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Poly(vinyl alcohol)–poly(acrylic acid) interpenetrating networks. Study on phase separation and molecular motions

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Abstract

We report on the preparation and characterization of interpenetrating polymer networks (IPNs) composed of poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAAc) formed by a sequential method. Interpolymer interactions were examined using ^{13}C CP/MAS NMR and DSC methods. Evidence on the formation of a PVA–PAAc complex through hydrogen bonds between the hydroxyl groups of the PVA chains and the carbonyl group of the PAAc chains was obtained. The existence of polymer interactions between PVA and PAAc and its effect on the molecular motion of polymer chains, was further investigated by means of the analysis of the ^{13}C spin–lattice relaxation times in the rotating frame, $T_{1\rho}^{\mathrm{C}}$. To elucidate the scale of the mixing in the PVA/PAAc IPNs, proton spin–lattice relaxation times in the rotating frame, $T_{1\rho}^{\mathrm{H}}$, were also investigated. The analysis of the results reveals the compatibility between the PVA and the PAAc polymer networks at low PVA concentrations and the occurrence of phase separation at relatively high PVA concentrations.

Keywords: Interpenetrating networks; Polymer interactions; Miscibility

1. Introduction

Interpenetrating polymer networks (IPNs) are a combination of two or more polymer networks synthesized in juxtaposition [1]. They can also be described as polymer networks held together by permanent entanglements. The networks are held by topological bonds, essentially without covalent bonds between them. By definition, an IPN structure is obtained when at least one polymer network is synthesized independently in the immediate presence of another. IPNs are an important class of materials attracting broad interest from both fundamental and application points of view [2,3].

The fundamental phenomenon associated with all IPN's is that phase separation occurs during the reaction. The timing and the extent of phase separation are determined by the thermodynamic immiscibility changes during the course of the reaction [4]. The extent of phase separation is limited by the spatial scale over which interpenetration occurs at the onset of phase separation, and this in turn is related to the rates of polymerization in the system.

Differential scanning calorimetry (DSC) has been mostly used to study polymer miscibility. The detection of a single glass transition temperature, T_g, is generally considered as evidence of compatibility [5]. The glass transition temperatures of miscible systems lay between the T_g values of the component polymers, and may go through a maximum as a function of concentration if strong specific interactions occur between polymers [6]. It is interesting to use this general approach to study the interpenetrating character of IPNs. Solid state NMR spectroscopy has an advantage over other techniques for studying multi component polymer systems: it can be used to determine not only the level of miscibility but also the motion of the individual homopolymers [7,8]. In the past, molecular motion in polymer blends has been studied by a number of techniques, e.g. DMA, dielectric spectroscopy and DSC. However, in principle these techniques allow only to study the bulk dynamic properties or the motion of only a single component of the blend. It is demonstrated that blends classified as miscible by the aforementioned methods may also display a pronounced heterogeneity of chain motion as determined by NMR spectroscopy [9].

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The ^{13}C cross polarization and magic angle spinning (CP/MAS) NMR technique enables one to obtain information on the molecular structure of polymers. While analysis of chemical shifts proved valuable, a potentially even more potent use of solid-state NMR for polymers is the study of molecular motions. NMR relaxation behavior provides details on molecular motion of the polymer chains [10], where the motional frequency studied is determined by the choice of the experiment.

^{13}C spin–lattice relaxation times in the rotating frame ($T_{1\rho}^{C}$) can be used to analyze the motion of polymer chain segments and side chains. Interactions between polymers change the molecular motion and these changes are reflected in the relaxation times. One can take advantage of the large chemical shift dispersion of ^{13}C to resolve nuclei in different chemical environments and measure relaxation rates at each resolvable carbon because the low abundance of ^{13}C precludes averaging of relaxation rates by spin diffusion. $T_{1\rho}^{C}$ relaxation times have been extensively used to study the local dynamics in bulk polymers below T_g [11,12]. A significant example is that of polycarbonate for which $T_{1\rho}^{C}$ determinations show that there is a large distribution of motions with frequencies of a few tens of kilohertz [13]. $T_{1\rho}^{C}$ has been measured in liquid-crystalline poly(ester amides) [14] and blends of poly(vinyl phenol) with poly(methyl acrylate or methacrylate) [15], and a variable temperature study of $T_{1\rho}^{C}$ in aromatic polyamide networks and swollen gels has also appeared [16].

^{1}H spin–lattice relaxation times in the rotating frame ($T_{1\rho}^{H}$) are a very powerful tool for monitoring the phase separated domains in immiscible polymer blends [17,18]. In a homogeneous sample, all protons relax at about the same rate via spin diffusion. In a blend, when the phase separated domains are larger than 1–2 nm, different proton relaxation rates may be observed. On the opposite, if carbon resonances associated to each homopolymer component exhibit the same $T_{1\rho}^{H}$ value, then the efficiency of the spin diffusion during the few milliseconds of the spin–lattice relaxation in the rotating frame indicates that the material is homogeneous at the length scale of 1–2 nm [19]. This criterion can be readily applied to investigate the chain environments of each IPN component [20].

On the other side, PVA and PAAc can form IPNs through a sequential method. These PVA/PAAc IPNs shows drastic swelling changes by external pH and temperature according to the repulsion of ionic groups and association–dissociation of hydrogen bonds between the two polymers. The release of drugs incorporated into these IPNs exhibits pulsatile patterns in response to both pH and temperature. Also, the permeabilities of various solutes through the PVA/PAAc IPNs are regulated as a function of temperature, pH, ionic strength, solute size and ionic properties of the solutes. These characteristics make these systems very interesting as controlled drug delivery systems [21–23]. However, the interpenetrating character of the PVA/PAAc IPNs has not been determined yet.

In this work, the preparation and the miscibility and microphase structure of these IPNs have been investigated by measuring the ^{1}H spin–lattice relaxation times in the rotating frame ($T_{1\rho}^{H}$) as well as through the T_g determination. The effect of the existence of polymer interactions between PVA and PAAc on the molecular motion of the polymer chains will be determined by the interpretation of ^{13}C spin–lattice relaxation times in the rotating frame ($T_{1\rho}^{C}$).

2. Experimental section

2.1. Materials and reagents

Acrylic acid monomer (AAc) was purchased from Aldrich and was purified under vacuum distillation to eliminate hydroquinone inhibitor. *N*,*N*′-methylenbisacrylamide (*N*-BAAm) used as crosslinker and potassium persulfate used as thermal initiator were employed without further purification. Poly(vinyl alcohol), >99% hydrolyzed, with a weight average molecular weight of 94.000 g/mol and a tacticity of syndio = 17.2%, hetero = 54.1% and iso = 28.7%, from Aldrich, was used without further purification.

2.2. Preparation of PVA/PAAc IPNs

PVA/PAAc IPNs were prepared by a sequential method: PVA solutions (polymer concentrations ranging from 3 to 10% (g/mL)) were prepared in hermetic Pyrex tubes by mixing the appropriate amount of polymer and water (milli-Q grade) at 100 °C under conditions of vigorous stirring until the polymer was completely dissolved. Aqueous solutions of acrylic acid monomer, containing the thermal initiator and the crosslinking agent, were added at room temperature. The degree of crosslinking, *X*, is defined as the ratio of moles of crosslinking agent to moles of PAAc repeating units. The crosslinking degree thus achieved was 3%. The solutions were poured into glass plates, sealed with paraffin and allowed to react at 50 °C for 24 h. After this, the specimens were subjected to a freezing-thawing cycle: they were frozen to −32 °C for 15 h and then, allowed to thaw at room temperature for 5 h. In order to eliminate reactants, gels were immersed in deionized water (pure gels) and kept there until equilibrium is attained at room temperature. Films were obtained by simple drying of the ‘swollen’ hydrogels at room temperature. The composition of the IPNs is shown in Table 1.

2.3. DSC measurements

The glass transition temperature (T_g) value of various samples were measured with a Perkin–Elmer DSC7 under nitrogen purge gas using a heating rate of 20 °C/min. Indium was used as a standard for calibration. Each sample was subjected to several heating/cooling cycles to obtain