European Polymer Journal 48 (2012) 1218–1229

Contents lists available at SciVerse ScienceDirect

European Polymer Journal

journal homepage: www.elsevier.com/locate/europolj

Influence of the organic compounds addition in the polymer free volume, gas sorption and diffusion

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ARTICLE INFO

Article history:
Received 2 December 2011
Received in revised form 29 March 2012
Accepted 24 April 2012
Available online 2 May 2012

Keywords:
Poly(hydroxyamino-ether) resin
Antiplasticizers
Free volume
Diffusion
Gas sorption

ABSTRACT

Three low molecular compounds were added to a glassy polymer, poly(amino-ether) resin, in order to change its free volume and to study the subsequent effect in transport properties. Free volume characterization was carried out using the positron annihilation lifetime spectroscopy technique. Two electrobalances were used to obtain carbon dioxide sorption kinetic. Diffusion coefficient variation is in good agreement with the additive antiplasticizer character, i.e. the reduction of the free volume fraction. However, solubility is affected by other variables too, as the balance of the interactions between penetrant, additive and polymer as well as the effect of coming closer the sorption temperature to the glass transition temperature in the sorption mode.

1. Introduction

Polymers contain lesser density domains as well as holes of molecular dimension, which arise from irregular molecular packing in the amorphous phase and molecular relaxation processes. These holes form the so-called free volume, which affects thermal, mechanical and relaxation properties, viscosity, diffusivity, among others [1,2]. In amorphous polymers, the holes form an excess free volume, as it also occurs with enthalpy, and physical ageing can be considered as an evolution from this non-equilibrium glassy state towards equilibrium. Thus, the influence of the polymer ageing in those properties has been extensively studied [3].

Addition of low molecular weight compounds into glassy polymers can usually produce similar changes in the above-mentioned properties: a glass transition temperature (T_g) decrease, but it also modifies the mechanical behavior, i.e. elastic modulus reduction as well as an impact resistance increase. However, in other cases, additive inclusion into a polymer raises the rigidity of the material. Apart of the mechanical properties, changes in other physical properties have been found such as suppression of sub-T_g relaxation processes, gas permeability decrease and gas selectivity increase [4–6]. This phenomenon, called antiplasticization, has been attributed to the reduction of the free volume due to the fact that additive molecules fill free volume holes [7,8]. Jackson and Caldwell [9] have pointed out that other effects as polymer–antiplasticizers interactions, which would originate stereo impediments hindering polymer mobility; as well as the suppression of the secondary relaxation process (sub-T_g) could also have influence in the antiplasticization effect. This behavior would also affect the diffusion process in which free volume plays an important role.

In relation to the solubility, gas isotherm in glassy polymers is usually described by dual mode [10] where the excess free volume is compiled in the Langmuir contribution. Even though more facts than changes in the free volume affect to the solubility, it could be interesting to analyse the relation between antiplasticization and solubility.

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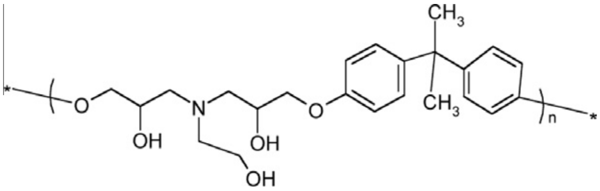
0014-3057/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.eurpolymj.2012.04.018

The antiplasticization effect depends on some characteristics of the additive such as size, shape, stiffness and its concentration in the mixture [5,6]. Furthermore, the secondary transition feature of pure polymer must be also taken into account [11,12]. In this work, we have studied a glassy polymer, namely the Poly(hydroxyamino-ether) resin (PHAE), while three low molecular weight compounds have been used as additives. PHAE could be considered as a good barrier material [13,14] but, as it will be showed later, diffusion coefficient suffers a large increase at high pressures of the penetrant. This fact could facilitate to observe more easily the antiplasticization effect on the diffusion process. In relation to the additive plasticizer-antiplasticizer nature, studies are usually based in the changes promoted in the free volume. Positron annihilation lifetime spectroscopy (PALS) has been used in order to characterize the free volume [1,2,15]. Then, carbon dioxide isotherm and diffusion coefficients have been carried out in order to relate the transport property changes to those observed in the free volume.

2. Experimental part

2.1. Materials

The polyhydroxyamino-ether resin (PHAE) was supplied by Dow Chemical. PHAE has a melt flow index (MFI) of 0.9 g/10 min, measured at 200° and with a 2.16 kg load [16]. Its chemical structure is shown below:



The additives were hydroquinone 99% (HyQ), 4,4′-(hexafluoroisopropylidene) diphenol 97% (HeFP) and 4-hydroxybenzophenone 98% (HyBP) and all of them were supplied by Aldrich and were used without further purification. Their chemical structure and melting points are compiled in Table 1.

All the blends were prepared using this procedure: first, the polymer was ground using a Retsch grinder with liquid nitrogen cooling. Then, polymer powder and additive were mixed in the appropriate weight ratio and dried under vacuum at room temperature for at least 4 days. Blending in molten state were carried out with a Minimax Molder mixer operating at 50 rpm at 230° for HeFP and at 160° for both HyQ and HyBP. The PALS samples were also obtained using the Minimax Molder. Membranes for sorption measurements and samples for PALS were prepared in a Graseby Specac hot-pressing device using molds of different thickness at the above given temperature for each blend and a pressure around 90 bar. Both Minimax Molder and hot-pressing devices were pre-heated at the desired temperature, after loading a time of 2 min was used to achieve the temperature, then devices operated during other 2 min after which samples were extruded in the case of the Minimax Molder and were cooled for 2 min before removing them in the case of the hot-pressing device. Membranes of 40–60 µm thickness were obtained and the PALS samples had at least a thickness of 1 mm. A DuoCheck ST-10 apparatus was used to determine film thickness. All the samples were kept in vacuum for at least 6 days before carrying out the corresponding measurement. Even though the glass transition temperatures in some mixtures were close to room temperature ageing behavior were not observed neither the possible loss of additives during the preparation, vacuum process and storage.

2.2. Apparatus

Glass transition temperatures, T_g, of the blends were determined in a Perkin–Elmer DSC-6 differential scanning calorimeter with a cooling water system and calibrated with an indium reference standard. All the measurements in the DSC were carried out at a heating rate of 20° min^{-1} and with approximately 8 mg of sample mass. The onset of the transition point of the heat capacity change from the second scan was chosen to determine the T_g, which are shown in Fig. 1.

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 µCu of ^{22}NaCl evaporated onto a Kapton foil, was used. The PALS experiments were carried out at 20°. More details about the procedure were described elsewhere [8]. The positron annihilation in the free-volume holes makes it possible to correlate the hole dimension with their measured lifetime. According to the model proposed by Eldrup [17], the lifetime, τ, is related to the free volume hole radius, R, by:

$$\tau_3 = 0.5\left(1 - \frac{R}{R_0} + \frac{\sin 2\pi \frac{R}{R_0}}{2\pi}\right)^{-1} \tag{1}$$

where $R_0 = R + \Delta R$ and τ is given in nanoseconds. The radius ΔR is an empirical parameter and the best value obtained fitting all known data is 1.656 Å [18]. Yu et al. have pointed out that lifetime of o-Ps can only consider as an average of the holes detected by o-PS's before their annihilation [19], as it will be assumed in this work. Anyway, the use of the Eq. (1) in order to calculate the hole size is the most usual procedure [1,2,15]. The mean free volume hole size, V_H, assuming a spherical form for the holes, may be estimated by using a simple equation:

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

The relative intensity corresponding to the annihilation lifetime in the free volume holes, I_3, is related to the number of the free volume holes. Furthermore, combining the number (I_3) and size of free volume holes (V_H), the fractional free volume (f) could be extracted by [20]:

$$f = c \cdot V_H \cdot I_3 \tag{3}$$

where c is a characteristic constant of each material, but it is difficult to know the value of c for many polymers. Moreover, there are other facts, besides the number of the free