Sorption and plasticization effects of ethanol–toluene–isooctane ternary mixtures in polyamide 6,6 and induced plasticization effects

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ABSTRACT

The equilibrium sorption of ethanol–toluene–isooctane ternary mixtures (EX) in polyamide 6,6 (PA66) films is studied. These mixtures being strongly non-ideal, the thermodynamical activity of each component must be determined in the vapor phase, so as to determine the equilibrium sorption in PA66. A GC (Gas Chromatography) analytical technique was used to quantify the composition of vapor phases at room temperature. After equilibrium sorption of PA66 films in contact with EX mixtures, the desorbing vapors were analyzed and quantified. It is found that, even though it is a non-polar solvent which is absorbed in relatively small amount in PA66, toluene has a stronger effect on the material than ethanol, relatively to its molar content. The presence of a small quantity of absorbed toluene increases ethanol sorption at a given ethanol activity. At a given molar content, the T_g drop induced by toluene is almost three times larger than that induced by ethanol. These observations indicate that toluene sorption is driven by complex molecular mechanisms and cannot be described by a mean-field picture.

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1. Introduction

In the past several years, an increasing interest on the research and development of polymeric materials intended to replace metallic alloys in the automotive industry has been observed. One can cite as an example the replacement of steel alloys in fuel tanks by a polymeric formula [1]. Polyamide 6,6 (PA66) may be a good candidate as a replacement material, thanks to its high mechanical performances and good barrier properties to toluene and isooctane, which are the main components of fuel. However, new fuel formulations, colloquially known as biofuels, are increasingly used worldwide. These fuels contain a certain quantity of ethanol. Thus, it is essential to measure and rationalize the barrier properties of PA66 to mixtures of

solvents containing ethanol in various proportions. This is a prerequisite on the way to elaborating PA66 based formulations with enhanced barrier properties. Note that the presence of water in the atmosphere may become an issue in the presence of ethanol.

Polyamides are semi-crystalline polymers possessing a crystalline, solvent-tight phase and an amorphous phase where solvent diffusion and sorption occur. The behavior and the properties of the amorphous phase have a major influence on polyamide properties, since their crystalline ratio is relatively low (35–40% in mass) compared to other polymers such as polyethylene and polypropylene [2]. Polyamides possess a physical network of amide–amide hydrogen (H) bonds in both the amorphous and the crystalline phases. The existence of this network, especially in the amorphous phase, presumably plays a major role in giving polyamides their good mechanical and thermal properties [3–8]. The effect of water on the properties of

polyamides is well documented [9–28]. In the presence of water, strong interactions between polyamide and this solvent can be formed, due to the presence of the polar amide groups along the polymer chains [9]. Indeed, it is most likely that H-bonds may be formed between water and the polyamide chains, disrupting the original interchain network and resulting in a large drop of the glass transition temperature T_g, thus modifying the polymer intrinsic properties. Indeed, a recent study of the dynamics of water absorbed in polyamides has shown that the diffusion coefficient of water is considerably reduced with respect to bulk water, which indicates strong interactions between water molecules and the polymer [29]. Also, the motion of amide–water complexes have been discriminated [29].

In a previous work, the effect of polar and non-polar solvents on the T_g of the amorphous phase of PA66 was investigated [30]. A series of polar solvents (alcohols) and various non-polar solvents (hydrocarbons) were studied. It was observed that polar solvents were absorbed in much larger amounts than non-polar solvents at sorption equilibrium. It was stated that polar solvents decreased significantly PA66 T_g by disrupting and substituting interchain H-bonds following a similar mechanism to that of water. More unexpected, it was also observed that, although non-polar solvents were absorbed in very small quantities, they induced a comparatively extremely large T_g drop, possibly because non-polar solvents might be able to modify the dynamics of PA66 interchain H-bonds through steric effects, decreasing their lifetime and thus inducing a T_g drop. This hypothesis, however, needs to be further tested.

In the same work, the sorption and desorption in PA66 films of the E10 mixture, composed of 10% ethanol, 45% toluene and 45% isooctane in volume, which models the commercial biofuel available in Europe, was assessed by Gas Chromatography equipped with a Flame Ionization Detection (GC-FID). The equilibrium sorption of these species was discussed. The obtained results were compared to data available in the literature [31–33], notably Dynamical Vapor Sorption (DVS) measurements for pure ethanol in PA66 as well as an approximate calculation of the ethanol chemical activity in the vapor phase for ethanol–toluene and ethanol–isooctane mixtures. These comparisons allowed us to observe an unexpectedly high ethanol intake in PA66 films in the presence of the E10 mixture.

In this work, we have studied the equilibrium sorption of a PA66 film put in the presence of a series of ternary ethanol–toluene–isooctane mixtures (hereafter named EX mixtures, in which X denotes the volume fraction of ethanol and in which toluene and isooctane are in equal volume fractions in the liquid mixture), at room temperature. The sorption kinetics is not discussed. To properly interpret the sorption curves, the composition of the vapor phase in equilibrium with the EX liquid mixtures must first be determined in order to determine the thermodynamical activities of each mixture components, because these mixtures are strongly non-ideal. The equilibrium sorption of each component in PA66 is measured quantitatively by Gas Chromatography (GC). Furthermore, the absorption of pure ethanol in PA66 at various activities, measured by DVS, is compared to the sorption–desorption values of samples saturated in EX mixtures (corresponding to various ethanol activities) obtained by GC-FID, relating the effects of the solvents at both the pure state and when contained in a solvent mixture. The effect of each solvent and of the mixtures on the glass transition temperature T_g of PA66 films has been measured. The very unusual, non-mean field features, of solvent sorption, specifically for a non-polar solvent (toluene), is discussed.

2. Experimental

Sixteen ethanol–toluene–isooctane (EX) mixtures with different compositions were considered. X stands for the volume fraction of ethanol in the mixture, while toluene and isooctane contents are kept in equal volume fractions (i.e. the E10 mixture contains 10 vol% ethanol, 45 vol% toluene, and 45 vol% isooctane). Analytical-grade solvents were used.

Extruded, 100 μm-thick standard-grade neat PA66 films were supplied by Rhodia/Solvay. The films were cut in 5×5 cm^2 square pieces and then dried under vacuum at 110 °C overnight. All samples were kept in air-tight envelopes after drying in order to avoid water intake prior to conditioning. Differential Scanning Calorimetry (DSC) measurements were performed with a TA Instruments Q2000 DSC on all films at 10 °C/min in order to obtain their crystalline mass fraction X_C. The heat of fusion per gram of crystal ΔH_f was taken as 188.4 J/g [11]. For all samples the crystalline ratio was found to be $X_C = 38 \pm 1\%$. To obtain the sorption at equilibrium of EX mixtures, the films were put in flasks containing one of the mixtures at room temperature (25 °C): E2.5, E5, E7.5, E10, E65, E75, E85 and E100 (pure ethanol). Gravimetric measurements were carried out at regular time intervals to measure the mass intake of the films, until the sorption equilibrium was reached. All relative mass intakes (mass fractions) Δm reported herein are referred to the total mass of PA66 samples and not to their amorphous fraction. The mass fractions were then converted in molar fractions Δn (expressed in equivalents) with respect to the number of amide groups within the amorphous phase of PA66 samples, defined according to Eq. (1):

$$\Delta n = \frac{\Delta m}{M_{solvent}} \frac{M_{PA66}}{100} \frac{1}{1 - X_C} \tag{1}$$

where $M_{solvent}$ is the molar mass of the absorbed solvent, M_{PA66} = 113 g/mol is the molar mass of PA66 per amide group (PA66 has two amide groups per monomer unit), and X_C = 38% is the crystalline mass fraction measured by DSC.

Glass transition temperatures (T_g) were measured by DSC, equipped with a liquid Nitrogen cooling system (LNCS). Even in the dry state, the T_g of PA66 is relatively hard to detect by standard DSC. Thus, the temperature-modulated mode (MDSC), which allows increasing the sensitivity and separating the glass transition process from other kinetic phenomena like solvent evaporation, was used. Dry or solvent-conditioned PA66 samples were introduced in non-hermetic aluminum pans and heated at 3 °C/min from −60 °C to 80 °C with a temperature modulation of ±2 °C each 60 s. The T_g was defined at the inflexion point