Effects of Antiplasticization on the Thermal, Volumetric, and Transport Properties of Polyethersulfone

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ABSTRACT: The aim of this work was to study the effects of the addition of low molar mass additives such as N-phenyl-2-naphthylamine (PNA) and hexafluoro-bisphenol-A (HFBPA) on the volumetric, thermal and transport properties of polyethersulfone (PES). The additive incorporation resulted in changes in molecular mobility and properties of the glassy PES matrix associated with antiplasticization. The changes in molecular mobility were accompanied by reductions in water vapor permeability of the PES of up to 93% for 30 wt % incorporation of PNA and of up to 70% for the addition of 20 wt % of HFBPA. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 2627–2633, 2007

Key words: polyethersulfone; additives; antiplasticization; molecular mobility; permeability

INTRODUCTION

When certain low molar mass additives are incorporated at low concentration in glassy polymers, it is observed a mobility restriction of the polymeric chains and effects on the mechanical behavior of the material, which is usually the opposite of that observed when plasticizers are added to a polymer at high concentration. This non usual behavior is called antiplasticization, and it is thought to be somehow related to a loss in free volume and a subsequent reduction in molecular mobility. Usually, the antiplasticization phenomenon also leads to a reduction on the gas and vapor permeability and an increase in gas selectivity properties of the material. The magnitude of these effects depends on some characteristics of the additives, such as size, shape, stiffness, and concentration in the polymer, as well as on the polymer's characteristics, particularly on the intensity of its secondary transition.[1]

In a previous work,[2] we studied the effects of low molar mass additives incorporation in a polysulfone (PSF) matrix regarding the water vapor permeation, dynamic mechanical, thermal, and volumetric properties. The results showed a reduction in T_g and free volume, increase in modulus, and diminution and/or suppression of secondary loss transition peak. It was found that antiplasticization is also accompanied by a significant decrease in water vapor permeability. This work extends our previous study to observe the antiplasticization phenomena in another polymer matrix with different chemical structure and properties, polyethersulfone (PES), and by using two different low molar mass additives PNA and HFBPA.

EXPERIMENTAL

Materials and films preparation

Table I shows the characteristics of the additives and polyethersulfone (PES) used in this work.

Films of PES-additives were produced by casting from dichloromethane solution. The additives PNA and HFBPA were used in the mixtures at 10, 20, and 30 wt % concentration and 5, 10, 15, and 20 wt %, respectively. The residual solvent was removed by drying the films in an oven at 70°C under vacuum for 4 days. To standardize the thermal history of the samples, the films were submitted to an annealing treatment at $T = T_g + 10°C$ for 60 min, followed by a quench to room temperature.
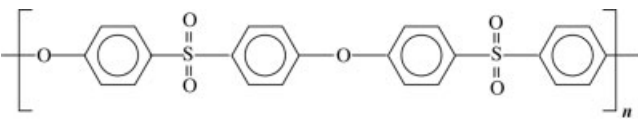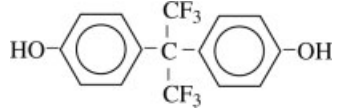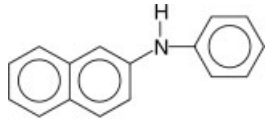
Thermal characterization

The glass transition temperature (T_g) were measured using a DSC V4.0 B DuPont 2100 calorimeter, heating rate of 20°C/min, in the temperature range from 25 to 300°C.

TABLE I
Structures of PES and Additives Used in This Work

Chemical structure	Materials
	Polyethersulfone (Ultrason E® (BASF))
	Hexafluoro-bisphenol A (HFBPA)
	N-phenyl-2-naphthylamine (PNA)

The mechanical relaxation spectra of PES and PES-additives mixtures were determined using DMTA PL Thermal Sciences, at a 2 Hz frequency, temperature range from −125 to 100°C, and heating rate of 3°C/min.

Volumetric characterization

For a detailed volumetric characterization of PES-additive mixtures, each component's specific volume must be determined in the amorphous state. In previous work, Larocca and Pessan[1] determined the specific volumes of the additives used in this study. The specific volumes for PES-additive mixtures at 25°C were measured by a flotation method, using a mixture of two miscible liquids with different densities (heptane and carbon tetrachloride). The liquids were mixed at an adequate ratio to promote the flotation of the film when the liquid solution density matched the film density. After 24 h of an equilibrium situation and therefore confirmation of flotation, the density of the liquid solution was determined using a pycnometer. Four distinct sections of the same film were analyzed for each PES-additive mixture. The temperature was controlled at (25.0 ± 0.5)°C in a thermostatic water bath.

Water vapor permeability

The water vapor permeabilities were determined by the microgravimetric method based on the ASTM standard E 96-90.[3] The permeability values were obtained from eqs. (1) and (2)

$$P = \frac{WVT \times e}{S(R_1 - R_2)} \quad (1)$$

$$WVT = \frac{G}{tA} \quad (2)$$

where G is the mass variation (g), t the time (h), A the permeation area (m^2), WVT the rate of water vapor transmission [g/(m^2 h)], e the film thickness (m), S the water vapor pressure saturation in the temperature of the essay (mmHg), and R_1 and R_2 is the air relative humidity inside and outside of the chambers.

RESULTS AND DISCUSSION

Solubility parameter (δ)—Evaluation of PES-additive interaction level

Table II shows solubility parameters of PES and those of PNA and HFBPA additives, as well as the $\Delta\delta$ values of polymer-additive mixtures. The values were determined by Hoy's method[4] and can be used to estimate the level of interaction between additives and PES. On the basis of this criterion, small differences in the values of δ parameter (<5 J/cm^3) indicate high interaction between polymer and additive (solubility).

It can be observed in Table II, a higher $\Delta\delta$ value for the PES–HFBPA mixtures indicating that this system is immiscible. In the calculation of the solubility parameter three different contributions, related to interactions between compounds (solubility), are considered: the parameter δ_H relative to hydrogen bonding, the parameter δ_P relative to dipole–dipole forces, and the contribution of dispersive forces δ_D (weak interactions). The first two parameters represent stronger interactions and are more representative of the solubility parameter.[4] The values of the solubility parameters ($\delta_{H,P}$ and $\Delta\delta_{H,P}$) considering only hydrogen bonding and dipole–dipole forces are also shown in Table II.

The $\Delta\delta$ and $\Delta\delta_{H,P}$ values for PES–PNA mixtures (Table II) are very similar. However, for HFBPA additive these values are very different ($\Delta\delta = 14.77$ and $\Delta\delta_{H,P} = 5.28$ J/cm^3). In this case, considering only

	δ_H (J/cm³)	δ_P (J/cm³)	δ_D (J/cm³)	δ (J/cm³)	$\Delta\delta$ (J/cm³)	$\delta_{H,P}$ (J/cm³)	$\Delta\delta_{H,P}$ (J/cm³)
PES	12.19	9.20	19.20	24.07	–	17.51	–
PNA	8.32	10.99	16.12	21.21	4.20	13.78	4.18
HFBPA	16.75	15.24	30.31	37.84	14.77	22.65	5.28

$\Delta\delta_{H,P}$ parameter the value obtained is close to that necessary to obtain a good solubility (<5 J/cm³). Because of the polar groups in the structure of the HFBPA additive it is possible the formation of hydrogen bonding, resulting in the solubility of HFBPA in the PES matrix.

The $\Delta\delta$ values in Table II indicate a higher interaction between PES and PNA additive than PES and HFBPA. Similar effect was observed in the preparation of the films, where PES–PNA mixtures showed no phase separation with the addition of up to 30 wt % of PNA. However, for the mixture PES–HFBPA it was not possible to exceed 20 wt % of HFBPA without phase separation.

Thermal characterization

Glass transition temperatures of the mixtures

Figure 1 shows the DSC curves for the PES-additives mixtures. It is observed in Figure 1 a reduction in the PES glass transition temperature due to additive incorporation, as observed in a previous study for PSF.[2] The T_g reduction observed in these polymer-additives systems is due to the increase in long-range molecular mobility conferred to the system by the additive.

Figure 2 shows the glass transition temperature for the PES-additives mixtures as a function of the additive concentration. The incorporation of PNA additive leads to a more significant reduction in T_g when compared with HFBPA (Fig. 2). For example, the mixtures containing 20 wt % of additive the T_g values observed were of 127°C and 144°C for the mixtures PES–PNA and PES–HFBPA, respectively.

The magnitude of reduction in T_g of PES matrix is not necessarily correlated with the glass transition temperatures of the additives. For example, the T_g of the system PES–PNA containing 20 wt % additive calculated by the additive rule of mixtures is 176°C, while the experimental data is 127°C. For the HFBPA additive these values are 178°C and 144°C, respectively. This deviation from the rule of mixtures was also observed in some other works of Maeda and Paul.[5,6] The additives glass transition temperature and degradation temperature was previously determined by Larocca and Pessan[1] (Table III).

Effects of additives in polyethersulfone sub-T_g transitions

The dynamic-mechanical behavior for the PES-additive mixtures can be visualized in Figure 3.

The DMTA curves for the PES-additive mixtures shows two sub-T_g transitions associated to segmental motions: transition γ at about -97°C and transition β near 20°C. The β transition is usually attributed to packing defects of the polymer molecules due to a fast cooling of the system (quenching). The antiplasticization phenomenon and their effects in materials properties depend on the magnitude of the γ transition. Figure 4 shows the tan δ curves for PES-additives mixtures in the γ transition region.

It can be observed a reduction in the γ transition peak intensity with additive incorporation, and even
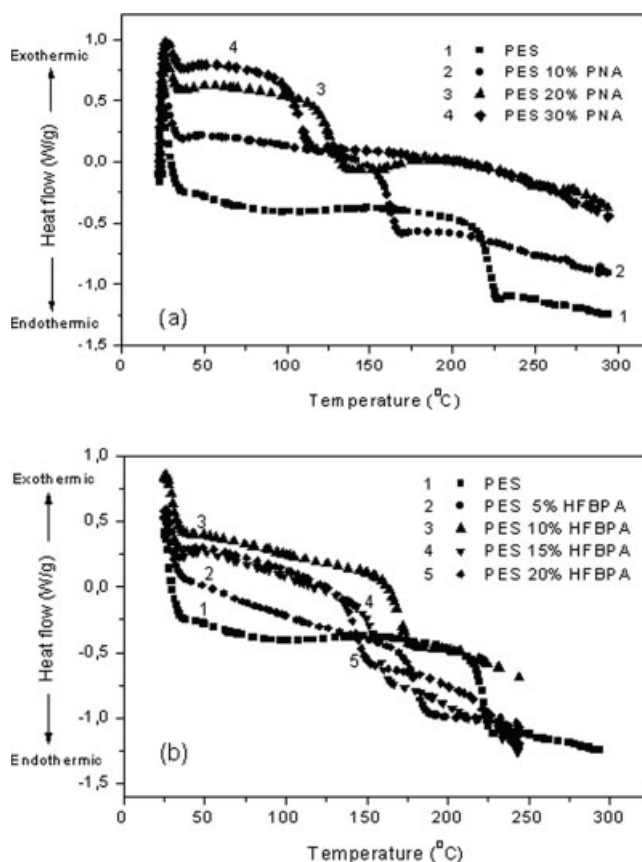

Figure 1 DSC scans for pure PES and PES-additive mixtures (a) PNA and (b) HFBPA.
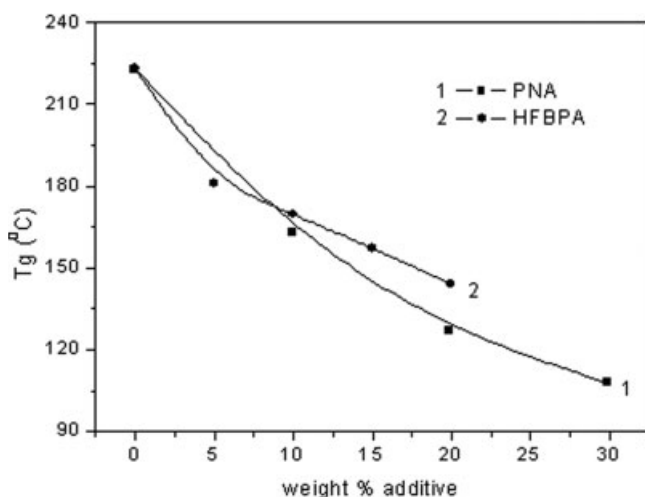
Figure 2 Glass transition temperatures of PES mixtures with PNA and HFBPA.

a suppression of this transition at high concentration of PNA additive. This suppression phenomenon is observed for PES at 30 wt % of PNA. The suppression of this transition is attributed to the mobility restriction of the aromatic rings and sulfone groups that occurs in the presence of additives. For the PES–HFBPA mixture [Fig. 4(b)] the effect of the γ transition suppression is not observed. Therefore, this additive is not as efficient antiplasticizer for PES as PNA.

The reduction in the magnitude of the sub-T_g transition with the incorporation of low molar mass additives in glassy polymers is attributed to the suppression of polymer chains local motions responsible for this transition. This behavior can be explained by the higher rigidity of the additives molecules. The aromatic rings presented in additives structure leads to local mobility restriction of polymer chains, as described by Ngai et al.[7] In other words, the additive interacts with PES aromatic rings and/or sulfone groups promoting higher cohesion between polymeric chains. Consequently, the movement of the chemical groups that is responsible for the γ transition is reduced.[8] Another parameter, that confirms the additive rigidity, is their higher glass transition temperature (T_g) (Table III) when compared with others additives.

The effects observed on the γ transition can also be explained considering the conceptual model de-

TABLE III
Additives Thermal Properties

Additive	T_m (°C)	T_g (°C)	T_d (°C)
PNA	111	−11	175
HFBPA	162	−2	175

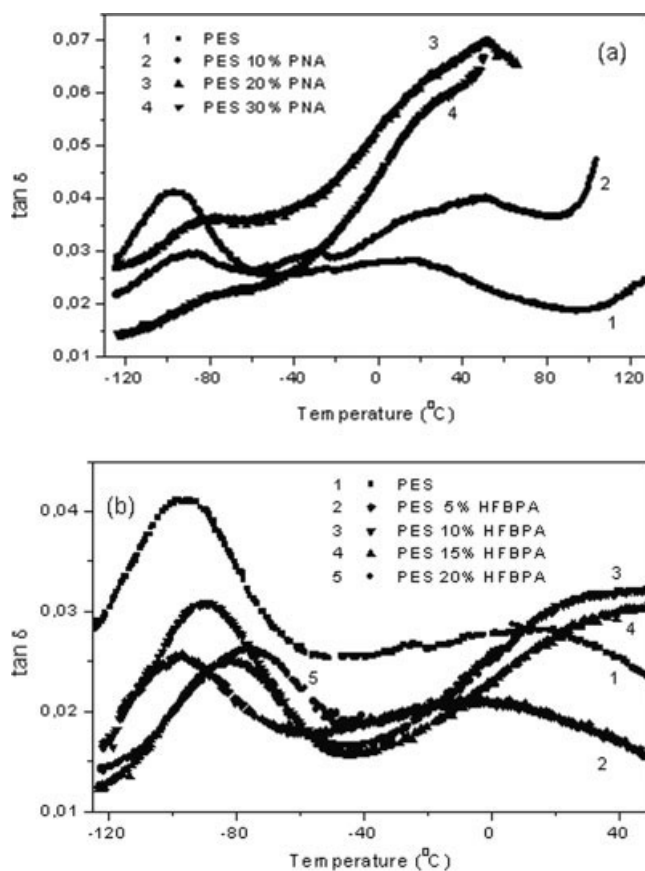T_m: melting temperature, T_d: thermal decomposition temperature.

Figure 3 Dynamic mechanical tan δ curves for (a) PES-PNA and (b) PES-HFBPA mixtures.

scribed by Liu et al.[10] According to this model, a polymer in the glassy state is constituted of regions with high density and low energy and regions with low density and high energy. Because of the higher local free volume, polymer segments of low density regions can have greater mobility which makes possible the local mobility of polymeric paths. The high-energy regions are originated from the difficulty of the polymeric chains to rearrange to an equilibrium state at temperatures below the glass transition temperature. Consequently, some of the polymeric paths with higher mobility, which could contribute to polymer γ transition, can be associated to these regions of high energy. If a small amount of additive is present during the glassy state formation, these high-energy regions can change into lower energy regions, because, next to the polymer glass transition temperature the additive mobility is higher than that of the polymeric chains. As a result, regions of higher density and lower energy are formed and paths movements around of these regions will be more difficult.

The effect attributed to antiplasticization phenomenon observed in sub-T_g transitions of PES caused by additives incorporation have also been described in literature for other polymer-additives systems.[1,2,5,6]
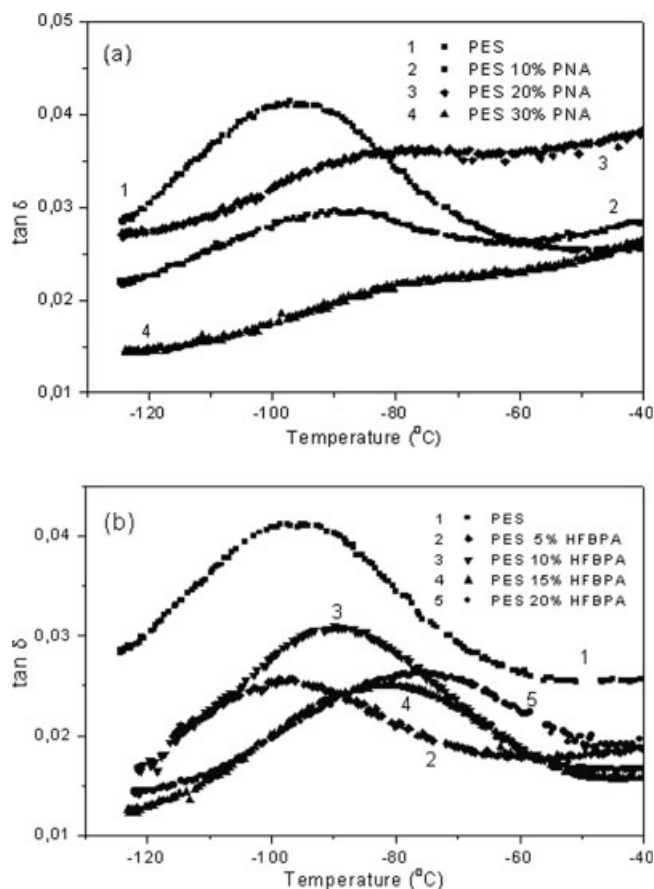
Figure 4 Dynamic mechanical tan δ curves for (a) PES-PNA and (b) PES-HFBPA mixtures in the region of transition γ.

Effects of additives on the polyethersulfone elastic modulus (E')

Figure 5 shows the elastic modulus curves of PES-additives mixtures. Similar values of elastic modulus were observed for pure PES and the PES–PNA mixture containing 10 wt % additive. At higher additive concentrations (20 and 30 wt % of PNA) it was observed a increase in elastic modulus. For HFBPA additive, similar behavior is observed for all mixtures, i.e., increase in the elastic modulus with additive concentration. The PES–PNA mixtures presented a higher increase in the elastic modulus compared to HFBPA mixtures. Therefore, PNA was found to be a more effective antiplasticizer for PES than HFBPA, as already verified by tan δ curves, where HFBPA additive showed lower efficiency in suppression of the γ transition of PES.

The differences in the antiplasticization effect observed can be understood by considering the physical chemistry characteristics of each additive. The level of interaction between polymer and additive is crucial on the level of the resulting antiplasticization effect. To evaluate the interaction between polymer and additive it is common to use a solubility parame-ter-based approach which predicts the compatibility between then.

Comparing the values shown in Table II it can be concluded that PNA molecules have a higher level of interaction with PES when compared with HFBPA molecules, as already discussed. The differences in the antiplasticization effects can be attributed to the presence of highly polar groups in the PNA molecules (amine group) that are able of interacting with the sulfone groups in the PES molecules. Although the additive HFBPA also have polar groups/atoms (hydroxyl and F), its interaction with PES can be complex due to stereo factors. As a result the differences in solubility parameters values for PES–HFBPA mixtures are larger than those for PNA mixtures.

As described earlier, it was expected that the HFBPA additives would have lower efficiency in hindering the mobility of PES molecules. The HFBPA rigidity is not high enough to compensate the effect of low interaction with PES and high specific volume. Therefore, in agreement with the previous discussion, the PES–HFBPA mixtures resulted in lower polymeric chains rigidity (Fig. 5).
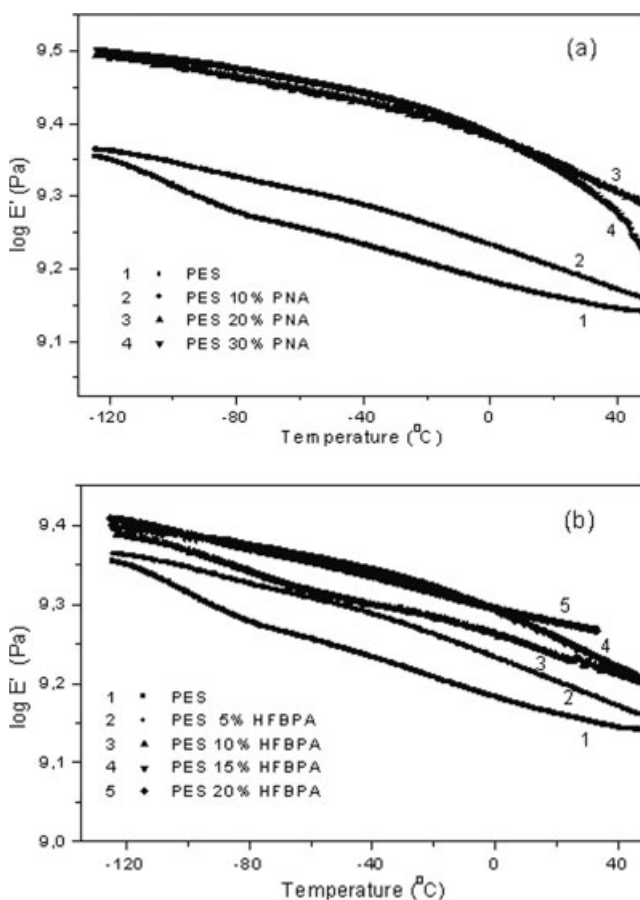

Figure 5 Elastic modulus (E') of PES-additive mixtures (a) PNA and (b) HFBPA.

TABLE IV
Volumetric Properties of PES, Additives, and Polymer-Additive Mixtures

	V_0 Bondi (cm^3/g)	V (25°C) (cm^3/g)	FFV
PNA	0.743	0.861	0.137
HFBPA	0.575	0.691	0.168
PES	0.626	0.726	0.137
PES 10% PNA	0.638	0.731	0.127
PES 20% PNA	0.650	0.739	0.121
PES 30% PNA	0.661	0.731	0.095
PES 5% HFBPA	0.624	0.717	0.130
PES 10% HFBPA	0.621	0.715	0.132
PES 15% HFBPA	0.619	0.713	0.132
PES 20% HFBPA	0.616	0.708	0.130

TABLE V
Water Vapor Permeability Values for PES-Mixtures

	P (10^{-9} g/ (Pa*s*m))	Permeability reduction (%)
PES	1.62	–
PES 10% PNA	0.45	72
PES 20% PNA	0.19	88
PES 30% PNA	0.11	93
PES 5% HFBPA	1.01	38
PES 10% HFBPA	0.83	49
PES 15% HFBPA	0.57	65
PES 20% HFBPA	0.48	70

Volumetric characterization

Table IV shows volumetric properties of the PNA and HFBPA additives, PES and PES-additives mixtures. Figure 6 shows the fractional free volume (FFV) variation for PES-additive mixtures.

It is observed in Figure 6 a reduction in the FFV of the materials due to the incorporation of the additives PNA and HFBPA. The more significant reduction in the FFV was observed for the PNA additive, in agreement with the higher elastic modulus obtained by DMTA analysis.

Compared to PES–PNA, the mixtures prepared with HFBPA additive shows a small FFV variation and lower increase in elastic modulus. Similar behavior is observed for the correlation between FFV and the effect of these additives in the PES γ transition (Fig. 4). PNA presented a high FFV reduction leading to the suppression of γ transition. For the HFBPA additive it was observed a less significant effect in the FFV reduction, leading to a small shift of the γ transition to higher temperatures and no suppression of this transition.
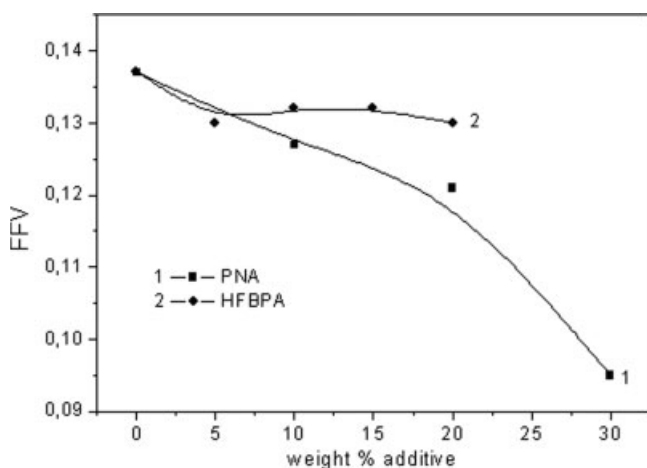
Water vapor permeability

Table V shows the values of water vapor permeability and the reduction in water vapor permeability for PES and PES-additives mixtures.

It can be observed that the additives incorporation lead to a significant reduction in water vapor permeability of up to 93% for the mixtures containing 30 wt % of PNA and of up to 70% for the mixtures containing 20 wt % of HFBPA.

As discussed previously, the PNA additive shows a stronger interaction with the PES compared to HFBPA additive resulting in a more significant reduction of the FFV and in the suppression of γ transition. The combination of these phenomena results in lower water vapor permeability for PES–PNA mixtures when compared with PES–HFBPA mixtures at the same additive concentration.

Figure 7 shows water permeability versus 1/FFV for PES-additive mixtures. The reduction of FFV leads to a reduction of the available free volume for the permeation process, and consequently to lower diffusion coefficient.

For the PES–HFBPA mixtures it is observed a small variation in the FFV which is correlated to a smaller
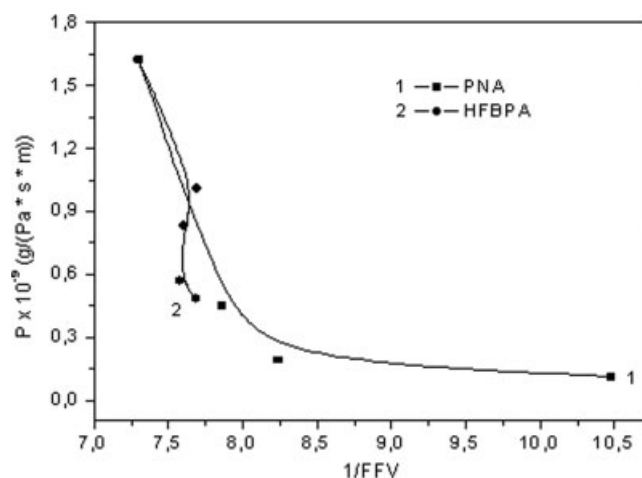

Figure 6 Fractional free volume (FFV) variation of the PES mixtures.

Figure 7 Water vapor permeability versus 1/FFV for PES-additives mixtures.

reduction in permeability than that observed for PES–PNA mixtures.

A significant reduction in permeability was observed for the mixtures containing up to 20 wt % of additive. Further additive incorporation leads to a less effective reduction (Table V). This phenomenon can be attributed to the possible formation of clusters at higher additives concentrations. It results in a loss of the additive efficiency to fulfill the polymeric matrix free volume or even to immobilize the polymeric chains leading to lower changes in permeability. It was possible to verify the efficiency of PNA and HFBPA additives in antiplasticizing and drastically reducing the water vapor permeability of PES. The reduction in water vapor permeability was observed in all additive concentrations (Table V), being more effective for PES–PNA mixtures.

CONCLUSIONS

The results of this work showed that the additives PNA and HFBPA, at the concentrations studied, lead to the antiplasticization of the PES matrix. The antiplasticization effects were more significant for the PES–PNA mixtures.

The antiplasticization effects observed with additive incorporation were: reduction in the T_g of mixtures; shift of the γ transition to higher temperatures, and even the suppression of this transition at some conditions; increase in the elastic modulus; reduction in the FFV of the mixtures and significant reduction in the water vapor permeability. For PES–PNA mix-

tures it was observed a reduction of up to 93% in water vapor permeability at 30 wt % of additive. For the HFBPA mixtures the reduction in permeability was of 70% for mixtures containing 20 wt % of additive.

On the basis of this work and from previous results obtained for PSF-additives mixtures, it can be concluded that PNA additive is the most efficient antiplasticizing agent compared to the other additives used in these systems.

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