

Effects of Low Molar Mass Additives on the Molecular Mobility and Transport Properties of Polysulfone

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ABSTRACT: The aim of this work was to study the effects of incorporation of low molar mass additives on the molecular mobility and water vapor transport properties of the polysulfone (PSF). The additives used in this work were *N*-phenyl-2-naphthylamine (PNA) at 10, 18, and 30 wt % concentration and 2,6-di-*tert*-butyl *p*-cresol (BHT) at 5, 10, 15, and 20 wt % concentration. The additive incorporation resulted in changes on molecular mobility and thermal properties of the polysulfone glassy matrix associated with antiplasticization phenomenon. The effects observed on the polysulfone were reduction in glass transition temperature, reduction in the magnitude of secondary loss transition

peak, changes in secondary loss transition peak for higher temperatures, and increase in elastic modulus E' as compared with those of the unmodified polymer. Changes in molecular mobility were correlated to reductions in PSF water vapor permeability. In PSF-PNA mixtures, the water vapor permeability was reduced up to 95% for 30 wt % additive incorporation and 81% for mixtures PSF-BHT with 20 wt % incorporation. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 101: 825–832, 2006

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

INTRODUCTION

Addition of low molar mass additives to a glassy polymer usually reduces its glass transition temperature and changes its behavior to a flexible one, with reduction in the elastic modulus and increase in impact resistance, when T_g drops below the ambient temperature. In several works,^{1–4} however, an opposing effect to the one described earlier is observed. On adding small amounts of low molar mass additive to a glassy polymer, a mobility restriction of the polymeric chains and changes in the material mechanical behavior, i.e., modulus increase, followed by impact strength reduction is observed. It is also observed that changes in the polymer transport properties, usually with a great reduction on the gas or vapor permeability and an increase in selectivity, are obtained.¹

This phenomenon, called “antiplasticization,” can be observed in several systems polymer-additive and has been attributed to the reduction in molecular mobility caused by reduction in free volumes in the material. These results reiterate the described hypothesis

of Anderson et al.,² that the phenomenon can be attributed to a chain end effect. Antiplasticizers initially fill unoccupied lower volume at the chain end and then the overall polymer free volume. Chain end mobility is restricted, resulting, thus, in higher modulus and resistance, generally followed by polymer hardness.¹

Another mechanism describing the antiplasticization phenomenon was considered by Jackson and Caldwell.^{5,6} According to these authors, antiplasticization can be attributed to a free volume reduction due to antiplasticizers; polymer-antiplasticizers interactions, creating stereo impediment and polymer paths mobility reduction; and to suppression of polymer secondary relaxation (sub- T_g).

Volumetric properties

The incorporation of additives can be a useful way to modify properties of polymeric materials. For example, changes in fractional free volume (FFV) of a polymer are expected to alter its transport properties such as vapor and gases permeability and selectivity. FFV is defined by eq. (1):⁷

$$\text{FFV} = \frac{V - V_o}{V} \quad (1)$$

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where V is the experimental mixtures specific volume, measure at 30°C; V_o is occupied volume calculated by van der Waals volume (V_w), using Bondi's empirical method.⁷

$$V_o = 1,3V_w \quad (2)$$

For polymer-additives mixtures, V_o was determined by assuming the following additive function:

$$V_o = w_d(V_o)_d + (1 - w_p)(V_o)_p \quad (3)$$

where w_i and V_{oi} are weight fraction and occupied volume of pure component i , respectively.

Solubility parameter (δ)

The level of interaction between polymers and additives has a crucial effect on the level of the antiplasticization. To evaluate the interaction between polymer and additives, it is common to use a solubility parameter-based approach, which predicts the compatibility between polymer and additive.

The thermodynamic criteria of solubility are based on the free energy of mixing ΔG_m . Two substances are mutually soluble if ΔG_m is negative. By definition,⁸

$$\Delta G_m = \Delta H_m - T\Delta S_m < 0 \quad (4)$$

where ΔH_m is the enthalpy of mixing and ΔS_m is the entropy of mixing.

As ΔS_m is generally positive, there is a certain limiting positive value of ΔH_m below which dissolution is possible.

The enthalpy of mixing can be calculated by

$$\Delta H_m = \phi_1\phi_2(\delta_1 - \delta_2)^2 \quad (5)$$

where ϕ_1 and ϕ_2 are volume fractions of components 1 and 2 and δ_1 and δ_2 are solubility parameters of components 1 and 2.

Two substances with equal solubility parameters should be mutually soluble due to negative entropy factor. As the difference between δ_1 and δ_2 increases, the tendency towards dissolution decreases. Therefore, a requirement for the solubility of a polymer P in a solvent S (or additive A) is that, the quantity $(\delta_p - \delta_{S,A})^2$ has to be as small as possible.

Formally, the solubility parameter may be divided into three parts, corresponding with the three types of interaction forces: δ_D contribution of dispersion forces; δ_H contribution of hydrogen bonding; δ_p contribution of polar forces.

These contributions can be obtained by Hoy's method.⁸ The polymer-additive systems solubility can be determined by eq. (6).

$$\Delta\delta = [(\delta_{Hp} - \delta_{Ha})^2 + (\delta_{Dp} - \delta_{Da})^2 + (\delta_{Pp} - \delta_{Pa})^2]^{\frac{1}{2}} \quad (6)$$

where p indicates polymer and a indicates additive.

The purpose of this article is to examine the effects of incorporation of low molar mass additives into polysulfone (PSF) by evaluating the changes in molecular mobility and water vapor transport properties of the polymeric matrix. The materials were characterized by differential scanning calorimetry (DSC), dynamic-mechanical thermal analysis (DMTA), and water vapor permeation. The FFV of PSF-additives was obtained by volumetric characterization.

EXPERIMENTAL

Materials and films preparation

Table I shows the characteristics of the additives and polysulfone used in this work.

PSF-additives films were produced by casting from dichloromethane solution. The additives PNA and BHT were used in the mixtures at 10, 18, and 30 wt % and 5, 10, 15, and 20, wt % concentrations, respectively. The residual solvent was removed by drying 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 at $T = T_g + 10^\circ\text{C}$ for 60 min followed by a quench to room temperature.

Thermal characterization

The glass transition temperature (T_g) was measured using a DSC V4.0 B DuPont 2100 calorimeter, heating rate of 20°C/min, at the temperature range from 25 to 250°C.

The mechanical relaxation spectra of PSF and PSF-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 PSF-additive mixtures, each component's specific volume must be determined in the amorphous state. In previous work, Larocca and Pessan³ determined the specific volumes of the additives used in this study. The specific volumes for PSF-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). Each liquid was mixed at an adequate ratio to promote the flotation of the film when the liquid solution density equaled film

TABLE I
PSF and Additives Used in This Work

Chemical structure	Materials
	Polysulfone (PSF Udel P3500 [®] Amoco)
	2,6-di-tert-butyl <i>p</i> -cresol (BHT)
	<i>N</i> -phenyl-2-naphthylamine (PNA)

density. After 24 h and confirmation of flotation, liquid solution densities were determined using a pycnometer. Four distinct sections of the same film were analyzed for each PSF-additive mixture. The temperature was controlled at $(25.0 \pm 0.5)^\circ\text{C}$ in a thermostatic water bath.

Water vapor permeability

Water vapor permeability were determined by the microgravimetric method based on the ASTM standard E 96–90.⁹ The permeability values were determined from eqs. (7) and (8):

$$P = \frac{WVT \times e}{S(R_1 - R_2)} \quad (7)$$

$$WVT = \frac{G}{tA} \quad (8)$$

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

Because of some necessary alterations in relation to the ASTM method (relative humidity of air in the

chamber and area of test of the membrane), the results presented here are discussed comparing the mixtures with the pure polymer, without the objective of correlating them with literature values. Relative permeability values (P_r) of the mixtures, in relation to pure PSF, were then obtained by eq. (9):

$$P_r = \frac{P_m}{P_p} = \frac{(WVT_m \times e_m)}{(WVT_p \times e_p)} \quad (9)$$

where m is mixture and p is pure polymer.

RESULTS AND DISCUSSION

Solubility parameter (δ)—evaluation of PSF-additive interaction level

To estimate the level of interaction between additives and PSF, the solubility parameters (δ) were calculated, considering dipole forces, dispersion forces, and hydrogen bonding, by Hoy's method (groups chemical contribution).⁸ The $\Delta\delta$ values of polymer-additive mixture obtained by eq. (6) are shown in Table II. Based on this criterion, a low value for this parameter is an indicative of high interaction between polymer and additive.

The $\Delta\delta$ values in Table II, shows that there is a higher interaction between PSF and PNA and so a higher chemical affinity than between PSF and BHT.

TABLE II
Solubility Parameters (δ) of Polysulfone and Additives Used in This Work

	δ_H (J/cm^3)	δ_p (J/cm^3)	δ_D (J/cm^3)	δ (J/cm^3)	$\Delta\delta$ (J/cm^3)
PSF	11.07	10.67	16.34	22.44	—
PNA	8.32	10.99	16.12	21.21	2.77
BHT	7.26	6.82	15.62	18.53	5.46

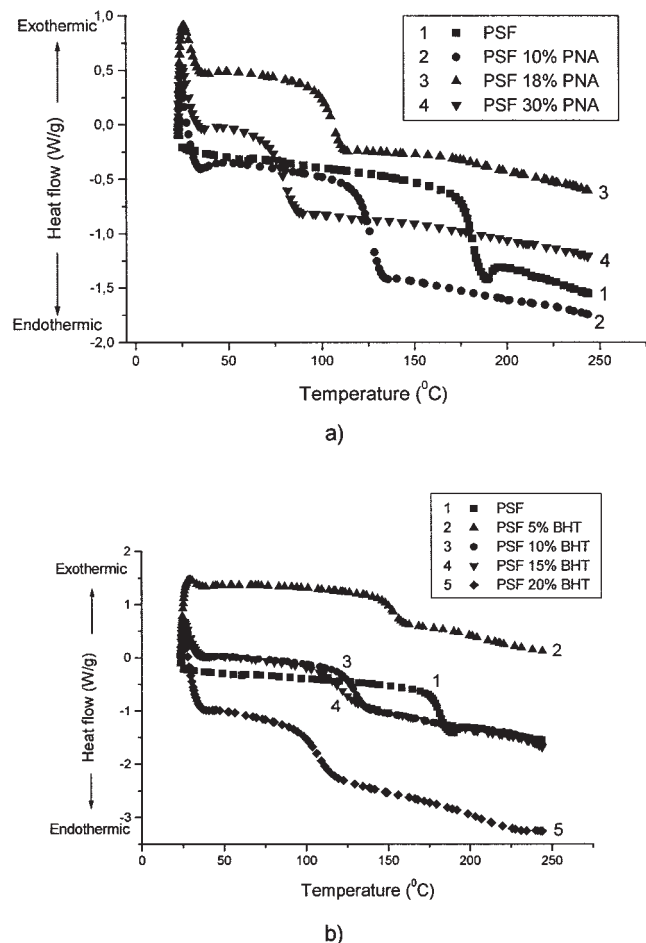


Figure 1 DSC thermograms for the pure PSF and its mixtures with (a) PNA and (b) BHT.

Thermal analysis

Glass transition temperatures of the mixtures

Figure 1 shows DSC scans for the PSF-additives mixtures.

A reduction in PSF glass transition temperature was observed due to the additive incorporation. The T_g reduction phenomena due to the addition of low molecular weight additives in glassy polymers can be understood if one considers the process of preparation of the glassy mixtures from solution. As the solvent is removed by drying, the relaxation of PSF macromolecular segments slows down to the point at which large-scale segments can no longer relax. This leads to the formation of high-energy frozen-in voids and the glassy phase formed is not at thermodynamic equilibrium. If a small amount of a low T_g additive is present while the glass is being formed, it can relax those high-energy regions because, as the additive's T_g is lower than the polymer's, its intrinsic mobility is higher than that of the polymer's.¹⁰ In other words, the additive promotes higher densification of the glassy phase, leading the polymer in the glassy state to ap-

proach its thermodynamic equilibrium state, which in turn implies a decrease of T_g .

Figure 2 shows the glass transition temperature for the mixtures with each additive as a function of the additive concentration.

The trend observed and the decreases in T_g values are comparable to those found for other vitreous polymer-additives systems.^{7,11–13} The PSF reduction in T_g magnitude due PNA and BHT addition is similar until 10 wt % additives concentration. For higher additive concentrations, a distinct behavior is observed, i.e., higher reduction in T_g for PNA additive.

Dynamic-mechanical thermal analysis

Effects of additives in polysulfone sub- T_g transitions

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

The dynamic-mechanical thermal analyses for the mixtures PSF-additive show two sub- T_g transitions associated with segmental motions: transition γ at about -97°C and transition β in the vicinity of 0°C , respectively. The β transition is usually attributed to packing defects in polymer molecules under fast cooling (quenching). Previous studies,^{1,7} presented different values for this transition, attributed to tensions relaxation process (annealing) that can reduce or inhibit this transition. Therefore, the T_β is highly dependent on the thermal history and on the sample preparation.

The antiplasticization phenomenon and effects caused in the materials, as modulus increase, matrix free volume, and permeability reductions depend on the γ transition magnitude. Therefore, this transition analysis is important to understanding polymer-antiplasticizer systems and its implications. Figure 4 shows the $\tan \delta$ curves in the γ transition region for the polymer mixtures.

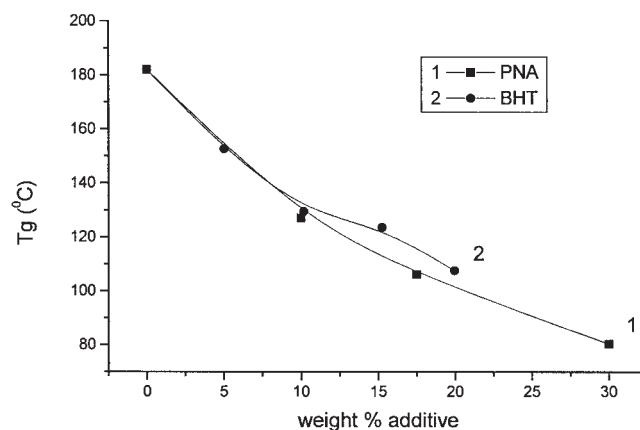
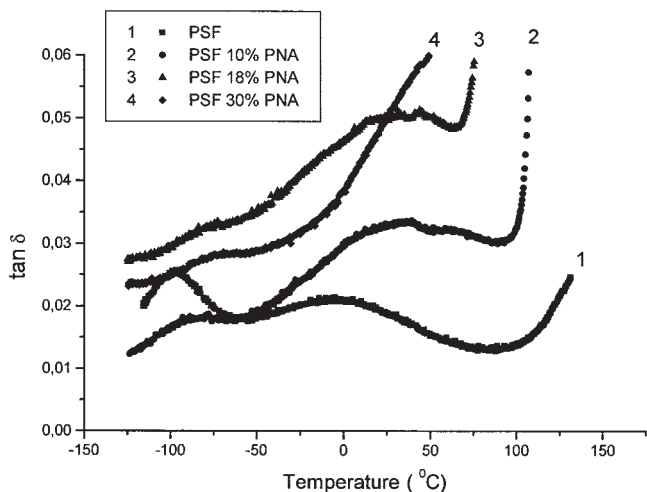
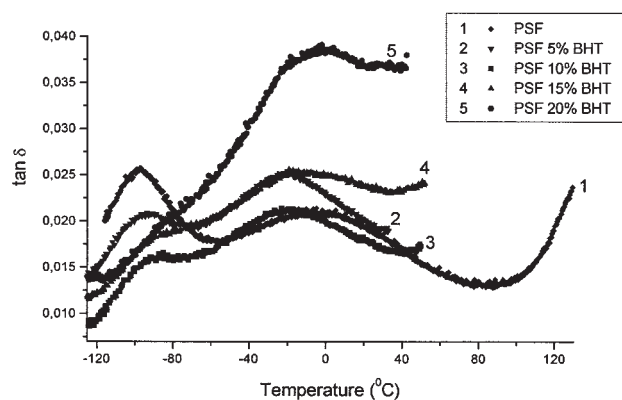


Figure 2 Glass transition temperatures of PSF and its mixtures with PNA and BHT.



a)



b)

Figure 3 Dynamic mechanical analysis curves for (a) PSF-PNA and (b) PSF-BHT mixtures.

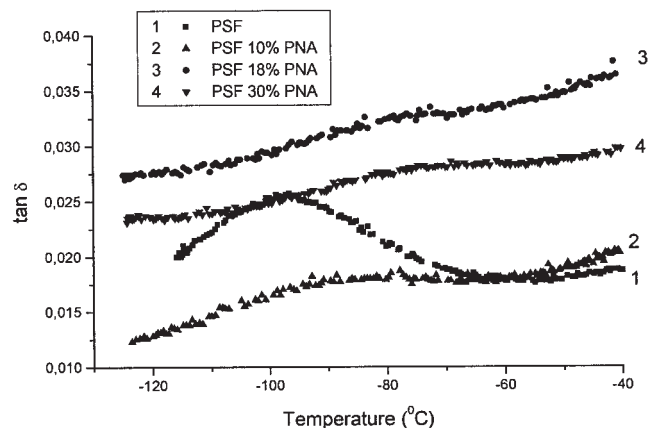
The additives modify the temperature and intensity of the γ transition, indicating that the PSF segmental mobility is also modified. The γ transition is shifted to higher temperatures with increasing amounts of additive, as shown in Figure 4, indicating that the additive restricts the segmental motions associated with this transition.

The magnitude of the transition peak also changes and the intensity of these changes depends on the sort of additive. This fact can be attributed to a higher movement restriction of aromatic rings and group diphenyl sulfone of the polymer structure, caused for additive incorporation.¹⁴

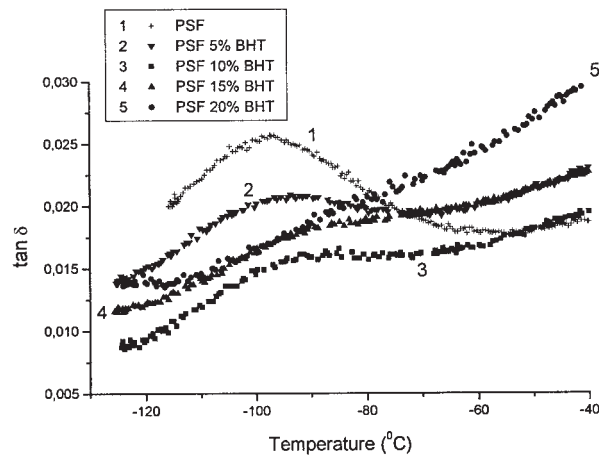
A reduction in γ transition magnitude by increasing the level of additive added in the PSF matrix is also observed, which lead to the suppression of this transition at high level of additives. This fact is observed above 10 wt % of PNA and 15 wt % of BHT. The effects of antiplasticization phenomenon

in the PSF sub- T_g transitions caused by additives incorporation have been described to other systems polymer-additive in literature.^{1,12}

Polymer-low molecular weight additive mixtures that undergo antiplasticization display another characteristic behavior, while the additive shifts the polymers α relaxation to shorter times, i.e., T_g is reduced, the secondary relaxation occurring at low temperatures shifts to longer times, representing an increase in the temperature for this transition.¹⁵ This behavior also prevails in the PSF-additive mixtures because, while additives cause the T_g of the PSF mixtures to drop, they also promote an increase of this system's T_γ . This increase of T_γ is also explained by the free volume approach considering that the densification promoted by the additives also suppresses free volume fluctuations in the glassy state.^{10,15} This suppression restricts the available space for the polymer segmental motions responsible for low temperature transitions, causing a



a)



b)

Figure 4 Dynamic mechanical analysis curves for (a) PSF-PNA and (b) PSF-BHT mixtures in the γ transition region.

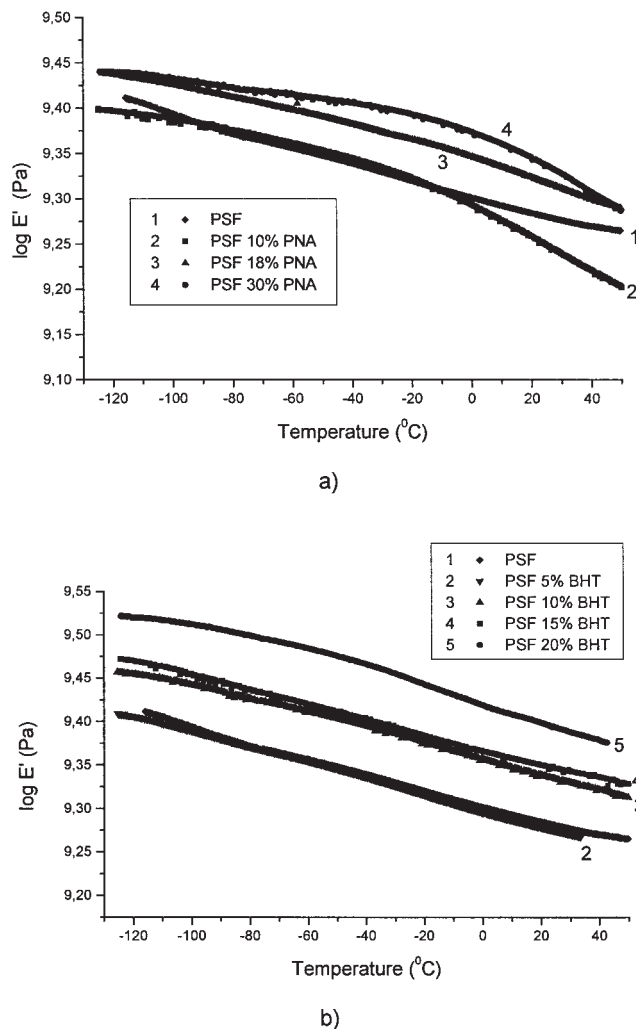


Figure 5 Elastic modulus (E') for the mixtures (a) PSF-PNA (b) PSF-BHT.

shift of the relaxation to longer times or, equivalently, a rise in the transition temperature.

Effects of additives in polysulfone elastic modulus (E')

Figure 5 shows the elastic modulus of PSF-additives mixtures.

Figure 5 indicates that all the additives actually promote stiffening of PSF glassy matrix. The level of this stiffening depends on the additive and apparently follows the sequence BHT > PNA. The stiffening of the PSF-additives mixtures can be attributed to the restriction in the movement of the polymeric chain, as observed in $\tan \delta$ curves (reduction in transition γ magnitude).

The enhanced long-range mobility (T_g decreasing) combined with stiffening of the glassy phase is a characteristic feature of an antiplasticized system. In

TABLE III
Volumetric Properties of PSF and Additives Used in This Work

	V_0 Bondi (cm^3/g)	V (25°C) (cm^3/g)	FFV
PNA	0.743	0.861	0.137
BHT	0.878	1.151	0.237
PSF	0.687	0.805	0.146
PSF 10% PNA	0.693	0.803	0.137
PSF 18% PNA	0.697	0.803	0.131
PSF 30% PNA	0.704	0.800	0.119
PSF 5% BHT	0.697	0.813	0.142
PSF 10% BHT	0.707	0.819	0.137
PSF 15% BHT	0.716	0.824	0.131
PSF 20% BHT	0.726	0.825	0.121

this case, it can be said that PSF was antiplasticized by incorporation of the additives PNA and BHT.

Volumetric analysis

Table III shows volumetric properties of the additives, PSF, and PSF-additives mixtures. The values were calculated by eqs. (1)–(3).

Figure 6 shows the fractional free volume (FFV) variation for mixtures as a function of the level of additive.

We can observe in Figure 6 a FFV reduction of materials by additive incorporation. This reduction can be correlated with other properties of the mixtures, as for example, dynamic-mechanical modulus and gases and vapors permeabilities.

As previously described, one can conclude that antiplasticization produces a reduction in the T_g and free volume of glassy polymers. This reduction in free volume increases the interchain cohesion and represents restricted freedom for the macromolecules to

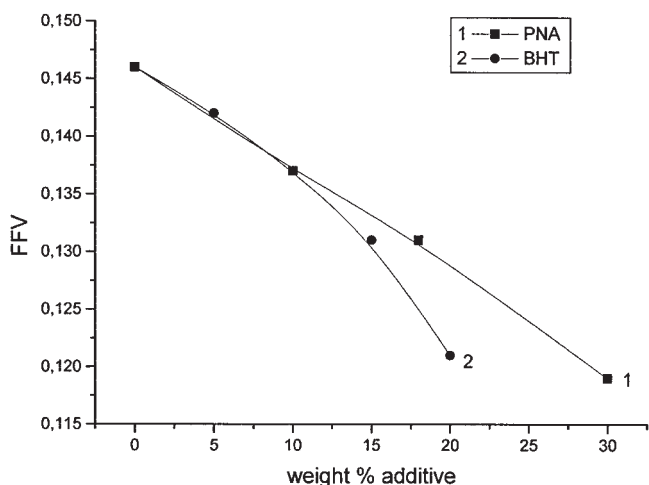


Figure 6 Fractional free volume (FFV) variation for the mixtures PSF-PNA and PSF-BHT.

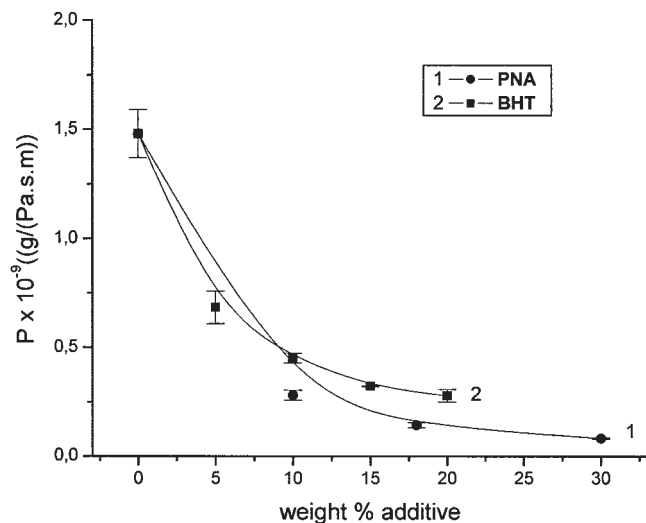


Figure 7 Water vapor permeability for the pure PSF and its mixtures with PNA and BHT.

absorb mechanical energy, which is reflected in the modulus increase. This correlation has also been found for other antiplasticized polymers.^{11,16} Figure 6 shows more significant FFV reduction in the PSF–BHT mixtures, which is in agreement with the increase in modulus for this mixture which is higher than for the PSF–PNA mixtures.

The FFV reduction results in a shift of the transition γ for higher temperatures, implying in greater energy necessary for the movement of the moieties or groups responsible for this transition, once, the holes density to these moieties lower. At higher additive concentrations, 20–30 wt %, the reduction in the FFV for the mixtures is more significant, resulting in the suppression of the γ transition. The holes around the moieties, responsible for this transition, are small and the transition is not observed. These results are in good agreement with those observed in the DMTA analysis, i.e., the transition γ shifts to higher temperatures (all additives) and for higher additive concentrations, the transition suppression is observed.

Water vapor permeability

The water vapor permeability values for pure PSF and for the PSF–PNA and PSF–BHT mixtures were calculated by eqs. (7) and (8). Figure 7 shows the permeability values obtained.

Through eq. (9), relative water vapor permeability values of pure PSF and PNA and BHT mixtures were calculated (Fig. 8).

It can be observed that there was a significant reduction in the water vapor permeability because of the incorporation of additives as compared with the values for the neat PSF. This behavior is more evident for the PNA additive compared with that of the BHT

additive at the same additive concentrations. The PNA molecules have a higher level of interaction with PSF macromolecules compared with that of the BHT molecules. The fact is evident by minor differences in values of solubility parameters, 2.77 and 5.46 (J/cm³), respectively. These values can be attributed to the presence of highly polar groups in the PNA molecules (group amine) and its possible interaction with the sulfone groups in the polymer structure. These interactions result in reduction of the water solubility coefficient in the polymer, once, hydrogen bonding between water and sulfone groups will occur at a lower intensity.

The permeability reduction in the mixtures can be related to the effects caused by antiplasticization phenomenon, as modulus increase, free volume reduction, and molecular mobility restriction. This fact is attributed to the additive effect in the polymer chain, described previously, as decrease in magnitude of the γ transition and the capacity of suppression of this transition by the additive.

Permeability is very dependent on the materials γ transition. Therefore, when any additive that can act on this transition is added, permeability is influenced. As observed in Figure 4, as the additive is incorporated in the polymer, the magnitude of the γ transition decreases or is shifted to higher temperatures, until suppression can occur, restricting the polymeric chains segmental mobility and penetrant diffusion, resulting in permeability reduction.

Another factor to be considered is the FFV reduction of the materials due to the additive incorporation. The reduction in the FFV results in the reduction of the penetrant diffusion coefficient, i.e., a reduction of the available free volume for the permeation process. Figure 9 shows water vapor permeability correlation with the inverse of the FFV of the materials.

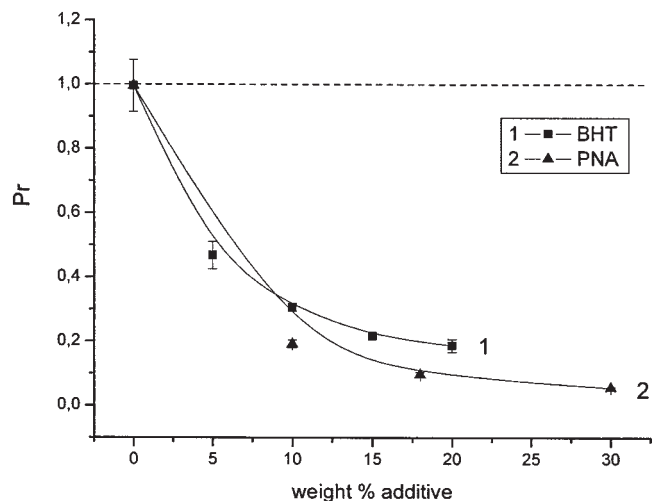


Figure 8 Relative permeability of PSF–PNA and PSF–BHT mixtures.

It can be observed that there is a good correlation between the water vapor permeability reduction and the reduction of the FFV for the mixtures. Gases or vapors permeability is highly affected by free volume. The penetrant permeation in polymer matrix depends on the diffusion coefficient and is directly related with the unoccupied volume in the matrix, which allows the formation of an activated state for the diffusional jump to occur. Higher fraction free volumes result in higher penetrant diffusion coefficient and higher materials permeability. For the PSF studied, a pronounced reduction in the permeability due to reduction in the FFV is observed for both systems.

Table IV shows water vapor permeability values obtained through eqs. (7) and (8), the FFV values obtained from eqs. (1)–(3), and the percentage in water vapor permeability reduction due to additives incorporation.

We can observe in Table IV and Figure 9, a more effective reduction in water vapor permeability at low additive concentrations (10–20 wt %) and a lower reduction at higher additives concentrations, reaching a plateau in the reduction of the property. This phenomenon can be attributed to a possible formation of clusters of additive molecule at high concentrations, resulting in lower additive solubility in the matrix. This way, the additive starts to be less efficient in fulfilling the unoccupied volume of polymeric matrix and immobilizing polymeric molecules. As a result, it is observed that there is a less efficient reduction in permeability at higher concentrations of the additives.

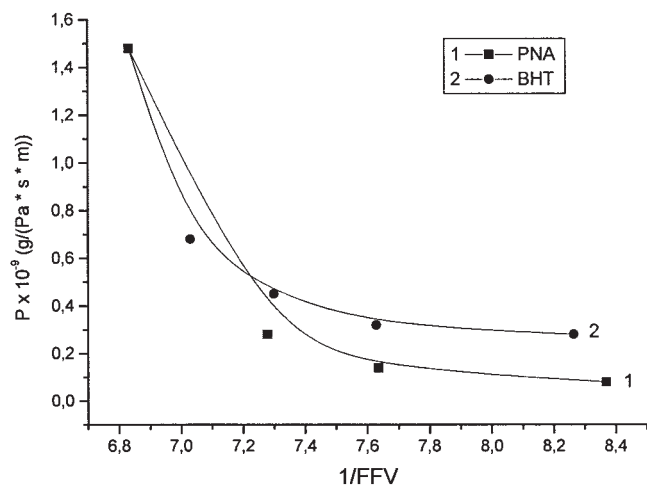


Figure 9 Water vapor permeability versus $1/\text{FFV}$ for the mixtures PSF-additives.

TABLE IV
Water Vapor Permeability, FFV, and Permeability Reduction for the Mixtures Studied

	FFV	P ($10^{-9}\text{g}/\text{Pa s m}$)	P reduction (%)
PSF	0.146	1.48	
PSF 10%PNA	0.137	0.28	81
PSF 18%PNA	0.131	0.14	91
PSF 30%PNA	0.119	0.08	95
PSF 5%BHT	0.142	0.68	54
PSF 10%BHT	0.137	0.45	70
PSF 15%BHT	0.131	0.32	78
PSF 20%BHT	0.121	0.28	81

CONCLUSIONS

Through this work, it was possible to verify the efficiency of PNA and BHT additives in antiplasticizing and significantly reducing the water vapor permeability of PSF. The reduction in water vapor permeability was observed for all additive concentrations, being more effective for the PSF–PNA mixtures.

The antiplasticization effects observed with additive incorporation were: reduction in T_g of mixtures; shift of the γ transition to higher temperatures, as well as, the suppression of the γ transition; increase in the elastic modulus; reduction of the FFV of the mixtures; and significant reduction in the water vapor permeability.

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