Journal of Membrane Science 421–422 (2012) 75–84

Contents lists available at SciVerse ScienceDirect

Journal of Membrane Science

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

Assembly of nanocomposite PEBAX membranes: A complementary study of affinity and clusterization phenomena

Luana De Lorenzo [a], Elena Tocci [a,*], Annarosa Gugliuzza [a,**], Enrico Drioli [a,b]

[a] *Institute on Membrane Technology, ITM-CNR, via P. Bucci, Cubo 17/C, c/o University of Calabria, 87030 Rende (CS), Italy*
[b] *Department of Chemical Engineering and Materials, University of Calabria, 87030 Rende (CS), Italy*

ARTICLE INFO

Article history:
Received 28 October 2011
Received in revised form
18 June 2012
Accepted 22 June 2012
Available online 8 July 2012

Keywords:
PEBAX
Filler
Nanocomposite membranes
MD simulations

ABSTRACT

The behaviour of a block *co*-poly(ether/amide) 80PTMO/PA12 (PEBAX) membrane blended with an amphiphilic filler, *N*-ethyl-*o*/*p*-toluene sulphonamide (KET), was studied both experimentally and theoretically in order to identify the affinity, the miscibility and the effective distribution and arrangement of KET molecules and the mechanism controlling water interactions on different length scales, from macro to nano. Both methods have also been used to establish the role of molecular rearrangement and clusterization phenomena of modifiers in packed membranes, and to relate this to the macroscopic affinity behaviour. The compatibility between KET and PEBAX and the presence of nanoclusters of KET inside the matrix have been studied at molecular level through modelling, calorimetry and infrared spectroscopy analyses. A good miscibility has been observed up to 50 wt% of modifier content but with discrepancies when KET is at 70 wt%, confirming a saturation of hydrophilic sites of the filler, resulting in a reduced affinity of the membranes to polar penetrant. An integrated experimental–theoretical approach has provided a more detailed investigation of three-component complex systems, in which the macroscopic properties and morphologies are determined by interactions in the nano-scale range, thus resulting in a reciprocal validation and useful correlations between MD and experimental analysis.

1. Introduction

The design of new functional polymeric membranes that exhibits perm-selective properties is an important target for membrane technology [1–4]. One of the most common strategies to change and improve the performance of raw materials foresees the incorporation of suitable structural and chemical elements into the polymer matrixes in order to control structure–property relationships [5,6]. A more flexible method for achieving this goal is to blend different compounds, selected on the basis of their intrinsic chemical and morphological characteristics [7], even if miscibility and compatibility are critical issues to be considered [8]. In any case, the possibility of manipulating the membrane affinity through blending strategies appears to be a promising tool for enhancing the process efficiency, especially when the sorption selectivity is the predominant parameter in the overall transport [7]. In this respect, thermoplastic elastomers (TPE) block *co*-poly(ether/amide) is a class of attractive solubility-selective membrane materials, which finds important applications in vapour and gas separation, packaging, coatings, biomedical devices and so on [7–18]. The performances of block *co*-poly(ether/amide) 80PTMO/PA12 (PEBAX@2533, PEBAX) membranes are well known because they can be changed from highly breathable [19] to a barrier film by blending the polymer with specific organic modifiers [4,5]. At the molecular level the affinity of PEBAX blended with *N*-ethyl-*o*/*p*-toluene sulphonamide (KET) membranes to specific polar species, including water molecules, was demonstrated to be the result of 'domino processes' involving hydrogen bonding [20]. However, a deeper understanding of how the local changes in the membrane structure, owing to the presence of the filler and the modification of filler–polymer and filler–penetrate–polymer interactions, can affect the performance of the membrane is needed: therefore it is necessary to turn the observation length from macro- to nano-scale. This is because it could facilitate the selection of new advanced materials on the basis of structural models. The focus of our research was to explain why water molecules prefer to interact with membranes containing 50 wt% in the first stage of the dissolution process. The subject of this combined study was the assessment of the determining factors which control miscibility and compatibility of the systems at molecular level, i.e., the interactions among chemical modifiers, polymeric matrix and guest molecules, in relation to the modifier/membrane/penetrant

---

[*] Corresponding author. Tel.: +39 984 492038; fax: +39 984 402103.
[**] Corresponding author. Tel.: +39 984 492026; fax: +39 984 402103.
E-mail addresses: e.tocci@itm.cnr.it (E. Tocci), a.gugliuzza@itm.cnr.it (A. Gugliuzza).

0376-7388/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2012.06.050

interactions and to solubility processes. Insightful indications about the effective distribution and arrangement of KET molecules, on multiple scales, from macro down to nano, are yielded by integrating experimental findings from calorimetry and infrared spectroscopy measurements with molecular dynamics (MD) simulations. Both approaches have also been used to establish the role of molecular rearrangement and clusterization phenomena in packed membranes that appears to be more evident on the nanoscale when a large amount of modifier is used. The type and frequency of intermolecular interactions between modifier–polymer, modifier–modifier and, then, modifier–polymer–water have been also examined and discussed, while analysing length scale more in depth.

2. Experimental and simulation sections

2.1. Materials and membrane preparation

PEBAX@2533 was used to prepare flat nanocomposite isotropic membranes from alcoholic mixtures (2-propanol/n-butanol 50/50 v/v) of the polymer and N-ethyl-*o*/*p*-toluene sulphonamide (KET), ranging in concentration from 30 wt% to 70 wt%. The solutions were stirred at 70 °C in order to guarantee complete dissolution of the polymer. The clear dopes were put into Petri dishes inside a pre-equilibrated climatic chamber (T=25 °C, RH=50%) until formation of isotropic membranes. Annealing at 70 °C for a further 24 h was effective in removing possible traces of residual solvents. The membrane thickness ranged from 20 to 40 mm. The measurements were taken using a digital gauge (Carl Mhar D 7300 Esslingen a. N.) for an average of 10 measurements with a deviation of ±1.5 µm.

Table 1
Details of simulations of the PEBAX/KET amorphous cells.

System	DP	No. of atoms	No. of KET	No. of H_2O molecules	ρ sim (g/cm^3)	Cell length (Å)
PEBAX/KET I 70/30	8	5037	46	5	0.9603	37.48
PEBAX/KET II 70/30	8	5037	46	5	0.9532	37.52
PEBAX/KET III 70/30	8	5037	46	5	0.9659	37.47
PEBAX/KET I 50/50	8	6609	106	9	1.008	42.15
PEBAX/KET II 50/50	8	6609	106	9	1.0150	41.36
PEBAX/KET III 50/50	8	6609	106	9	1.0120	41.32
PEBAX/KET I 30/70	8	10,286	248	4	1.0708	48.32
PEBAX/KET II 30/70	8	10,286	248	4	1.0692	48.33
PEBAX/KET III 30/70	8	10,286	248	4	1.0715	48.29

2.2. Membrane characterization

2.2.1. SEM

The surface morphologies of PEBAX were examined by scanning electron microscopy (SEM) and optical microscope (Perkin Elmer Instruments).

2.2.2. FTIR

Infrared spectra were collected directly from the sample surface at a pixel size of 6.25 × 6.25 µm over 550 × 550 µm sampling area by using Spectrum Spotlight Chemical Imaging Instrument by Perkin Elmer. FT-IR Chemical Imaging maps were extracted by comparing the spectrum exhibiting the highest modifier content with the others. For all samples the scale was nearly unity.

2.2.3. DSC

The distribution of the materials was also studied by thermal analyses using a Diamond Pyris DSC (Perkin Elmer Instrument). In order to establish an identical thermal history, each sample, removed from the siliconised support, was cooled down to −100 °C, heated up to 200 °C at 15 °C/min, cooled again down to −100 °C and finally heated up to 200 °C at rate of 15 °C/min. In this work the second heating runs were evaluated and compared. In order to obtain an indication of the extent of the materials compatibility, the glass transition temperature (T_g) was also measured for all samples by DSC and the experimental values were compared with theoretical ones calculated by the Fox equation, traditionally used to estimate the ability of the compounds to mix [5].

$$\frac{1}{T_g} = \frac{w_a}{T_{ga}} + \frac{w_b}{T_{gb}} \tag{1}$$

where w_a and w_b are the weight fractions of components a and b, T_g is the glass transition temperature of the blend, and T_{ga} and T_{gb} are the glass transition temperatures of the components. The weighted amount of sample for each experiment was approximately 10.5 mg.

2.2.4. Hildebrand solubility parameters. To investigate the miscibility/immiscibility behaviour, the cohesive energy density and the solubility parameter as affinity indicators were calculated. The cohesive energy density (CED) is the amount of energy needed to remove completely the unit volume of molecules from their neighbours to infinite separation [21,22]. The solubility parameter (δ) is used to predict miscibility of binary solutions since the difference in the components solubility parameters is related to the enthalpy change on mixing [23]. Materials with similar solubility parameters will be able to interact with each other, resulting in solvation, miscibility or swelling [24,25]. In order to dissolve a material, these same interactions need to be overcome as

Table 2
Thermal analysis data for PEBAX/KET nanocomposite membranes.

PEBAX/KET (wt%)	T_g Onset[a] (°C)	T_g Theoretical[b] (°C)	ΔC_p (J/g °C)	T_m-PTMO[a] (°C)	ΔH Melting (J/g)	T_m-PA[a] (°C)	ΔH Melting (J/g)
0	-83.5 ± 0.8	-76 [50]	0.15 ± 0.03	8.1 ± 0.3	33.8 ± 0.4	135.2 ± 0.9	4.8 ± 0.1
30	-71.5 ± 0.2	-71.5	0.39 ± 0.06	11.8 ± 0.9	20.0 ± 1.0	114.4 ± 0.4	2.9 ± 0.5
50	-68.51 ± 0.03	-65.2	0.46 ± 0.06	10.1 ± 0.2	21.0 ± 1.0	104.7 ± 0.7	3.6 ± 0.4
70	-33.6 ± 0.4	-60.0	0.40 ± 0.08			122.0 ± 1.0	0.23 ± 0.01
100	-53.6 ± 0.1		0.45 ± 0.06			–	

[a] T_m values detected during first heating run, T_g values detected during second heating run.
[b] T_g values predicted by Fox equation.