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# Antiplasticization of a polyamide: a positron annihilation lifetime spectroscopy study

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**Abstract**

In order to modify the transport properties of the amorphous polyamide Trogamid-T™, several additives with structural characteristics that produce antiplasticization have been tested. Positron annihilation lifetime spectroscopy (PALS) has been used to determine both the size of free volume holes and the number of holes (free fractional free volume). Polyvinyl phenol (PVPh), 1,5 dihydroxy naphthalene (Ndiol) and a hexafluorinated Bisphenol A (HFBA) were chosen according to the results of a preliminary study based on density and PALS measurements with 15% of additive blends. Their blends with Trogamid show different behaviours: HFBA behaves clearly as a plasticizer while the polyvinyl phenol acts as an antiplasticizer. Ndiol has a more special effect: blend densities are greater than additive whereas the hole size decreases.

*Keywords:* Antiplasticization; Positron annihilation lifetime spectroscopy; Polyamide

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## 1. Introduction

The incorporation of small amounts of low molecular additives into glassy polymers often leads to an increase in stiffness as a result of the phenomenon that has been termed as antiplasticization. Variations of free volume have been used to explain the effects of this phenomenon [1,2] in polymeric materials. In that case, the inclusion of small molecules into a polymer raises the rigidity of the material with a subsequent suppression of motions in the polymer chain. Because of that, there are changes in physical properties of the polymeric materials. For instance, modulus and strength increase whereas ductility and permeability to gases decrease [3–13], there is a suppression of sub-$T_g$ relaxation processes [14], etc.

Investigations of the antiplasticization phenomenon have been mainly carried out in poly(vinyl chloride) (PVC) and polycarbonate (PC) [6,7,15–18]. It is however known that certain kinds of polyamides [15], poly(methyl methacrylate) [15], polysulfone [19], polyhydroxyether [19] and polystyrene [1,15] may be antiplasticized as well. The effect of various antiplasticizers on the gas permeability of polysulfone (PSF) and poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was studied in detail by Maeda and Paul [10–12].

In a given polymer, the degree of the antiplasticizing effect, depends on the type and quantity of the additives used. Additives that act as antiplasticizers should be compatible with the polymer and their structures usually possess some of the following characteristics: they are relatively planar, rigid and contain specific atoms such as halogen, nitrogen, oxygen, etc. The majority of the existing antiplasticizers are low molecular weight substances and most studies of antiplasticization have been devoted to the polymer–diluent interactions.

On the other hand, until few years ago, attributing antiplasticization to a decrease in free volume was solely based on density measurements and theoretical calculations. Now, positron annihilation lifetime spectroscopy (PALS) should be considered as the unique method that gives most direct and detailed information on free volume. The PALS technique has been widely used in the study of polymeric systems at molecular level in the recent years [20–23].

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Although it has been observed an increase of the number of papers concerning PALS applications in the study of microstructure of polymers and polymeric blends, little attention has been addressed to the effect of plasticization and antiplasticization of polymers [1,24–30].

In this work we present the results of free volume variations due to antiplasticization of an amorphous polyamide, the poly(trimethyl hexamethylene terephthalamide), commercialised as Trogamid-T™ which will be denoted as Trogamid or T in this paper. These variations have been obtained from positron annihilation lifetime spectroscopy (PALS) experiments. Trogamid was selected for this investigation due to two main reasons. Firstly, to our knowledge, there are no reports in the literature about antiplasticization of this polymer by low molecular weight diluents. And secondly, it would be of interest to learn whether antiplasticization might provide an alternative for modifying the properties of this polymer as a membrane material to improve its selectivity while retaining in some degree its advantageous barrier properties.

## 2. Experimental

### 2.1. Positron annihilation lifetime spectroscopy

In recent years positron annihilation spectroscopy (PALS) has shown to be a unique and very good tool to study the free volume properties of polymers. In general, positrons are sensitive to open volume type defects present in materials, and the positron lifetime is proportional to the size of the open volume [31]. In the case of polymers, positrons also form positronium, Ps (a bound atom which consists of an electron and the positron). Because of the relatively small size of Ps (1.59 Å) compared to others probes, PALS is particularly sensitive to small holes and free volume in a size of Å, capable of determining the holes and free volume in a polymer without being significantly interfered by the bulk. In molecular systems, a large fraction of Ps formation is observed in the free-volume regions. The long lifetime of *o*-Ps (*ortho*-Ps, the triplet state), which is localised in the free-volume holes, makes possible to correlate the hole dimension with the measured lifetime. According with the model proposed by Eldrup [32], the *o*-Ps lifetime, $\tau$, as a function of free-volume radius, $R$, is given by:

$$\tau = 0.5\left[1 - \frac{R}{R_0} + \frac{\sin 2\pi(R/R_0)}{2\pi}\right]^{-1} \tag{1}$$

where $R_0 = R + \Delta R$ and $\tau$ is given in nanoseconds. The radius $\Delta R$ is an empirical parameter which best value obtained fitting all known data is 1.656 Å [33]. The mean free volume hole size, $V_H$, assuming a spherical form for the holes, may be estimated by using a simple equation:

$$V_H = (4\pi R^3)/3 \tag{2}$$

The experimental data of a positron lifetime experiment in polymers are the convolution of three exponential decays (i.e. three different lifetimes) being the resolution a function of the spectrometer. Each lifetime corresponds to the average annihilation rate of a positron in a different state: the shortest lifetime ($\tau_1 \approx 0.12$ ns) is due to singlet *para*-positronimun (*p*-Ps), the intermediate lifetime ($\tau_2 \approx 0.40$ ns) is due to positrons annihilated in molecule species, and the longest lifetime ($\tau_3 \geq 0.5$ ns) is due to *o*-Ps localised in free volume holes. In this analysis, the $\tau_3$ component is used to determine the mean free-volume hole size. The relative intensity corresponding to this lifetime, $I_3$, contains information related to the number of the free-volume holes. In this sense, combining the number ($I_3$) and size ($\tau_3$) of free volume holes an estimation of the free volume fraction ($f$) could be extracted by [34]:

$$f = AV_H I_3 \tag{3}$$

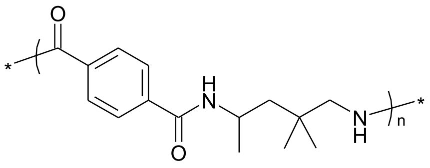
where $A$ is a proportionality constant which can be determined by calibrating with other physical parameters [35,36]. However, due to the fact that is difficult to know the value of $A$ for many polymers, Li et al. [37] have defined an apparent fractional free volume ($f_{app}$) by the following equation:

$$f_{app} = V_H I_3 \tag{4}$$

On other hand, some authors [38–42] have shown that $I_3$ depends also on other variables as activity of the positron source and the chemical composition of the polymer [38,39,42] as well as elapsed times for temperatures far below $T_g$ [40–42], so, $I_3$ could not uniquely be ascribed to the free-volume hole number. Taking into account these comments, the absolute value of free volume fraction would not be available from $I_3$. But if the aim of the PALS study were to know the variation of free volume fraction with the composition in the blends, as is our case, $f_{app}$ would be an adequate magnitude in order to estimate the free fractional volume variation.

### 2.2. Materials

Trogamid-T-5000™ was supplied by Dynamit Nobel. It is an aromatic amorphous polyamide, poly(2,2,4-trimethyl hexamethylene terephthalamide). Its chemical structure is shown below



Like other polyamides, Trogamid absorbs water at a rate that depends on the temperature and relative humidity. Before any study or measurement it must be properly dehydrated in vacuum in order to eliminate the possible influences of the water content.

The additives fluorene 98%, 4,4′-(9-fluorenylidene) diphenol 97%, 1,5-dihydroxynaphthalene 97%, 1,1′-bi-2-naphtol 99%, 4,4′-(hexafluoroisopropylidene) diphenol 97% and poly(4-vinylphenol) (average $M_w$ ca. 20,000) were supplied by Aldrich. Chemical structure and melting points of these additives are compiled and described in Table 1.

### 2.3. Procedure

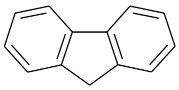
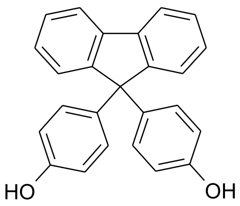
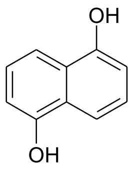
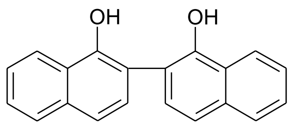
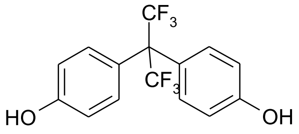
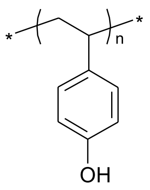
All the blends used in this work have been prepared by laboratory-scale melt-extrusion. For this, the polymer was first ground into powder using a Retsch grinder with liquid nitrogen cooling. The polymer powder and each additive were mixed in the appropriate weight ratio, then dried under vacuum at room temperature for at least 7 days. Samples were removed from the vacuum oven only prior to extrusion. Blends in molten state were carried out with a MINIMAX MOLDER mixer operating at 50 rpm at 225 °C.

Glass transition temperatures, $T_g$, of the blends and pure Trogamid were determined by differential scanning calorimetry (DSC) using a Perkin–Elmer DSC6 calibrated with an indium reference standard. Thermal data were taken from the DSC trace of the second run that was scanned at a heating rate of 20 °C/min from room temperature to 200 °C. All samples were run in air.

Films have been prepared by moulding the powders of each blend by hot-pressing following the next method: First of all, the empty mould is pre-heated at the moulding temperature (roughly 40 °C above $T_g$), then an amount enough to cover the inside of mould is put in it and it is closed. The charged mould is heated for 1 min at moulding temperature, then a pressure of 92 bar is applied for 2 min after which the sample is cooled for 2 min and, finally, the film is carefully removed from the mould.

Densities of films have been determined in a gradient

Table 1
Description of potential antiplasticizers additives

| Name | Acronym | Structure | $T_m$ (°C) |
|---|---|---|---|
| Fluorene | Fluorene |  | 115 |
| 4,4′-(9-Fluorenylidene) diphenol | FDPh |  | 225 |
| 1,5-Dihydroxy naphthalene | Ndiol |  | 260 |
| 1,1′-Binaphtol | Binaphtol |  | 216 |
| 4,4′-(Hexa fluoroisopropylidene) diphenol | HFBA |  | 162 |
| Poly(4-vinylphenol) | PVPh |  | 174[a] |

[a] Instead of mp the $T_g$ has been reported.

density column with a dissolution of KBr in water at 23 °C, in ranges not higher than 0.15 g/cm$^3$. Three films of each sample have been placed on the liquid column and the reading has been done the following day in order to let the solution to wet the films.

### 2.4. Apparatus

Positron lifetime spectra were recorded using a conventional fast–fast nuclear spectrometer with a resolution (full width at half maximum) of 230 ps. As positron source, 10 μCi of $^{22}$NaCl evaporated onto a Kapton foil was used. All lifetime spectra were resolved in three components after subtracting the source contribution to the data. Because we are interested in the evolution of free volume, only the long component, $\tau_3$, was taken into account in the analysis of the spectra. The values for the two other components are in agreement with *p*-Ps and bulk annihilation events. Because we have used a finite term analysis, the parameters of the long component, lifetime and intensity, represent an average of free volume distribution present in the sample.

## 3. Results and discussion

### 3.1. Additive selection

As it has been mentioned above, certain additives may cause the phenomenon of antiplasticization in polymers. Some of the best groups of additives that fit the structural conditions required to give such type of effect, are naphthalene, fluorene and bisphenol derivatives, successfully used, for example, with polysulfones [8]. We have selected some members of these series with melting points high enough to allow us to prepare the blends at temperatures over 200 °C. Table 1 shows the additives used and their structures. An important factor to consider when they are used as additives is the effect of the hydroxyl groups, which can interact strongly by hydrogen bonding with other adequate groups, such as carbonyl groups.

Besides the low weight additives, we have found interesting to carry out a parallel study with a polymer, poly(4-vinylphenol) (PVPh), which has similar chemical characteristics to those of the above-cited additives: it has a planar and polar structure and, furthermore, it has been found to be miscible in any range of composition with Trogamid [43]. However, it could be expected that the mechanism of antiplasticization by polymer chains [44] may be different to that of small molecules, due principally to the polymer size, although this macromolecular character could avoid the plasticizer migration.

Previous works have indicated that greatest effect of antiplasticization is at percentages of additive in the blends around 10–20% in weight [10,44,45]. We have made blends of Trogamid with every compound described in Table 1 at 15% in weight in order to study this effect. Blends were made by melt mixing of the pure components since this is the most fast and versatile way of blending. In all cases a unique glass transition, $T_g$, lower than that of pure Trogamid was obtained, except in the PVPh case due to the higher value for pure PVPh (see Table 1). All the measured $T_g$ are shown in Table 2.

We can conclude that miscible blends have been obtained in all cases; therefore, the required compatibility with the compounds selected as potential antiplasticizers is fulfilled.

Thermal study shows the compatibility of the components of the system but not if the additive acts as an antiplasticizer. As a first test of this effect we have measured the density of the different systems. The density of Trogamid was measured in a gradient column giving a value of 1.1308 g/cm$^3$. The measured densities of pure additives ($\rho_2$) and blends ($\rho_b$) are shown in Table 3. Using the experimental densities and the van der Waals volumes calculated by the Bondi group contribution method [46], it is possible to obtain a theoretical free fractional volume ($f_{theo}$) using:

$$f_{theo} = (V_{SP} - 1.3V_W)/V_{SP} \tag{5}$$

being $V_{SP}$ and $V_w$ the specific volume and the van der Waals volume. Except fluorene and Ndiol for which extremely low $f_{theo}$ values have been predicted, all the other materials would have similar values, around of 10%. Moreover, the theoretical density $\rho_{theo}$, if blends would follow this additive rule:

$$\rho_{theo} = 0.85\rho_T + 0.15\rho_2 \tag{6}$$

where $\rho_T$ and $\rho_2$ are the densities of pure Trogamid and additive, respectively. $\rho_{theo}$ allows us to calculate the $\rho_{theo} - \rho_b$, a magnitude expressing the deviation of the experimental density from additivity. According to the data of this magnitude, the unique additive able to increase density with respect to the expected one ($\rho_{theo}$) and therefore decreasing the free volume is the polymeric one (PVPh). Fluorene and Ndiol increase significantly the free volume (decrease the density). These pure additives have low theoretical fractional free volumes values and, at the low composition of the blends, their own arrangement would be highly hindered. Consequently, these additives could contribute with an additional free volume to the blend free volume. Besides, densities of pure Ndiol and HFBA have been determined using picnometric method. The powdered nature of these two additives hinders the density measurements given large errors, so, in our opinion, the column measurements are more accurate than this second method.

Table 2
Glass transition temperature ($T_g$) of pure Trogamid and its blends with 15% of the different additives

| Additive | — | Fluorene | FDPh | Ndiol | Binaphtol | HFBA | PVPh |
|---|---|---|---|---|---|---|---|
| $T_g$ (°C) | 146 | 136 | 144 | 122 | 133 | 133 | 157 |

Table 3
Density of pure substances ($\rho_2$) and their blends with Trogamid ($\rho_b$) and deviations from the additivity rule ($\rho_{theo} - \rho_b$)

| Additive | $\rho_2$ (g/cm$^3$) | $f_{theo}$[a] | $\rho_b$ (g/cm$^3$) | $\rho_{theo} - \rho_b$ (g/cm$^3$)$10^{-3}$ |
|---|---|---|---|---|
| | 1.1308 | 0.1094 | | |
| Fluorene | 1.2893[b] | 0.0334 | 1.1350 | 19.5 |
| FDPh | 1.2596[b] | 0.1038 | 1.1486 | 1.5 |
| Ndiol | 1.40[c] | 0.0331 | 1.1581 | 13 |
| Binaphtol | 1.2791[b] | 0.1051 | 1.1512 | 1.8 |
| HFBA | 1.56[c] | 0.1126 | 1.1743 | 20 |
| PVPh | 1.16[d] | 0.1408 | 1.1430 | −7.8 |

[a] The free fractional volume calculated by Bondi.
[b] Measured in gradient column.
[c] Measured picnometrically.
[d] Provided by the manufacturer.

In this sense, the large deviation from additivity would come, at least partially, from differences in the experimental technique.

Other data directly related to the free volume can be obtained from the PALS technique: the free volume hole size as well as the density of holes. Both magnitudes would play a major role in the transport properties of the materials, being the variation of these properties the aim of further studies. Table 4 shows the mean radii of the holes in the blends and their volume ($V_H$), supposing spherical holes obtained from the lifetime $\tau_3$ by the Eq. (1). In the case of the Trogamid (T)/PVPh blend, it would be interesting to determine also the value for pure PVPh, but its powdered nature impeded the preparation of appropriate films.

In Table 4, we can observe that the hole size decreases in all the blends except in the T/HFBA one. The HFBA additive seems to act as a classical plasticizer because it produces an increase of $V_H$ and a reduction of the density. In the other blends, while the addition of fluorene hardly affects de $V_H$, the smallest hole size is obtained in the blend of T/Ndiol with a reduction of 10%. In the blends with Binaphtol, FDPh and PVPh the hole size decreased with respect to the pure polyamide in a minor quantity (around 4%). If we observe the chemical structures of these additives, less grade of freedom the molecule has, better antiplasticizer is. However, fluorene, though being a quite rigid structure, do not act as antiplasticizer nor plasticizer possibly due to its apolar nature, which does not promote interactions with the polymer. In conclusion, the presences of hydroxyl groups as well as the rigidity of the molecules are the most important conditions for getting antiplasticization in Trogamid. Turning to HFBA, although it fulfils these conditions, its plasticizer character would be related to the fact that the larger volume of fluoride atoms and the high mobility associated to isopropylidene bridge could hinder to fill the holes of the polymer.

Table 4
Mean radii ($R$) and mean hole volume ($V_H$) of Trogamid and its blends

| Sample | Radius (Å) | $V_H$ (Å$^3$) |
|---|---|---|
| Trogamid (T) | 2.69 | 81.4 |
| T/fluorene | 2.69 | 81.2 |
| T/FDPh | 2.65 | 78.0 |
| T/Ndiol | 2.60 | 73.9 |
| T/binaphtol | 2.65 | 77.6 |
| T/HFBA | 2.72 | 84.7 |
| T/PVPh | 2.67 | 79.3 |

It is interesting to point out that despite the fact that density measurements seem to contradict PALS results in the T/fluorene and T/Ndiol blends, this contradiction could be explained by the fact that density is directly related to the free fractional volume ($f$) whereas the parameter given by the PALS technique is the hole size. Even if the $V_H$ remains constant or decreases, the number of holes (and therefore $f$) could vary in a different way, as we will show later.

At this stage, in order to carry out a deeper study of the Trogamid antiplasticization, we selected among the additives the more (Ndiol) and less (HFBA) efficient antiplasticizers according to previous PALS results, in order to compare their effect in both free volume and transport properties. We selected also the polymeric additive, PVPh, because of its different nature and also because despite the fact of being a large molecule and the difficulty of accommodation in the holes, it produces an appreciable decrease in both the density and the $V_H$. PVPh, thus, behaves as an antiplasticizer and, from this point of view, it could be also interesting to study the behaviour of this blend.

### 3.2. Effect of additives in the free volume of Trogamid

According to the previous paragraph, we have prepared samples with different compositions up to 25% in weight for low weight additives and in the whole range of composition in the case of PVPh, using the same methodology described for the 15% blends. First of all, thermal analysis has been carried and the determined $T_g^{\prime}$s of each blend are shown in the Fig. 1.

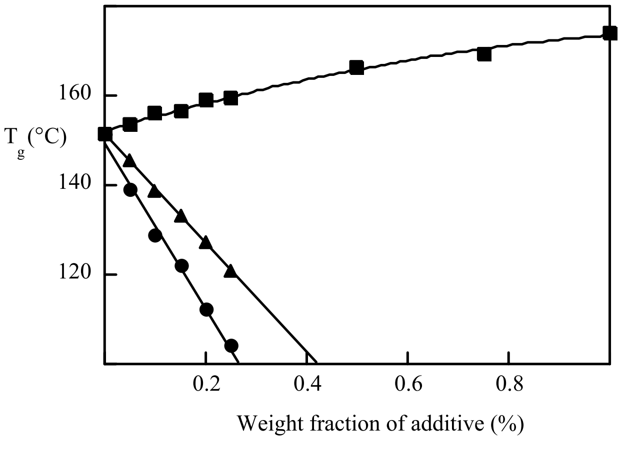


Fig. 1. Glass transition temperatures ($T_g$) of blends of Trogamid with: ● Ndiol; ▲ HFBA; ■ PVPh. Solid lines are regression lines in both Ndiol and HFBA blends and the curve fitted in the PVPh case.

In the three blends, a unique value for each composition is obtained, probing that the required compatibility is fulfilled in all cases. It can be also observed that the addition of substances of low molecular weight produces a linear decrease with composition in $T_g$, as occurs for both plasticizers and antiplasticizers. However the variation of $T_g$ with the composition of the polymeric additive is just the opposite because the $T_g$ value of the pure PVPh is higher than that of Trogamid. More interesting is its slightly curve form. In these cases, the Gordon–Taylor equation is usually applied to fit the experimental data [47]:

$$T_{g_{12}} = T_{g_1} + \frac{kw_2}{w_1}(T_{g_2} - T_{g_{12}}) \tag{7}$$

where $T_{g12}$ is the $T_g$ of the blend, $T_{gi}$ and $w_i$ are the $T_g$ of the pure components and the weight fraction, respectively, and $k$ is an adjustable parameter which fits the deviation from the additivity. The $k$ parameter has been related to the strength of the interactions between both components [48,49]; i.e. for systems where the chain mobility is impeded by the interactions values higher than 1 are usually obtained for $k$. In our case, $k$ parameter takes a value of 1.37, which reflects the strong interactions present in the T/PVPh blend, in good agreement to the values obtained for other mixtures constituted by PVPh [50].

Once the miscibility has been established, we have focused on the variation of the density of the blends, shown in Fig. 2. If antiplasticization occurs, we would expected a density of the blends higher than that of Trogamid. This is true in absolute value, but we must not forget that density of pure additives is quite higher as well. If we draw a straight line between densities of pure components of the blends, it can be seen that in the case of blends of additives of low molecular weight the densities deviate negatively from the linear dependence. Nevertheless, blends with PVPh show densities above linearity; in fact, the blend with a 75% of PVPh has a density higher than those of the pure components. Reminding that the specific volume of pure compounds or blends ($V_{SP} = 1/\rho$) can be express as:

$$V_{SP} = V_o + V_F \tag{8}$$

where $V_0$ is the volume physically occupied by atoms and $V_F$ is the free volume and taking into account that $V_0$ could be considered additive but different for each blend and composition because there was not a chemical reaction in the formation of blends, $V_F$ is the only variable that affects density. With the additives of low molecular weight the obtained density is lower than the additive one. We can consequently conclude that there was an increase in $V_F$ as a consequence of blending Trogamid with these additives. This points out that there has been plasticization instead of antiplasticization. In the PVPh blends, the density measurements indicate the opposite behaviour, then it seems that in that case there has been antiplasticization.

In order to confirm the conclusions about $V_F$, we have also completed the PALS measurements. By one hand, PALS gives us the lifetime of positronium in each blend and, from it, using the relation described in Eqs. (1) and (2), we get the mean free volume hole size ($V_H$) that we have represented in Fig. 3.

According to preliminary results (Table 4), the hole size decreases strongly in the Trogamid/Ndiol blends and, in less quantity, in the blends with PVPh. However, in the Trogamid/HFBA blends the hole size increases. As it has been mentioned above, Ndiol is a small and planar molecule with polar groups, conditions that fit the common characteristics of antiplasticizers. If these compacted molecules are able to fit inside the holes of the polymer, then we will get a reduction in $V_H$, as it is obtained experimentally. This result is not in agreement with the density increase observed for the blend Trogamid/Ndiol, but we will discuss this point later.

HFBA has also structural characteristics of antiplasticizer, but, due to its greater mobility and bulky groups, its van der Waals volume, calculated by Bondi, is greater (nearly twice) than the value of the Ndiol. Consequently, it could be hindered to go into the holes of the polymer and,

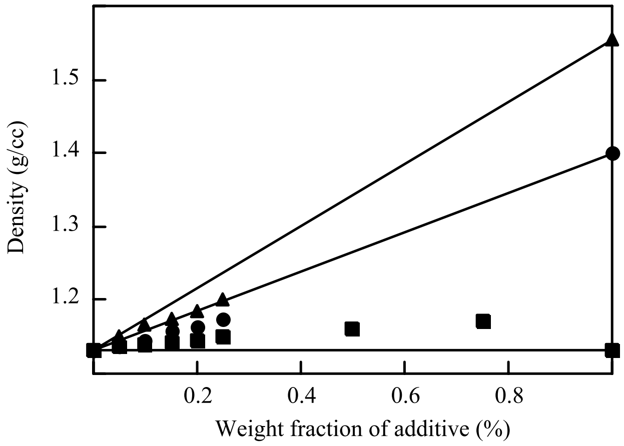


Fig. 2. Density of blends of Trogamid with: ● Ndiol; ▲ HFBA; ■ PVPh. Solid lines are straight lines between pure component densities.

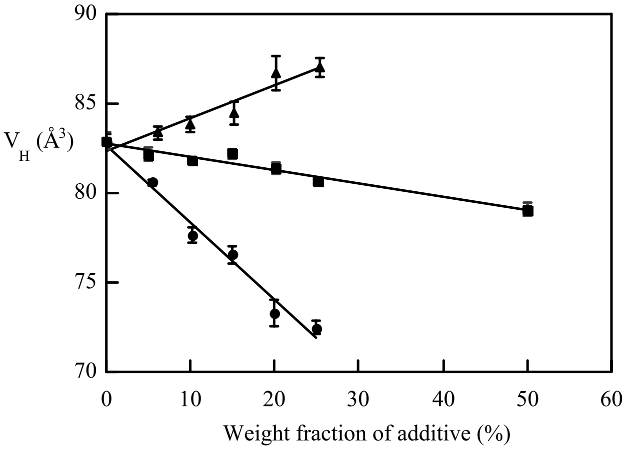


Fig. 3. Mean free volume hole size with error bars of blends of Trogamid with: ● Ndiol; ▲ HFBA; ■ PVPh. Solid lines are regression lines.

moreover, the mobility associated to isopropylidene bridge could generate greater holes. In conclusion, HFBA behaves as a plasticizer, increasing the dynamic free volume [51].

In the case of the PVPh, its hydroxyl group, which gives interactions between both materials and its planar conformation drive to decrease the blend hole volume ($V_H$). Unfortunately, the PALS measurements cannot be carried out for pure PVPh due to its powdered nature, thus, we could not affirm if this decrease also implies a negative deviation from the additivity, as occurs in the majority of miscible polymer blends [52–56].

PALS gives us additional information from intensity of $\tau_3, I_3$. In Fig. 4, the variation of $I_3$ in the three studied blends are shown. In all the cases $I_3$ increases with the additive concentration even though the behaviour for T/Ndiol case is more peculiar since it could be considered that $I_3$ takes a constant value from 10% additive fraction weight. Moreover, in the reported data for miscible polymer blends, $I_3$ has not a systematic tendency as occurs for $\tau_3$ [53,54] even though $I_3$ tends to be either an average of pure components or to have a slight negative deviation [52].

Focusing on the low weight additive mixtures, the variation of $I_3$ corresponding to HFBA agrees with the plasticization effect of this additive. By other way, reminding that $\tau_3$ is directly related to the magnitudes used in this work as mean free volume hole radius, $R$, by Eq. (1), and mean free volume hole size, $V_H$, by Eq. (2), in the case of Trogamid/Ndiol blend both $I_3$ and $\tau_3$ variations do not correspond to the different behaviour observed in the scarce polymer/additives systems reported: in some cases, when $\tau_3$ decreases comparing to pure polymer, $I_3$ also decreases [24–27]; in other case both increase [29]. Finally, we have found only one case where $I_3$ and $\tau_3$ had a similar behaviour to the T/Ndiol one, the PMMA/PEO system, where the polyethylene oxide has a relatively low molecular weight and it would take as an intermediate compound between plasticizer and polymer [54]. In that case, $I_3$ increases and $\tau_3$ decreases up to compositions of 25% in PEO. But, for higher PEO composition $I_3$ starts to decrease while $\tau_3$ increases up to take a constant value. The differences to our case are that $I_3$ takes a constant value from 10% of Ndiol and $\tau_3$ decreases monotonously even though our concentration range covers only up to 25% of Ndiol.

On other hand, in all the above-cited cases strong interactions are not expected, while they would be present in the Trogamid/Ndiol system. In such type of blends, Cowie et al. [53] have found a pronounced change in the variation of $I_3$ with composition. They quoted a ‘collapse’ of the matrix depending of the balance of hydrogen bonds, which drives to a new amorphous structure. But, in principle, this explanation is not adequate for our system because they have also observed a similar behaviour for $\tau_3$, whereas in our case, $\tau_3$ decreases monotonously with composition and $I_3$ does not show such type of behaviour.

As the holes number could play a major role than hole size ($\tau_3$) in the transport properties [57] and because, as has been cited above $I_3$ is related to the holes number, even though other variables also contributes to $I_3$, we have decided to apply Eq. (4) in order to estimate the apparent free fractional volume ($f_{app}$), assuming its uncertainty. As we can see in Fig. 5, the larger increase is found for the T/HFBA and this result is in a good agreement to the plasticization behaviour of the HBFA additive. The variation of $f_{app}$ has a more moderate rate in the Trogamid /PVPh system and, due to the decrease observed for $V_H$, it would be ascribed to a hole number increase, but the lack of the pure PVPh PALS data impede us to conclude if there is a positive or negative deviation from additivity. Anyway, the estimated hole number increase would not be enough to balance the free fractional volume reduction due to hole size decrease in order to agree the observed densification.

The most interesting behaviour is observed for the T/Ndiol system, where $f_{app}$ raises initially up to 10% Ndiol and then it decreases even though all the blends have slightly higher values than pure Trogamid. The evolution of the estimated apparent free fractional volume reveals a

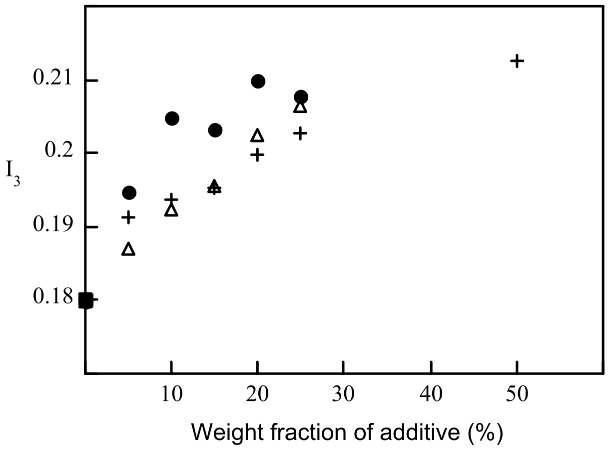


Fig. 4. The o-PS intensity, $I_3$, of blends of Trogamid with: (a) ● Ndiol; (b) △ HFBA; (c) + PVPh.

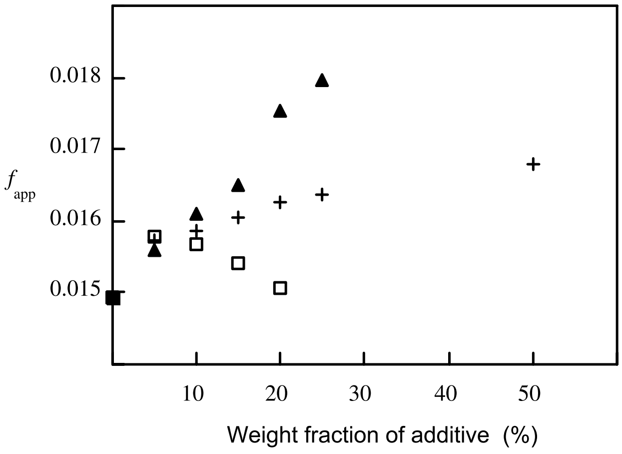


Fig. 5. Estimation of the apparent free fractional volume of blends of Trogamid with: (a) □ Ndiol; (b) ▲ HFBA; (c) + PVPh.

change of the packing of the molecules that would affect the transport properties, particularly in both the diffusion and permeability, that it must be proved in further works.

Taking into account all the data related to the free volume, we can discuss the disagreement between density and PALS measurements found in the T/Ndiol system. PALS measurements show a reduction of the free volume hole size while density shows a large positive deviation from additivity from which an increase for free volume, $V_F$, defined in Eq. (8), can be deduced. In our opinion, this disagreement could come from the fact that the density for pure Ndiol has been measured in the crystalline state and, in the low compositions used, Ndiol would have considerable difficulties to crystallize. For instance, DSC thermograms do not show melting peaks for Ndiol neither for HFBA. In this sense, the density of Ndiol in glassy state, which would be substantially lower than in the crystallised state, should be more appropriate in order to determine the additive density of the T/Ndiol blend, Eq. (6).

We have already pointed out that the free fractional volume for Ndiol calculated by Bondi radii is extremely low ($f_{theo} = 0.033$) comparing to other compounds which have values of approximately 0.10. If we take this value as representative of its glassy state, the density of Ndiol of that state would be around 1.30 g/cm$^3$. Curiously, if we fit T/Ndiol experimental densities by a straight line the pure Ndiol density would take also the same value: 1.30 g/cm$^3$. This rough estimation of the pure glassy Ndiol density would reflect that the crystalline state Ndiol has a free fractional volume extremely low or that its experimental error involved in picnometric method is so large. Unfortunately, the experimental determination of the Ndiol density in glassy state from extrapolation of liquid density data is not available, due to its high melting temperature. In the T/HFBA case, even the use of the HFBA crystalline phase density instead of glassy one in the density measurements would affect in a similar way of Ndiol, the PALS results reveal its plasticizer nature of this additive when used with Trogamid.

Another fact that could play an important role is the distribution of hole size. However, at this moment we do not dispose the required software in order to extract this information and, thus, to check this possible influence in that discrepancy.

Independently of these problems, the opposite variation of $\tau_3$ and $I_3$ for T/Ndiol and T/PVPh blends would be a good chance to test which magnitude (free hole size or number of holes) plays a major role in the transport properties. It would be also interesting to confirm the correlation between the data extracted from PALS and the transport properties, as reported for other systems [56–60]. Furthermore, changes in both $\tau_3$ and $I_3$ could affect permselectivity without decreasing permeability because the reduction of the hole size could favour the diffusion of smaller molecules besides the increase of number of holes maintain the permeability [61]. The real influence of such variation of free volume in the transport properties will be the principle aim of further studies.

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