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Miscibility of dextran and poly(ethylene glycol) in solid state: Effect of the solvent choice

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Abstract

The miscibility of dextran, Dx, and poly(ethylene glycol), PEG, have been studied in solid state by FTIR, Raman, DSC and XRD methods. In order to investigate the effect of solvent on the miscibility of Dx and PEG, their homopolymers and blends having different compositions were cast from aqueous and DMSO solutions. Following the above mentioned experimental methods, it has been seen that specific interactions causing partial miscibility exist between Dx and PEG and these interactions occur to a higher extent by choosing DMSO as the solvent, that is, the choice of solvent has a great influence on the miscibility behavior of the polymer blends.

Keywords: Dextran-poly(ethylene glycol) blends; Miscibility; Effect of solvent on polymer miscibility

1. Introduction

In search of new polymeric materials either new monomers are polymerized or co-polymerization technique is used to 'tailor make' a new product. An alternative method has been to blend existing polymers to produce materials with desired properties. An obvious advantage of this approach is that it usually requires little or no extra capital expenditure relative to new polymers. The miscibility between the constituents of a polymer mixture is an important factor in the development of new materials based on polymeric blends (Utracki, 2002). Among other factors, miscibility of polymer blends depends on the solvents used to dissolve the polymers (Miller-Chou & Koenig, 2003), that is, polymer dissolution in solvents plays an important role in polymer miscibility.

Dextran (Dx) is a naturally occurring non-toxic, biodegradable and microbial polysaccharide. Dextran and its derivatives are used as plasma expanders, blood substitutes, bone healing promoters, and also for dermal and subcutaneous augmentations (Cascone, Polacco, Lazzeri, & Barbani, 1997; Lafont et al., 1994; Prouchayret et al., 1992). Furthermore, dextran is widely under investigation as a polymeric carrier in novel drug delivery systems. Poly(ethylene glycol) (PEG) is used in almost all applications of aqueous phase partitioning. PEG is a biocompatible and biodegradable polymer and has adhesive and flocculent properties (Yılmaz, Erdenizci, & Yılmaz, 2003). For biochemical separations on the laboratory scale the most commonly used aqueous phase system is composed of Dx and PEG (Albertsson, 1986; Zaslavsky, 1995). Thus, studying molecular interactions between these two polymers is of technological importance especially for the purpose of biomedical, pharmaceutical and cosmetic applications.

In a previous study of ours, effects of temperature and composition on the miscibility of Dx and PEG were investigated in aqueous solutions by viscometry and FTIR methods (Barsbay & Güner, 2006). In this study, not only the investigation of the miscibility of Dx and PEG in solid state is aimed, but also a comparison of the results of DSC, XRD, FTIR and Raman studies of Dx/PEG blends cast from two different solvents, DMSO and water, is reported in order to investigate the effect of solvent on the miscibility.

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2. Experimental

2.1. Chemicals

Two water-soluble polymers; Poly(ethylene glycol), PEG ($M_n = 5.400$ g/mol) supplied from British Drug Houses Ltd, (BDH) and Dextran, Dx, ($M_n = 6.400$ g/mol) supplied from Pharmacia were used in this study. Dimethyl sulfoxide (DMSO), C_2H_6OS, supplied from MERCK and bidistilled and deionized water having almost zero conductivity were used as the solvents.

2.2. Preparation of solid samples

Solution of each blend sample was prepared by dissolving the required amounts of the polymers to the same concentration with our previously published study investigating the miscibility of Dx and PEG in solution, 0.8 g/dl (Barsbay & Güner, 2006). Solid samples of the blends were regenerated from their aqueous and DMSO solutions by solvent evaporation at room temperature. The obtained solids were powdered and dried at 35 °C under vacuum for three weeks.

2.3. FTIR analysis

Fourier transform infrared (FTIR) spectra of KBr pellets of the samples prepared in both solvents were taken by Mattson 1000 FTIR spectrophotometer in the 4000–400 cm^{-1} range, where 40 scans were taken at 16 cm^{-1} resolution.

2.4. Raman measurements

Raman spectra of samples were recorded using Labram 800 HR Raman spectrometer (Jobin Yvon) with a He–Ne Laser source emitting at 633 nm and a CCD charge coupled device detector.

2.5. Thermal analysis

DSC measurements were performed by means of a Universal V3.0G TA instrument at the following conditions: heating rate 5 °C min^{-1}, nitrogen flow 50 ml min^{-1}, sample mass 6.20–6.70 mg, temperature range (−100)–(250) °C.

2.6. XRD analysis

Wide-angle X-ray diffraction patterns were obtained by using a Rigaku DMAX 2200 model X-ray powder diffractometer. Each sample was measured in duplicate to ensure reproducibility.

3. Results and discussion

3.1. FTIR analysis

Fourier transform infrared (FTIR) spectroscopy has been widely used by many researchers to study the formation of blends (Wanchoo & Sharma, 2003). FTIR spectrum provides information regarding intermolecular interaction via analysis of FTIR spectra corresponding to stretching or bending vibrations of particular bonds and the positions at which these peaks appear depends directly on the force constant or bond strength. Hydrogen bonding or other secondary interactions between chemical groups on the dissimilar polymers should theoretically cause a shift in peak position of the participating groups. Hydrogen bonding interactions usually move the stretching frequencies of the participating groups e.g. O–H towards lower wavenumbers usually with increased intensity and peak broadening. The shift in peak position will depend on the strength of the interaction.

The FTIR spectra of Dx, PEG and their studied blends cast from DMSO solutions are compared to each other in Fig. 1. As can be seen in the figure, the spectra of blend samples display characteristic absorption bands of Dx and PEG. The detailed analysis of these characteristic bands and the spectra of water cast samples can be found in our previous study (Barsbay & Güner, 2006).

For the polymers studied, –O–H stretching, –C–O stretching and –O–H bending vibrations are the IR peaks of the particular interest. There are three different hydroxyl groups in Dx, and these groups take part in inter- and intramolecular hydrogen bonding. As can be followed from Fig. 1, Dx displays a broad IR peak as a result of these different OH stretching vibrations. Table 1 presents the peak maxima of –O–H stretching vibrations for the studied systems cast from both solvents. For the broad –O–H stretching vibrations, the peak maxima were taken as the values where the maximum transmittance values were observed. As can be followed in Table 1, the –O–H stretching vibration maxima of each DMSO cast blend was observed at lower wavenumbers than those of pure homopolymers. The water cast blends except for Dx/PEG (90/10) showed the same trend too. This shift towards lower wavenumbers reveals that there is a favorable interaction between Dx and PEG through the hydroxyl group of Dx and etheric oxygen of PEG as presented in Fig. 2.

Table 1 also presents the difference between the –O–H stretching vibration maxima of water and DMSO cast samples ($\Delta\nu_{\text{–OH}}$). As can be followed from $\Delta\nu_{\text{–OH}}$ values, the peak maxima of DMSO cast blends observed at lower wavenumbers by up to 65 cm^{-1} from the position of –OH absorption band of the same blend cast from water. Although this observation is also illustrated in the spectra of pure Dx and PEG (especially in Dx), this cannot account for the full difference observed for the blends. In other words, it is clear that there must be some extra interactions forming between Dx and PEG when they are blended and these interactions should be more pronounced for the DMSO cast blends.

Table 2 and Fig. 3 present one of the IR peaks of particular interest, –C–O stretching vibrations, for the studied samples cast from both solvents. As can be followed from

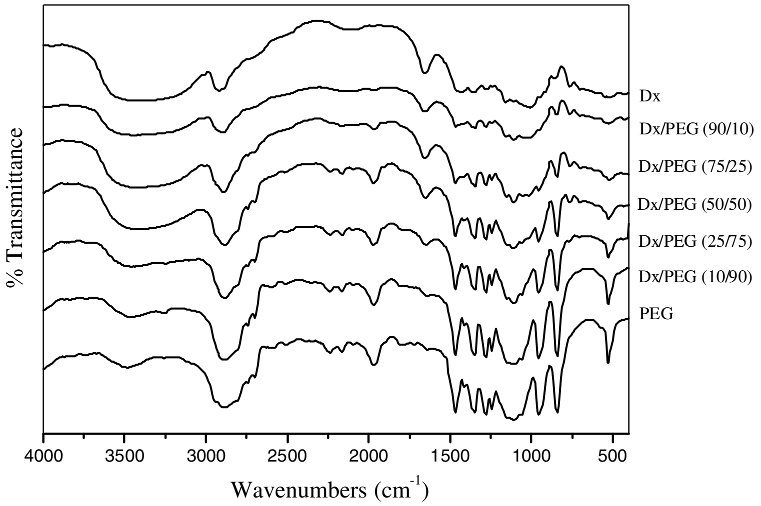

Fig. 1. FTIR spectra of studied systems cast from DMSO.

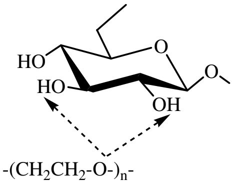

Fig. 2. Proposed hydrogen bonds between Dx and PEG.

Table 1
FTIR data for different polymer blend systems: –OH absorption frequency maxima (cm^{-1})

Polymer system	$\nu_{\text{-OH}}$ (cm^{-1}) water cast samples	$\nu_{\text{-OH}}$ (cm^{-1}) DMSO cast samples	$\Delta\nu_{\text{-OH}}$ (cm^{-1})
Dx	3522	3460	62
Dx/PEG 90/10	3518	3453	65
Dx/PEG 75/25	3486	3421	65
Dx/PEG 50/50	3480	3417	63
Dx/PEG 25/75	3461	3438	23
Dx/PEG 10/90	3465	3453	12
PEG	3490	3488	2

both Table 2 and Fig. 3, for the blends cast from DMSO there is a shift up to 8 cm^{-1} to lower wavenumbers when compared with the spectrum of pure PEG cast from the same solvent. This shift is less pronounced for the blends cast from water (2 cm^{-1}). These results support the idea that –OH groups in Dx engage in a hydrogen bonding interaction with the ether oxygen on PEG skeleton as proposed in Fig. 2 and indicate that miscibility is observed to a higher extent in DMSO cast blends.

Table 2
FTIR data for different polymer blend systems: –C–O stretching vibrations (cm^{-1})

Polymer system	$\nu_{\text{-C-O}}$ stretching water cast samples	$\nu_{\text{-C-O}}$ stretching DMSO cast samples
Dx	1160, 1107	1157, 1104
Dx/PEG 90/10	1148, 1099, 1058	1151, 1102, 1056
Dx/PEG 75/25	1148, 1099, 1058	1149, 1102, 1056
Dx/PEG 50/50	1148, 1099, 1058	1149, 1102, 1056
Dx/PEG 25/75	1148, 1099, 1058	1149, 1102, 1059
Dx/PEG 10/90	1149, 1099, 1060	1149, 1102, 1061
PEG	1149, 1100, 1060	1149, 1102, 1064

3.2. Raman analysis

The spectral features of the studied systems were also investigated by Raman spectroscopy. The Raman spectra of PEG cast from water and DMSO are presented in Fig. 4 as the representative examples among others. For the simplicity, the observed Raman shifts are summarized in Tables 3 and 4 for PEG and Dx cast from both solvents, respectively. The Raman spectra of the blend samples displayed the characteristic absorption bands of Dx and PEG. It is well known that any interaction, e.g. hydrogen bond formed between the ether oxygen of PEG and hydroxyl groups of Dx will affect the Raman shifts. For the investigation of these interactions, one of the regions of Raman spectra of particular interest is the region containing OH…O bending and CCO angle bending vibrations (Fig. 5). When the spectral behavior observed in this region was investigated for the blends cast from DMSO and water, it was easily seen that the peak maxima for DMSO cast blends were observed at higher frequencies than those observed for the water cast blends (Table 5). It is strictly expected that CCO angle bending vibrations become more difficult to occur with the formation of hydrogen bonds and hence shift to higher frequencies. Thus, the presented shifts should be caused by the formation of the proposed hydrogen bonds in Fig. 2, and again these shits support the claim that DMSO is a better solvent for the observation of a higher miscibility between the polymer pair.

In the Raman spectra, OH…O bending vibrations are observed along the 50–60 cm^{-1} frequency interval (Walrafen, 1989). During the Raman studies this band was displayed for certain blends containing higher PEG amount, e.g. Dx/PEG; (25/75) and (10/90) at a little bit above 60 cm^{-1} (Fig. 5A, B), and gave higher wavenumbers for DMSO cast samples. It is expected that OH…O bending vibrations will be more difficult with the formation of

Table 3
Characterization of Raman bands of PEG

PEG cast from water		PEG cast from DMSO		Responsive vibrations
Vibration frequency (cm^{-1})	Relative intensity	Vibration frequency (cm^{-1})	Relative intensity	
85.8	s	85.6	s	OH…O, bending (Walrafen, 1989); CCO, angle bending (Bailey & Koleske, 1976)
238.8	w	237.9	w	C–O, internal rotations (Bailey & Koleske, 1976); C–C–O, bending
283.0	s	282.5	s	C–O–C, in plane bending
365.8	w	367.7	m	C–C–O, in plane bending
538.1	w	539.6	w	C–O–C, in plane bending
588.0	w	586.4	w	CH$_2$, rocking
848.7	m	848.7	s	C–O–C, symmetric stretching
938.2	w	938.2	w	CH$_2$, rocking; C–C, stretching
1067.2[a]	w	1066.0[a]	m–w	C–O–C, asymmetric stretching
1144.6[b]	m	1143.5[b]	m	C–O–C, asymmetric stretching
1235.1	s	1235.1	s	CH$_2$, twisting
1282.8	s	1282.8	s	CH$_2$, twisting
1399.5	m–w	1399.5	m–w	CH$_2$, wagging
1482.8	s	1482.8	s	CH$_2$, scissoring

s, strong; m, medium; w, weak.

[a] Intermolecular H-bonding (Morssli et al., 1991).

[b] Intramolecular H-bonding (Morssli et al., 1991).

Table 4
Characterization of Raman bands of Dx

Dx cast from water		Dx cast from DMSO		Responsive vibrations
Vibration frequency (cm^{-1})	Relative intensity	Vibration frequency (cm^{-1})	Relative intensity	
80.6	s	80.2	s	OH…O, bending (Walrafen, 1989); CCO, angle bending (Bailey & Koleske, 1976)
232.6	w	232.0	w	C–O, internal rotations (Bailey & Koleske, 1976); C–C–O, bending
310.2	w	307.5	m	C–O–C, in plane bending
410.2	m	410.0	w	C–O–C, symmetric deformation
436.8	m	430.9	w	C–O–C, symmetric deformation
513.8	m	514.9	m	C–O–C, in plane bending
546.7	s	550.6	m	CH$_2$, rocking; C–O–C, in plane bending
771.5	w	771.0	w	C–C–O, symmetric stretching
853.0	s	859.9	m	C–O–C, symmetric stretching
923.0	s	924.3	m	CH$_2$, rocking; C–C, stretching
1083.4[a]	s	1083.4[a]	m	C–O–C, asymmetric stretching
1133.5[b]	s	1134.2[b]	s	C–O–C, asymmetric stretching
1271.6	m–w	1276.9	w	CH$_2$, twisting
1343.9	s	1350.4	m	CH$_2$, wagging
1466.1	m	1472.2	w	CH$_2$, scissoring

s, strong; m, medium; w, weak.

[a] Intermolecular H-bonding (Morssli et al., 1991).

[b] Intramolecular H-bonding (Morssli et al., 1991).

Table 5
Peak maxima for the polymer systems cast from water and DMSO (cm^{-1}): CCO angle bending

Polymer system	v (cm^{-1}) DMSO cast samples	v (cm^{-1}) water cast samples
Dx	80.2	80.6
Dx/PEG (90/10)	78.0	72.8
Dx/PEG (75/25)	80.0	80.4
Dx/PEG (50/50)	81.0	79.0
Dx/PEG (25/75)	82.3	78.5
Dx/PEG (10/90)	85.4	76.0
PEG	85.6	85.8

hydrogen bonds. This expectation is illustrated by the shift towards a higher frequency for the blends cast from DMSO. Appearance of the OH…O in plane deformation vibrations for the blends containing higher PEG amounts, e.g. Dx/PEG (25/75) and (10/90) may be an indicative of increasing miscibility with the increasing amount of PEG in the blend composition.

It is clear that C–O–C asymmetric stretching vibrations are observed at 1060–1085 cm^{-1} and the changes observed in this region are the basic proofs of the formation of hydrogen bonds (Morssli, Cassanas, & Bardet, 1991). With the formation of intermolecular hydrogen bonds, C–O–C asymmetric stretching vibrations weaken and shift to lower frequencies. As can be seen in Table 6, the peak maxima of DMSO cast blends was observed at lower frequencies when compared with those of same blends cast from water. This observation supports the above discussions.

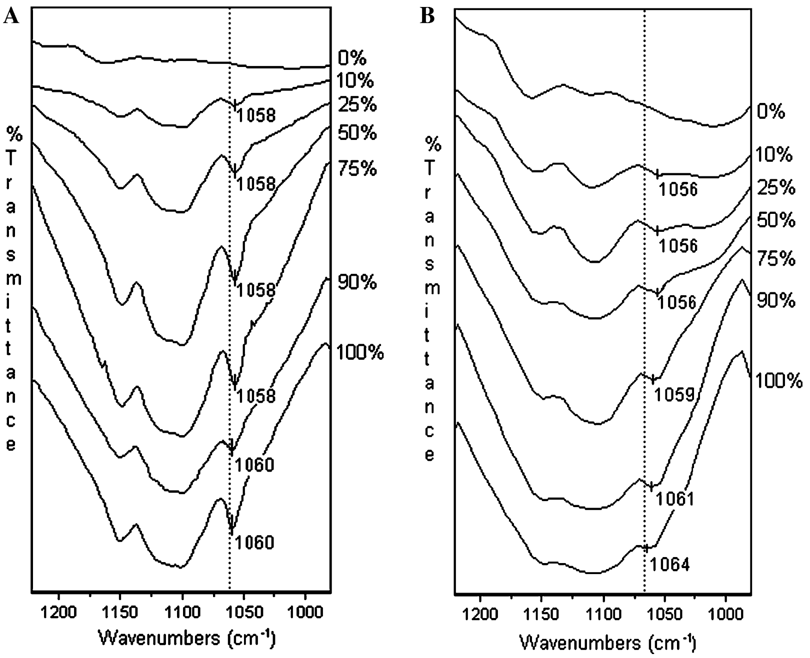

Fig. 3. Change of the IR spectra of C–O–C stretching frequencies in studied systems cast from (A) water and (B) DMSO. The percentages refer to the amount of PEG in each sample.

Table 6
Peak maxima for the polymer systems cast from water and DMSO: C–O–C asymmetric stretching; affected by intermolecular H-bonding (Morssli et al., 1991)

Polymer system	v (cm^{-1}) DMSO cast samples	v (cm^{-1}) water cast samples
Dx	1083.4	1083.4
Dx/PEG (90/10)	1076.0	1079.0
Dx/PEG (75/25)	1061.0	1061.9
Dx/PEG (50/50)	1064.4	1066.0
Dx/PEG (25/75)	1065.1	1067.7
Dx/PEG (10/90)	1065.3	1066.4
PEG	1066.0	1067.2

Table 7
Peak maxima for the systems cast from water and DMSO: C–O internal rotations

Polymer system	v (cm^{-1}) DMSO cast samples	v (cm^{-1}) water cast samples
Dx	232.0	232.6
Dx/PEG (90/10)	232.0	223.9
Dx/PEG (75/25)	233.1	224.4
Dx/PEG (50/50)	235.6	229.4
Dx/PEG (25/75)	235.8	231.5
Dx/PEG (10/90)	237.2	236.4
PEG	237.9	238.8

Table 8
Intrinsic viscosity, [η], values of studied polymers in water and DMSO at 25 °C

Polymer	[η] in water, (dl/g)	[η] in DMSO, (dl/g)
Dx	0.0844	0.1405
PEG	0.2525	0.2135

It is known that bending and rotating vibrations are hindered and shifted to higher frequencies by the formation of hydrogen bonds. Table 7 shows the peak maxima of C–O internal rotation vibrations for the blends cast from both solvents. As can be followed from the table, the values obtained for DMSO cast blends are higher than those observed for water cast blends. These results clearly accomplish the above discussions.

At this point, it would be helpful to mention the differences between two solvents used, DMSO and water, in order to understand their effects on the miscibility of the polymer pair. Table 8 presents the intrinsic viscosity, [η], values of Dx and PEG in both solvents at 25 °C. It is generally assumed that the value of intrinsic viscosity, [η], can be used as an experimental criterion of the solvent power. The larger values of [η] imply that the polymer–solvent interactions are stronger. As can be seen in Table 8, [η] value of Dx is greater in DMSO meaning that DMSO is a better solvent for Dx. On the contrary, from the [η] values it is seen that water is a stronger solvent for PEG. In a powerful solvent, macromolecules exist in a state of open swelled coil whereas in a poor solvent, they collapse into a very compact particle (Cragg & Bigdow, 1955). Considering the structures of the studied polymers, it is easily seen that Dx has a higher functionality than PEG owing to its hydroxyl groups and etheric oxygen. Thus, when these two polymers are blended, for the chains of Dx interactions with the polymer chains of their own kind via intra- or inter-segmental hydrogen bonds should be more probable than the interactions with dissimilar polymer chains, e.g. PEG. Consequently, high-dense H-bonding structure of Dx may be thought as one of the major factors preventing the miscibility between the polymer pair and this behavior of Dx makes its dissolution more important when

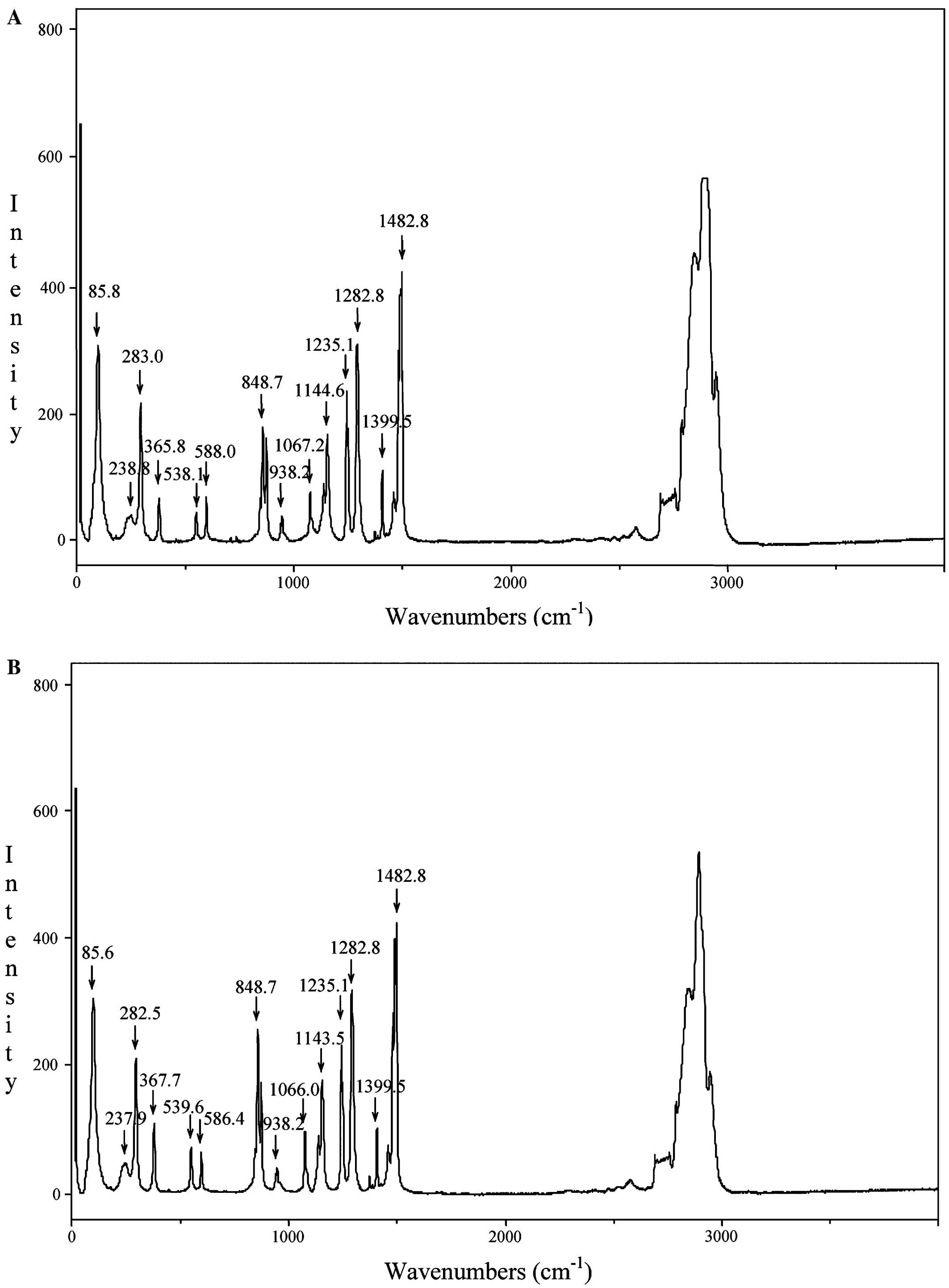

Fig. 4. Raman spectra of PEG cast from (A) water and (B) DMSO.

compared with the dissolution of PEG. More expanded Dx chains in DMSO solutions cause an increase in interaction and hence in miscibility between Dx and PEG by facilitating the diffusion of PEG into Dx. The smaller PEG chains in DMSO may also facilitate that diffusion process. The hetero-parts formed by the easier diffusion of two polymers into each other should be the reason of greater miscibility behavior observed for DMSO cast blends after the solvent evaporation.

3.3. Thermal analysis

One of the most direct experimental evidence of polymer miscibility in solid state is the occurrence of a single glass transition temperature, which is intermediate between the two T_gs corresponding to the blend components (Utracki, 2002). In miscible blends, the glass transition temperature generally depends on blend composition through a simple rule of mixing, outlined by the Fox equation (Fox, 1956).

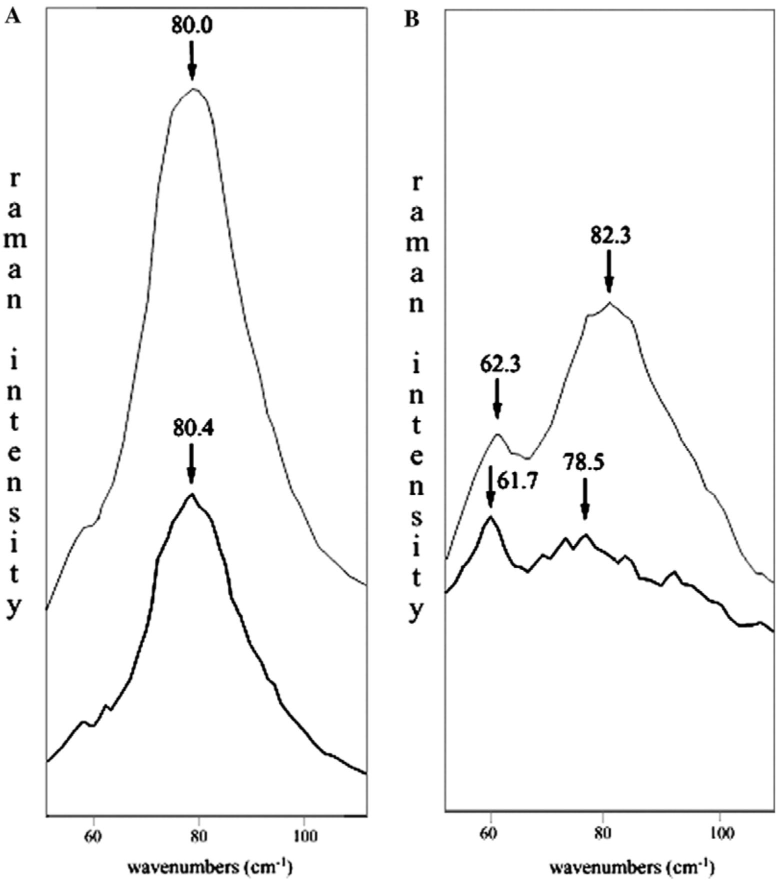

Fig. 5. Change of the Raman spectra of OH…O bending and CCO angle bending frequencies in (A) Dx/PEG (75/25), (B) Dx/PEG (25/75) blends. The upper of each pair refers to the spectra of DMSO cast blends whereas the lower refers to water cast blends.

At the other extreme, blends of immiscible polymers that segregate into distinct phases exhibit glass transitions identical in their temperature to that of the unblended components. In the intermediate cases of partial polymer miscibility or if the size of the dispersed phase is very small, the T_gs of individual components may be shifted, hindering the distinction between miscible blends and the systems of where only partial miscibility is present. Despite the fact that the thermograms of the studied blends do not provide a single T_g value, some tentative differences have been extracted after careful analysis of them with the help of other studied methods.

Fig. 6 illustrates the glass transition process of PEG for the blends studied; Dx/PEG (75/25) and (25/75) cast from both DMSO and water. Regarding the DSC data, blends exhibit a T_g value for the glass transition process of PEG at (−62)–(−65) °C interval in a good agreement with that of PEG reported in literature for −65 °C (Zheng, Huang, Li, & Guo, 1997) – this value is controversial due to some properties of the polymer such as MW. Glass transition width (ΔT_g), is defined as the difference between onset and end of the glass transition process. ΔT_g reflects the number of relaxation processes associated with the glass transition. If the system exhibits microenvironments caused by hydrogen bonding or dipole–dipole interactions, then this should undergo relaxation processes with different relaxation times, resulting in broadening of the glass transition. ΔT_g values may increase because of the heterogeneities at the molecular level (Rocco, Pereira, & Felisberti, 2001). Table 9 summaries the T_g and ΔT_g data of the studied blends for the glass transition process of PEG.

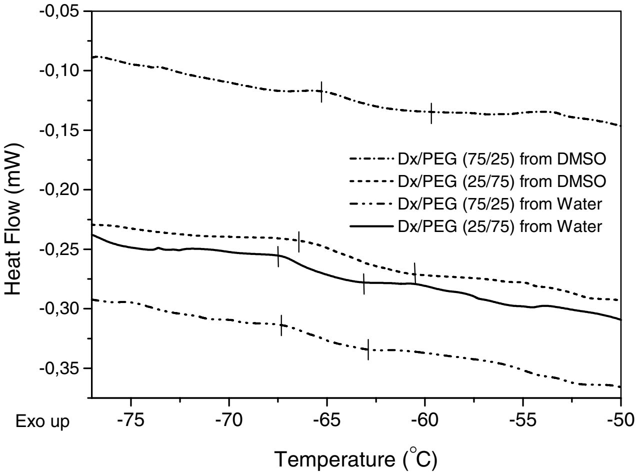

Fig. 6. Glass transition process of PEG in the studied blends.

As can be seen from Table 9, ΔT_g values of the same blends are greater for those cast from DMSO. In the studied blends there are some chain regions richer in Dx and

Table 9
T_g and ΔT_g data for the glass transition process of PEG

Blend system	$T_{g,\,PEG}$ (°C)	ΔT_g of the glass transition process of PEG
Dx/PEG (25/75) cast from water	−65.4	4.4
Dx/PEG (25/75) cast from DMSO	−63.5	6.0
Dx/PEG (75/25) cast from water	−65.2	4.5
Dx/PEG (75/25) cast from DMSO	−62.1	5.6

some regions richer in PEG. In other words, although these two polymers are not completely miscible with each other, there should be some hetero-parts formed with the diffusion of the two polymers into each other. These different chain regions should undergo different relaxation times and this would cause the broadening of the ΔT_g observed. As mentioned, Dx is more expanded in DMSO whereas PEG is less, which causes easier diffusion of the polymer pair into each other. These diffusions increase the heterogeneities at the molecular level and cause more broadened ΔT_g values in DMSO cast blend which is in good agreement with the results observed from FTIR and Raman.

In a two-phase polymer blend, an elevation in temperature of the low-T_g transition and a depression of the high-T_g transition may indicate that the system is close to miscibility. On the other hand, the coincidence of the component T_gs with those of the unblended polymers is indicative of phase separation (Feldstein, Roos, Chevallier, Creton, & Dormidontova, 2003). As can be followed from both Fig. 6 and Table 9, for the glass transition process of PEG, the T_g values of the same blends are greater for those cast from DMSO. This observation may be another evidence of the greater miscibility for the blends cast from DMSO. The T_g value for the glass transition process of Dx was observed at 143 °C for only Dx/PEG (75/25) blend cast from DMSO which is in a relatively good agreement with that of Dx reported in literature for 115 °C (Bumbu, Vasile, Chitanu, & Carpov, 2001). However, for other studied blends a definite T_g value could not be observed for the glass transition process of Dx. Thus, the change in the T_g value of Dx was not possible to investigate.

Dextran is an amorphous polymer, while PEG is capable of forming a crystalline phase (Feldstein et al., 2003; Bumbu et al., 2001). Fig. 7 shows the melting process of PEG in the studied blend systems. As illustrated in Fig. 7, DSC traces of the studied blends reveal that the melting temperature of PEG decreased with increasing Dx content. Table 10 shows this decrease more clearly. As can be followed from both Fig. 7 and Table 10, the obtained melting temperature for Dx/PEG (75/25) blend cast from one solvent gives a lower value than that obtained for Dx/PEG (25/75) blend cast from the same solvent. This indicates that less stable crystals result from increasing Dx amount which may be caused by increased miscibility in the amorphous regions. The decrease was similar for blends obtained from both DMSO and water, however blends cast from DMSO gave lower melting points throughout the composition range. The observed lower melting temperatures in DMSO-cast blends might indicate increased miscibility in the amorphous regions of these blends when compared with the water-cast blends which confirms the conclusions made up to now. Table 10 also presents the quantity of PEG melting, as indicated by the melting enthalpy. As can be seen from the table, ΔH_m value of a blend cast from DMSO is lower than that of the same blend cast from water. This decrease of crystallisable amount of PEG may be another evidence of the increase of interactions and hence miscibility in the amorphous regions when the blends are cast from DMSO.

3.4. X-ray diffraction (XRD) analysis

XRD studies have been achieved as a complimentary work of crystallinity behavior of PEG obtained from DSC measurements. X-ray diffraction patterns of studied samples cast from water and DMSO are presented in Fig. 8. From Fig. 8A, B and C which are all drawn by using the same intensity scale, it is easy to see that crystallinity decreases with decreasing PEG content for the samples cast from both solvents. This relationship is expected because the content of crystallisable polymer is decreasing. The dependence of crystallinity on solvent is very clear that PEG is more able to crystallize when the samples are cast from water. Computational XRD patterns (Fig. 8C) clearly shows the decrease of crystallinity when the samples are cast from DMSO. The decrease is illustrated for all studied samples (even in pure PEG), however, the decrease observed for pure PEG cannot account

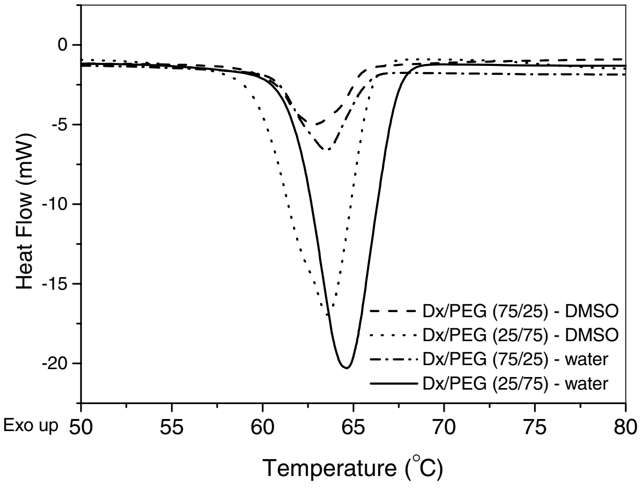

Fig. 7. Melting process of PEG in the studied blends.

Table 10
Data for the melting process of PEG in the studied blends

Blend system	$T_{m,\,PEG}$ (°C)	$\Delta H_{m,\,PEG}$ (J/g)
Dx/PEG (25/75) cast from water	64.6	132.1
Dx/PEG (25/75) cast from DMSO	63.6	117.7
Dx/PEG (75/25) cast from water	63.5	28.0
Dx/PEG (75/25) cast from DMSO	62.8	24.5

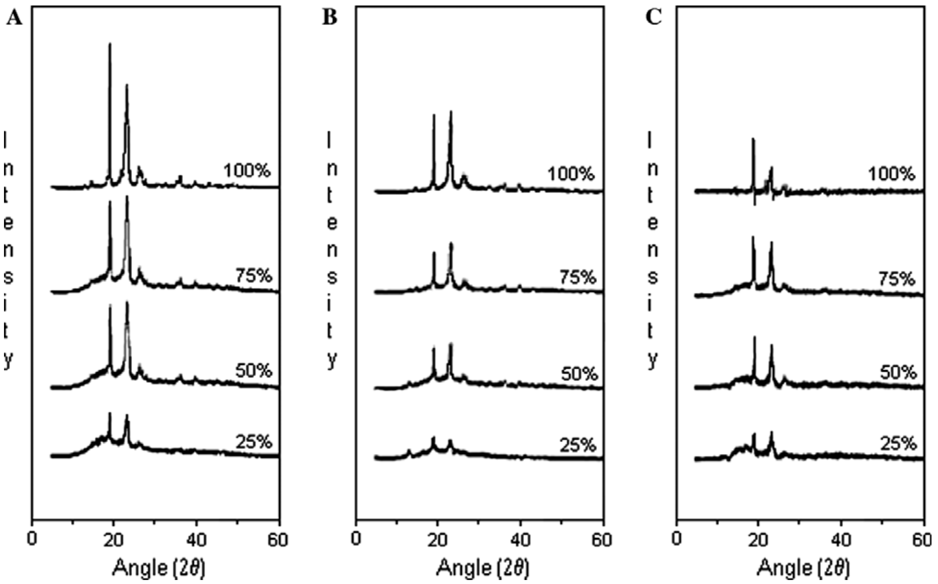

Fig. 8. XRD patterns: (A) water-cast samples; (B) DMSO-cast samples; (C) computational patterns. The percentages refer to the amount of PEG in each blend. XRD pattern of a DMSO cast blend has been subtracted from the XRD pattern of the same blend cast from water to calculate the computational patterns.

for the full difference observed for the blends. Thus, in occurrence with the results of DSC it may be concluded that Dx hinders the crystallization of PEG, to some degree, during the casting in binary blends cast from DMSO since the interactions and hence miscibility between PEG and Dx is greater in DMSO.

4. Conclusion

We have performed FTIR, Raman, DSC and XRD methods to investigate the miscibility of Dx/PEG blends. The presented investigation showed the great effect of solvent on the polymer–polymer interactions and hence on the miscibility. FTIR and Raman results clearly indicated specific interactions existing between the polymer pairs and increasing miscibility behavior observed when the blends cast from DMSO. The DSC and XRD data were in good agreement and demonstrated the differences between the samples cast from different solvents, that is, the PEG in binary blends is less able to crystallize when the samples are cast from DMSO, one of whose reasons may be the stronger interactions between PEG and Dx when the blends were cast from this solvent. The greater miscibility behavior observed for DMSO cast blends has been explained by the higher solvent power of DMSO for high-dense hydrogen bonded Dx which causes easier diffusion of PEG into Dx due to the more expanded state of the Dx chains in this solvent.

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