Sulfonation of Polyetheretherketone and Its Effects on Permeation Behavior to Nitrogen and Water Vapor

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SYNOPSIS

The novel polyetheretherketone (PEK-C) prepared from phenolphthalein in our institute is an amorphous, rigid, tough material with good mechanical properties over a wide temperature range. To improve its water vapor permeability for the application of gas drying, PEK-C was sulfonated with concentrated sulfuric acid and transferred in sodium, cupric, and ferric salt forms. Sulfonation degree can be regulated by controlling the temperature and reaction time. Characterization of sulfonated PEK-C in sodium form was made by infrared spectroscopy. Some properties of the sulfonated PEK-C, such as solubility, glass transition temperature, thermal stability, mechanical properties, and transport properties to nitrogen and water vapor, are also discussed. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polyetherketone with Cardo (PEK-C) synthesized from phenolphthalein in our institute is a novel polyetheretherketone (PEEK) with the structure[1]
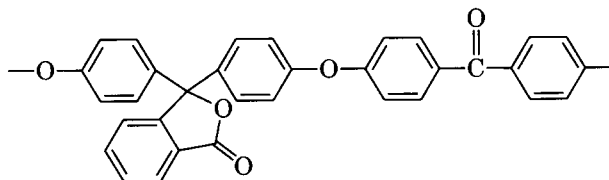
Although most of the PEEK compounds that exhibit partial crystallinity and thus are difficult to proceed solution processes, PEK-C is an amorphous polymer and is soluble in a few aprotic polar solvents such as N,N-dimethylformamide (DMF), N-methylpyrrolidone (NMP), and some chlorohydrocarbons and thus can be solution casted into membranes. In the meantime, it is a match for PEEK in mechanical and thermal properties. Furthermore, it can be modified easily by various chemical reactions, and thus its applications in membrane separation process will be found. In fact, the permeabilities for various gases through PEK-C membranes are fairly low, but the separate factors for some gas pairs are rather high, for example, the permeability for oxygen is only about 1 barrer (1 barrer = 1×10^{-10} cm^3-cm/ cm^2-s-cm Hg) and the selectivity for oxygen over nitrogen is 6.2.[2] It has been proven that the sulfonation of polymers is an effective method to increase both the permeability of water vapor and the selectivity for water vapor over nitrogen.[3–5] Therefore, the sulfonated PEK-C could be used in the air drying and natural dehydration that is one of the emerging application of membranes.

EXPERIMENTAL

Materials

PEK-C samples (η_{sp}/C = 0.97, M_w = 300,000, T_g = 228°C) were synthesized in our laboratory. H$_2$SO$_4$, 98%. Other solvents and reagents have been purchased and used without further purification.

Sulfonation

PEK-C in powder form was dissolved in H$_2$SO$_4$ to form a 10% w/v solution and stirred at 40–60°C for a certain period of time. The resulting sulfonated polymer (SPEK-C) was precipitated by dropping it in water under stirring. After removing the excess

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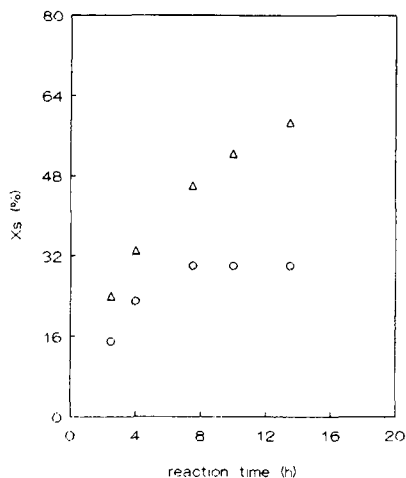
Figure 1 The changes in sulfonation degree (X_s) with reaction time at (O) 40°C and (△) 60°C.

acid by washing, the polymer was cut up and shredded in a blender, washed thoroughly free from acid, and then filtered and dried under vacuum at 60°C. A yellow-brown product was obtained. Polymers with higher degree of sulfonation were difficult to wash due to their swelling in water.

Neutralization

The SPEK-C samples were neutralized with enough $1N$ NaOH aqueous solution. The neutralized polymers were filtered, washed several times with water, and then dried under vacuum to give SPEK-C-Na polymers. The cupric and ferric salt forms of SPEK-C were transferred by immersing the SPEK-C in acid form in $1N$ $CuCl_2$ and $FeCl_3$ aqueous solution for a week, respectively.

Determination of Sulfonation Degree

Average degree of sulfonation (X_s) per repeating unit (containing four phenyl rings) was calculated from sulfur content determined by DIONEX 2120i ion-exchange chromatography (USA).[3]

Structure Characterization

Infrared (IR) spectra were obtained on a DIGILAB FTS-20E spectrometer (USA), and samples were prepared from solution cast film on NaCl plates.

Thermal Properties

The glass transition temperature (T_g) and thermogravimetric analysis (TGA) were obtained on Per-

kin-Elmer DSC-2C and TGS-2 (USA), respectively, at a 10°C/min heating rate in nitrogen atmosphere.

Permeability of Nitrogen and Water Vapor

The permeability of nitrogen was measured on a model K315-N-03 manometric permeation apparatus (Japan) and the permeability of water vapor was measured by the cap method that has been described in detail elsewhere.[4]

RESULTS AND DISCUSSION

Sulfonation of PEK-C and Characterization of SPEK-C

Sulfonation of PEK-C

The X_s can be regulated by controlling the temperature and reaction time. The results obtained from reaction at 40–60°C for different reaction time are shown in Figure 1. It is seen from Figure 1 that reaction temperature is a decisive factor controlling the sulfonation degree, which cannot be in excess of 0.3 at 40°C whatever prolonged period of reaction time. The products with high sulfonation degree $(X_s > 0.8)$ could be obtained at higher reaction temperature (e.g., 70–80°C); however, such being the case, degradation of polymer chains may have occurred and thus the mechanical properties of the membranes made from the products may be deteriorated. This can be found from the plots of reduced specific viscosity (η_{sp}/C) versus reaction time at 40 and 60°C as shown in Figure 2. It is clear that the values of
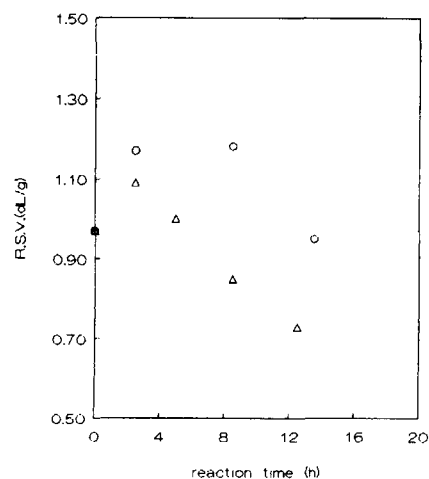

Figure 2 The changes in reduced specific viscosity (RSV) (η_{sp}/C) in DMF at 25°C with reaction time at (O) 40°C and (△) 60°C.

η_{sp}/C initially increase with time, mainly because the polar-SO_3H groups introduced into the polymer backbone interact with each other and cause the polymer chain to extend, leading to an increase in viscosity. The values of η_{sp}/C then rapidly decrease, which is mainly caused by the acid-catalytic hydrolysis of the phenolic ether bonds on the polymer backbone and the possible rupture of the phenolphthalein groups. Therefore, there is a competition between the degradation of chains and the increase in interaction among the polar groups.

The two opposite action factors will be offset by each other at a certain period of reaction time, leading to a constant value of η_{sp}/C. It is noteworthy from Figures 1 and 2 that the value of η_{sp}/C is still reduced with time after 8 h at 40°C, even though the sulfonation degree is no longer changed with time. It indicates that the degradation of chains is mainly dependent on the sulfonation agent used and reaction time but independent of the sulfonation degree, because it is learned from the literature[6] that if a moderate sulfonating agent, such as SO_3/triethyl-phosphite (TEP) is used, the values of η_{sp}/C will linearly increase with the increase in X_s, indicating no degradation of chains during the sulfonation.

On the other hand, however, the values of T_g are linearly changed with sulfonation degree except at higher values of X_s (>0.35) (as shown in Fig. 3), which is common to almost all sulfonated polymers.[3,6-8] The main factors affecting T_g values for a polymer with high enough molecular weight (MW) are the intermolecular interaction and the bulkiness of side groups, whereas the effect of MW on the T_g values is secondary as the MW values are high enough. The introduction of $-SO_3H$ groups into the polymer chains increase both the intermolecular interaction through polar ionic sites, that is, an ionomer effect, and the bulkiness of side groups,[7,8] leading to the increase in T_g values being proportional to sulfonation degree. Moreover, the ion sites in ionomers aggregate into clusters or ionic domains acting as cross-linking points also leading to the increase in T_g.[6-8] But at higher X_s (>0.35), the values of T_g underlie the straight line (Fig. 3), which can be attributed to the two possible factors: the degradation of chains in the system studied here and the plasticization by sorbed water at ambient humidity caused by strong interaction between the polar groups of the chains and water molecule.

Characterization of SPEK-C

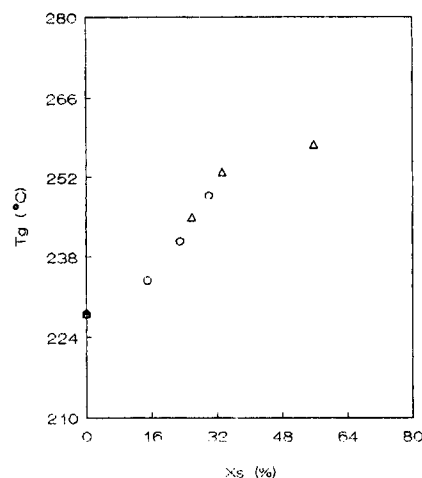The IR spectra of SPEK-C are shown is Figure 4. The distinguished feature of the IR spectra of

Figure 3 The relationship between glass transition temperature (T_g) and the sulfonation degree (X_s) for the SPEK-C obtained at (O) 40°C and (△) 60°C.

SPEK-C is the presence of absorption at 1029 cm^{-1} assigned to symmetric $S=O$ stretching caused by introduction of $-SO_3H$ groups into the polymer chains. However, determination of the sulfonation position using ^{13}C-NMR seems to be more complex and is discussed elsewhere in detail.

Physical and Chemical Properties of SPEK-C

Solubility

The solubility characteristics of PEK-C and SPEK-C in the free acid and sodium salt form are shown in Table I. It is obvious that the SPEK-C (both the free acid and the sodium salt form) is only soluble in strong polar aprotic solvents, such as DMF, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), and NMP, and insoluble in some chlorohydrocarbons, such as chloroform, 1,1,2-trichloroethane in which the amorphous PEK-C is soluble. It stands to reason that the introduction of strong polar $-SO_3H$ groups into PEK-C chains makes it lose solubility in nonpolar solvents, such as some chlorohydrocarbons.

Thermal Stability

PEK-C is a highly heat-resistant polymer. The onset of significant weight loss is at about 450°C (as shown in Fig. 5), which might be caused by main chain decomposition of the polymer occurring at the quaternary carbon atoms connected with Cardo groups. It is evident from Figure 5 that there are two weight loss steps on TGA curves for SPEK-C: one is in the temperature range of 150–300°C, which is associated
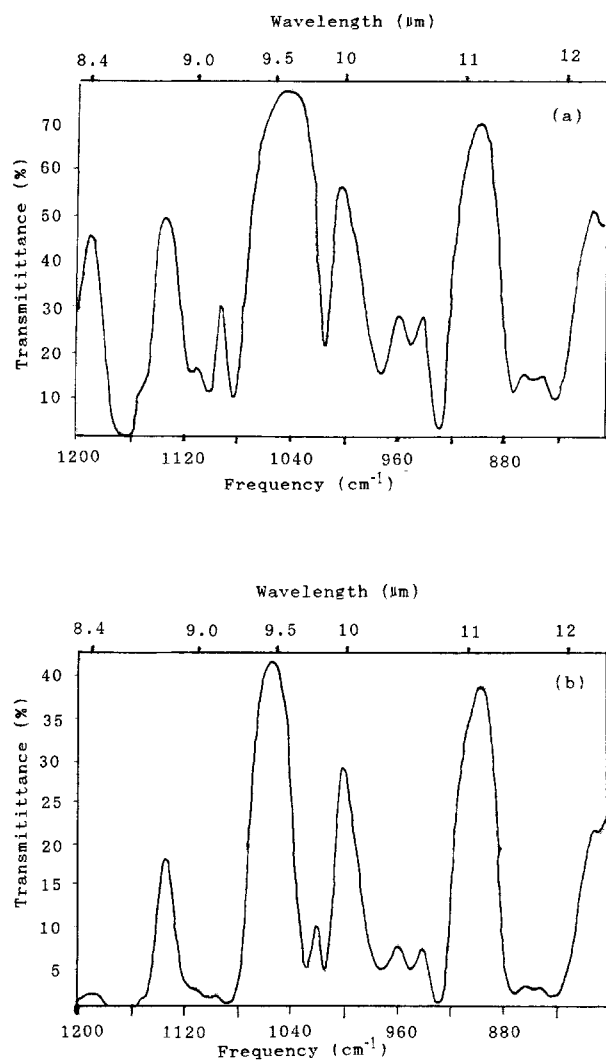
Wavelength (μm)

Figure 4 The IR spectra of the (a) PEK-C and (b) SPEK-C.

Table I Solubility of PEK-C and SPEK-C at 25°C

Solvent	SPEK-C(H)	SPEK-C(Na)	PEK-C
DMF	S	S	S
DMAc	S	S	S
NMP	S	S	S
DMSO	S	S	S
1,1,2-Trichloroethane	I	I	S
Chloroform	I	I	S
THF	I	I	SW
Ethanol	I	I	I
Acetone	I	I	I
Toluene	I	I	I

S, Soluble; I, insoluble; SW, swollen.

decreases and gradually levels off with the increase in sulfonation degree as shown in Figure 6(b). Comparing Figure 6(b) with Figure 3, it can be found that the changes in the yield stress and T_g with the sulfonation degree are the exact opposite. It looks a little strange, because the mechanical properties of polymer materials depend on the difference between the test temperature and T_g, the more the values of the difference, the higher the stress and the lower the strain.[9] It very likely resulted from the plasticization by sorbed water[7] at ambient humidity in SPEK-C, because strong interaction between the water molecule and the — SO_3H groups in SPEK-C makes the modified polymers tend to sorb water at ambient humidity and water is an effective plasticizer for many polymers.[9] It can be verified from TGA spectra (Fig.
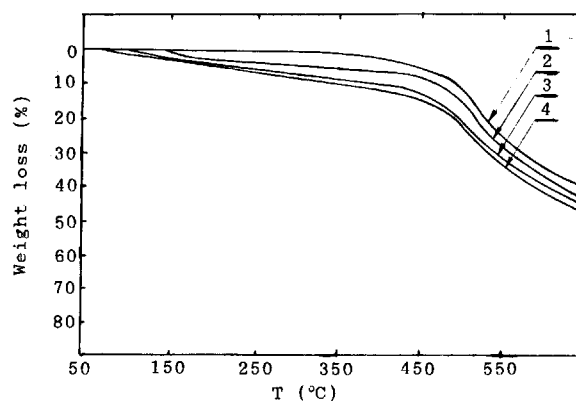
with the decomposition of sulfonic acid groups, because the bond energy of C — S bond (66.0 kcal/mol) is lower than that of C — C bond (83.1 kcal/mol). Another step appears at about 450°C, which seems to be similar to that for PEK-C, indicating no effect of sulfonation on main chain decomposition of the polymers.

Mechanical Properties

The changes in mechanical properties of SPEK-C-Na with the sulfonation degree are shown in Figure 6. It is found from Figure 6(a) that both the yield (ϵ_y) and break strains (ϵ_b) increase with the increase in sulfonation degree, but the former changes slightly compared with the latter. On the other hand, however, the yield stress (σ_y) initially

Figure 5 TGA spectra for SPEK-C of different X_s (in nitrogen atmosphere at a 10°C/min heating rate). X_s: (1) 0; (2) 0.08; (3) 0.16; (4) 0.38.
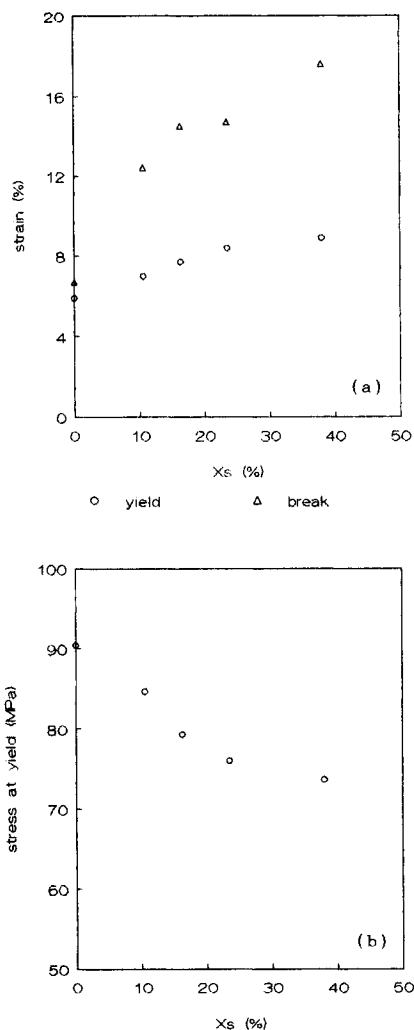
Figure 6 The changes in (a) (○) ε_y and (△) ε_b and (b) σ_y with X_s for SPEK-C-Na.

5) that the weight loss before 150°C, which is attributed to the loss of sorbed water, increases with increasing X_s. The other possible factor is the decrease in molecular weight after sulfonation in the system studied here (see Fig. 2), leading to a more flow by interchain slip and a lower fracture surface energy.[10]

Fortunately, the σ_y decreases only by 18%, whereas the ε_y increased by 47% for a sulfonated product with the sulfonation degree of 0.38. This indicates that within a certain scope of reasonably high degree of sulfonation, the SPEK-C is more ductile at ambient humidity than the original PEK-C without serious damage to its strength and is still an excellent membrane-formation polymer material.

Transport Behavior of Nitrogen and Water Vapor

Free Acid Form of SPEK-C (SPEK-C-H)

The changes in the permeability of water vapor and nitrogen through the SPEK-C-H membranes and the selectivity for water vapor over nitrogen with the degree of sulfonation are shown in Figure 7. It is obvious that the permeability for water vapor (P_w) through SPEK-C-H increased linearly with the increase in X_s whereas the permeability for nitrogen (P_N) decreased, thus leading to the increase in the selectivity for water vapor over nitrogen ($\alpha_{W/N}$) with the increase in X_s. Compared with the original PEK-C, the P_w for the SPEK-C-H sample with X_s being 0.38 increases by a factor of 6 and the selectivity for water vapor over nitrogen reaches as high as 10^5, a 10-fold increase over the PEK-C. Thus, the SPEK-C could be another excellent candidate membrane material for the air drying and natural gas dehydration. Furthermore, it was again verified from the results above that sulfonation of some polymers increases not only its permeability to water vapor but also its selectivity for water vapor over other gases. The reason is roughly the same as the case for sulfonation of poly(phenylene oxide).[5]

Effect of Ionic Interaction on Transport Behavior of Water Vapor and Nitrogen

The dependence of P_w, P_N, and $\alpha_{W/N}$ for the SPEK-C-H and its salts at 25°C on sulfonation degree are also shown in Figure 7. It is found from Figure 7(a) that the P_w values can be arranged in the following order for data acquired at the same X_s: Na ≥ H > Fe > Cu, which is caused by di- and trivalent interpolymer linkage (e.g., —SO₃—Cu—SO₃—) and water clusters assembled near the two cations that have high coordination numbers. Whereas the rank order of the P_N values follows roughly the opposite trend as the P_w: Fe ≫ Cu > H > Na (see Fig. 7(b)). Probably, it can be attributed to the larger volume of ions Cu and Fe compared with ions Na and H, leading to more free volume in SPEK-C-Cu and SPEK-C-Fe. Therefore, the $\alpha_{W/N}$ for SPEK-C-H and SPEK-C-Na membranes are larger than that for SPEK-C-Cu and SPEK-C-Fe (see Fig. 7).

Dependence of P_w on Temperature

Figure 8 shows the relationship between log P_w for PEK-C and SPEK-C-H with a sulfonation degree of about 0.5 and the reciprocal of absolute temperature, $1/T(K)$. It is obvious that there exists a linear relationship between log P_w and $1/T$ in each case, that is, the Arrhenius equation holds:
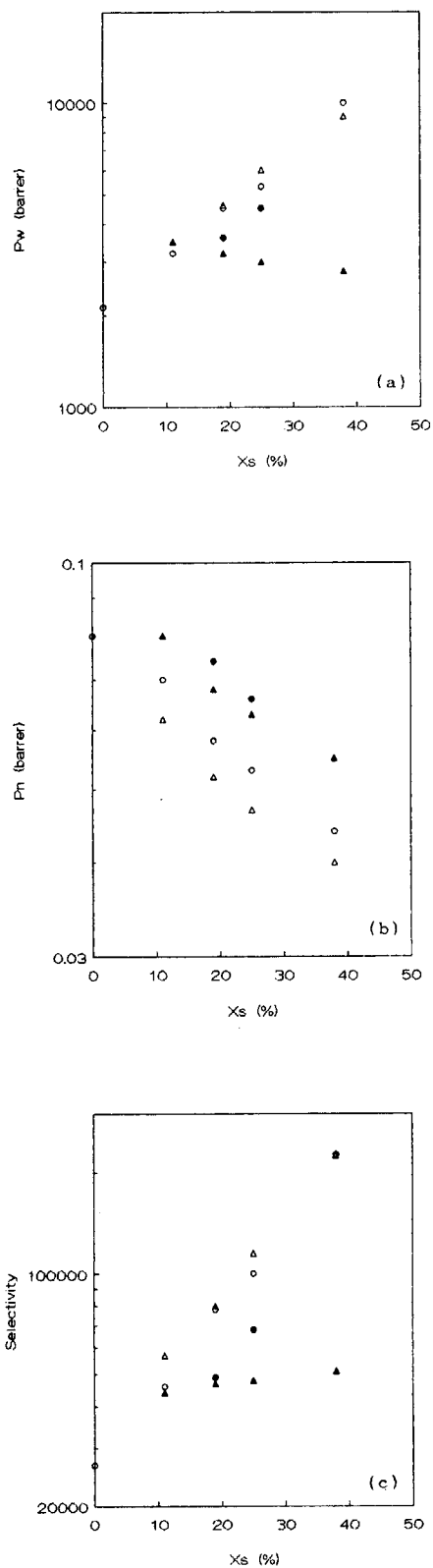
$$P_w = P_0 \exp(-E_p/RT)$$

where R is the universal gas constant and E_p is the apparent activation energy of water vapor permeation. It is well known that the permeation of gases and water vapor through a polymer matrix is a coupled process involving the dissolution and diffusion, that is, the permeability of a polymer membrane is the product of the diffusivity D (kinetic component) and the solubility S (thermodynamic component) of the permeating substances:

$$P = DS$$

Similarly,

$$D_w = D_o \exp(-E_d/RT)$$

and

$$S_w = S_o \exp(-\Delta H_s/RT)$$

Thus,

$$E_p = E_d + \Delta H_s$$

here E_d and ΔH_s are the apparent activation energy for diffusion process and the heat of solution, respectively. In general, E_d is larger than E_p for water vapor and thus ΔHs is negative, indicating that the heat generated in sorption process is provided for energy requirements for diffusion of water molecule in polymers. The values of E_p calculated from the slopes of the straight lines shown in Figure 8 are 1.4 and 8.9 kJ/mol for PEK-C-H and SPEK-C-H, re-
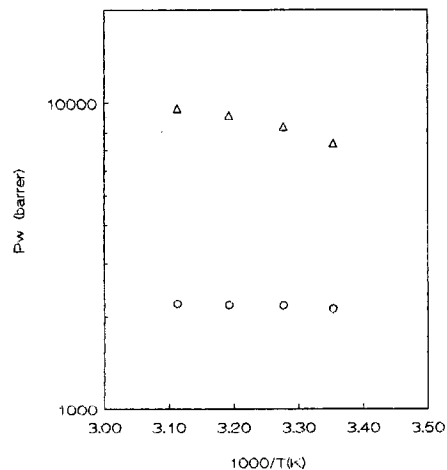
Figure 7   The changes in (a) P_w (b) P_N and (c) $\alpha_{W/N}$ with X_s for SPEK-C with different counter ions: (O) H$^+$; (△) Na$^+$; (▲) Cu^{+2}; (●) Fe^{+3}.

Figure 8   The relationship between log P_w and $1/T$ for (O) PEK-C and (△) SPEK-C.

spectively. The small value of E_p for PEK-C indicates that the permeation performance of the polymer membrane is less sensitive to changes in temperature, but its permeability of water vapor is also small. It is not surprising if the water molecule clustering making the diffusion coefficient of water vapor reduce in the hydrophobic polymer PEK-C is considered. On the other hand, E_p increases significantly after sulfonation of PEK-C, which mainly comes from the increase in E_d caused by introducing the — SO₃H groups into polymer chains. The — SO₃H groups may make the average gap size generated reduce and the chain stiffness increase as reflected by T_g increasing linearly with the increase in X_s (see Fig. 3). Both the factors lead to the increase in E_d. Whereas the increase in P_w after sulfonation of PEK-C can be mainly attributed to the increase in hydrophilicity, thus reducing the water molecule clustering and increasing the diffusion coefficient, caused by the strong interaction between — SO₃H groups in SPEK-C and water molecule. This situation is very similar to that encountered in the sulfonation of poly(phenylene oxide) (PPO).[5]

Conclusions

It has been proven that sulfonation of PEK-C using concentrated sulfuric acid is good practice to improve its gas/water vapor separation performance. The SPEK-C products are soluble only in strong polar aprotic solvents, such as DMF, DMAc, DMSO, and NMP, and insoluble in some chlorohydrocarbons in which the PEK-C is soluble. The T_g of the SPEK-C increases linearly with the increase in sulfonation degree at lower X_s (<0.5), and its thermal stability and the mechanical properties are slightly

poorer than that of the PEK-C. On the other hand, however, both its permeability for water vapor and the selectivity for water vapor over nitrogen are significantly enhanced. Therefore, the SPEK-C could be a good candidate membrane material for gas drying applications.

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