



Effect of compatibilizer on compatibility and pervaporation performance of PC/PHEMA blend membranes

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ABSTRACT

This study made use of the technique of positron annihilation spectroscopy (PALS) to examine the effect of a compatibilizer additive on the compatibility in a blend membrane of polycarbonate (PC) and poly(2-hydroxyethyl methacrylate) (PHEMA) and on the pervaporation (PV) performance of the compatibilized blend membrane. Scanning electron microscopy (SEM) showed that a blend membrane consisting of only PC and PHEMA apparently had some extent of incompatibility between the component polymers. An attempt to improve the compatibility was done by adding a graft copolymer (PC-g-PHEMA) compatibilizer. Results indicated that the addition of this compatibilizer could increase the extent of compatibility in the blend as shown by the SEM micrographs, strengthen thermal stability based on the thermal gravimetric analysis (TGA) thermograms, and effectively improve the pervaporation performance of the compatibilized blend membranes. The improvement in the compatibility, associated with better interfacial adhesion, was correlated with the microstructural properties obtained from PALS, such as ortho-positronium (o-Ps) lifetime and intensity, free volume size and distribution, and fractional free volume.

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1. Introduction

Polymer blends have improved processing characteristics as a result of integrating the properties of the constituent polymers. However, desirable blend properties depend highly on the degree of molecular interaction between the components [1], and many polymer pairs tend to form a multiphase mixture because of the thermodynamic incompatibility, resulting in poor interfacial adhesion and unstable phase morphology [2–4]. To control the phase separation in incompatible blends, either physical or chemical compatibilization is required [5–10].

Physical compatibilization consists of introducing a third component into the polymer/polymer interface. Different types of a third component have been added as a compatibilizing agent: a graft [5] and diblock [6] copolymer, random and triblock [7] copolymers, and even a homopolymer [8]. On the other hand, chemical compatibilization entails the occurrence of a reaction in the process of polymer blending, leading to the formation of an in situ compatibilizer [9,10].

Most studies on the compatibility in polymer blends involve the preparative method of melt mixing (without use of a solvent)

[3–5,7,8,11–21]; rather few researches deal with solution blending (use of a solvent to dissolve the polymers) [2,6,22,23]. These studies commonly utilize analytical and conventional techniques [1–8,11–15,22]. On a molecular level of analyzing compatibility, however, a sophisticated probe, positron annihilation lifetime spectroscopy (PALS), should be used. PALS has emerged as a powerful and straightforward technique for measuring microstructural properties such as free volumes in polymers, and it has only been used recently for investigating compatibility in polymer blends [16–21]. A positron tends to be localized in the polymer free volume, forms a positronium (Ps) by picking up an electron from the free volume wall, and annihilates in the free volume hole. This annihilation characteristic is related to the free volume size in polymers by the following semi-empirical equation.

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

where τ_3 is ortho-positronium (o-Ps) lifetime (ns), R is free volume radius (Å), and ΔR is fitted empirical electron layer thickness (1.66 Å).

An engineering polymer that frequently requires either polymer blending or grafting is polycarbonate (PC). This is to extend its performance by improving hydrophilicity and impact resistance. PC is a glassy polymer that possesses high chemical resistance and robust mechanical and thermal properties, which make it a potential

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water-selective pervaporation (PV) membrane for solvent dehydration [22]. However, in order to be applied as a PV membrane for dehydration of alcohols, PC has to undergo either surface or bulk modification. PC surface has been modified by means of grafting hydrophilic monomers, and owing to the improved hydrophilicity, the modified PC membrane performance in dehydrating alcohol solutions has been demonstrated to compare well with other PV membranes previously investigated [23,24].

PC modification by polymer blending has also been carried out, and majority of the studies on this are about melt mixing of PC and other polymers with and without a compatibilizing agent [5,8,11–15,25–27]; relatively few studies are on solution blending [2,28–30]. Limited investigations have extended their discussion to include the use of free volume information in examining the compatibility in PC blend membranes [27,30–32], and the pervaporation performance of these blend membranes is yet to be reported. Hence, the present study was conducted to analyze on a molecular level the compatibilizing action of a PC-g-PHEMA graft copolymer in a solution blend membrane of PC and a hydrophilic PHEMA, with the purpose of exploring the compatibilizer effect on the compatibility in terms of correlating the compatibilized blend membrane morphology, thermal stability, and pervaporation performance with the free volume characteristics.

2. Experimental

2.1. Materials

The PC used in this study was supplied by Sigma–Aldrich Co. Ltd., and its weight average molecular weight was 64,000 g/mole. PHEMA was purchased from Polysciences, Inc., and it had a weight average molecular weight of 200,000 g/mole. The solvents 1,2-dichloroethane (DCE) and 1-methyl-2-pyrrolidinone (NMP) and the monomer 2-hydroxyethyl methacrylate (HEMA) were obtained from Sigma–Aldrich Co. Ltd and Tedia Co., respectively. The chemical initiator benzoyl peroxide (BPO) was a product of the Fluka Co.

2.2. Preparation of blend membranes and compatibilizer

The compatibilizing agent for the blend membranes was prepared by means of a homogeneous grafting polymerization. A solution consisting of 5 g PC (as 10 wt% solution in DCE), HEMA (10–40 wt% based on PC), and BPO (5 wt% based on PC) added as a chemical initiator was contained in a reactor and degassed by purging it with nitrogen gas. The reactor was then placed in an oil bath, which was heated at 80 °C and stirred for 4 h by a combined hot-plate and magnetic-stirrer device. To precipitate the PC grafted with PHEMA and to remove any unreacted monomer and the chemical initiator, the procedure [33] was to pour the reaction mixture into an excess methanol and allow it to stand at room temperature with constant stirring for a total of 8 h. The precipitated grafted PC was filtered and vacuum dried at 80 °C for at least 8 h, and it was then subjected to Soxhlet extraction with ethanol for 48 h to remove the homopolymer. The degree of grafting was calculated according to the following equation [34]:

$$\text{Degree of grafting (\%)} = \frac{A - B}{B} \times 100$$

where *A* is the weight of the grafted PC (after Soxhlet extraction) and *B* is the weight of the PC before grafting.

The PC/compatibilizer/PHEMA blend membranes were prepared by dry casting a solution of the three polymers in an NMP solvent. The resulting blend membranes were vacuum dried at 80 °C for at least 8 h, and their thickness measured with a

Table 1

Composition of compatibilized PC/PHEMA blend membranes.

PC/PHEMA + compatibilizer ^a	PC (wt%)	Compatibilizer ^a (wt%)	PHEMA (wt%)
99.5/0.5 + 0.5 phr	99.00	0.5	0.50
95/5 + 1 phr	94.05	1.0	4.95
95/5 + 2 phr	93.10	2.0	4.90
95/5 + 5 phr	90.25	5.0	4.75
90/10 + 5 phr	85.50	5.0	9.50
85/15 + 5 phr	80.75	5.0	14.25
80/20 + 5 phr	76.00	5.0	19.00

^a PC-g-PHEMA, degree of grafting = 10.4%; phr = parts per hundred parts resin.

micrometer was in the 15–20 μm range. The composition of each compatibilized blend membrane prepared in this study is given in Table 1, where the degree of grafting (10.4%) in the compatibilizer added is the same in all the blend membranes.

2.3. Characterization of blend membranes

The chemical structure of pristine PC, graft copolymer compatibilizer, and pure PHEMA was characterized using an attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR; Perkin-Elmer Spectrum One). The blend membrane morphology was examined with a scanning electron microscope (SEM) (Hitachi, Model s4800). Prior to the SEM examination, a membrane sample was fractured in liquid nitrogen and coated with platinum. The thermal degradation temperatures of the blend membranes were measured using a Perkin-Elmer Thermal Gravimetric Analyzer, model TGA-7. The heating was conducted in an N₂ atmosphere at a rate of 10 °C/min in the 50–850 °C temperature range. To determine the surface hydrophilicity of the blend membranes, the water contact angle was estimated with an automatic interfacial tensiometer (FACE Mode 1 PD-VP).

2.4. Pervaporation (PV) performance assessment

A conventional pervaporation process [34] was used for the dehydration of a 90 wt% aqueous solution of methanol. The experiments were conducted at 25 °C. The determination of water and alcohol concentrations in the feed and permeate solutions was carried out with gas chromatography (GC, China chromatography 9800). The permeability was normalized based on the blend membrane thickness and calculated as follows: permeability = permeation rate × membrane thickness.

2.5. Positron annihilation lifetime spectroscopy (PALS)

The positron annihilation lifetimes of the blend membranes were determined by detecting the prompt γ-rays (1.28 MeV) from the nuclear decay that accompanies the emission of a positron from the ²²Na radioisotope and the subsequent annihilation of the γ-rays (0.511 MeV). A fast–fast coincidence circuit of the PAL spectrometer with a lifetime resolution of 260 ps as monitored by means of a ⁶⁰Co source was used to record all the PAL spectra. Each spectrum was collected at a fixed total count of 2 × 10⁶. All of the PAL spectra obtained were analyzed by a finite-term lifetime analysis method using the PATFIT program [35] to give the lifetime and intensity data and the MELT program [36] to obtain the free volume size distribution. In the current PAL method, we used the results of the o-Ps lifetime to determine the mean free volume radius with the use of the semi-empirical equation described in the introduction part of this paper. The free volume was calculated from $V_f = 4\pi R^3/3$, where *R* is a spherical radius. The fractional free volume (FFV) is expressed as an equation: $\text{FFV} = CV_f/l_3$, where *V_f* is the free volume calculated

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