of resistance to chemicals such as acidic and alkali substances. PEEK resistance to many aggressive solvents makes it a very promising candidate for membrane preparation. A support solves many of the handling problems and creates new opportunities for developing differently shaped membranes.

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