



A miscibility study on biodegradable poly butylene succinate/polydioxanone blends

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Abstract

Poly (butylene succinate) (PBS) and poly (dioxanone) (PDO) blends, both biodegradable semi crystalline polyester and poly (ether-ester) respectively, were prepared with the ratio of PBS/PDO ranging from 80/20 to 20/80 by the solvent evaporation method. The miscibility behavior of PBS/PDO blends in aqueous solution has been determined by dilute solution viscometry. Huggins plots of each homopolymer and polymer blend have been determined in aqueous solution at 25, 30 and 40 °C temperatures. From the data obtained from Huggins plots the miscibility parameters ΔB , α , and μ have been calculated. In addition to solution viscosity measurements, blend films were tested by SEM and FTIR analysis methods for the investigation of blend miscibility in the solid state. The results have shown that PBS/PDO blend with a blend composition of (80/20) is immiscible in solution with negative miscibility parameter values for ΔB , α , and μ respectively. SEM results indicate this immiscibility as well.

Keywords Poly (butylene succinate) · Poly (dioxanone) · Miscibility · Viscosity

Introduction

Biodegradable polymers, which have received more and more attention recently are used in wide range of applications such as tissue engineering, pharmaceutical, drug delivery, composites and membrane technologies [1–5]. Only a few works have been reported on PBS, mainly on its miscibility, crystal structure, crystallization and melting behavior [6–11]. Polymer blending is often performed in order to improve the physical properties and extend the application fields of PBS. PBS was found to be miscible with poly (vinylidene fluoride), poly(vinylidene chloride-co vinylchloride) and poly (ethylene oxide). On the other hand, PBS was found to show no miscibility with poly (hydroxybutyrate) (PHB) and poly(3-hydroxybutyrateco- hydroxyvalerate) (PHBV) [6].

Compatibility and miscibility of polymers in dilute solution is of scientific interest and technological importance since it provides evidence on thermodynamic interactions between polymers, and gives key on further industrial processing possibilities and applicability of the polymer mixtures [12].

Dilute solution viscometry is a practical and inexpensive tool to investigate polymer miscibility. Viscometric analysis of polymer-polymer miscibility in dilute solution is based upon the well-known Huggins equation, which reflects the relationship between the specific viscosity and polymer concentration [13]. This work aims at studying miscibility of poly (butylene succinate) (PBS) and poly (dioxanone) (PDO) in dilute aqueous solution by viscometry. The method is useful to examine intermolecular interactions in solution. Understanding intermolecular interactions in PBS/PDO blends would serve in designing new systems for biomedical, pharmaceutical, membrane technology and other applications.

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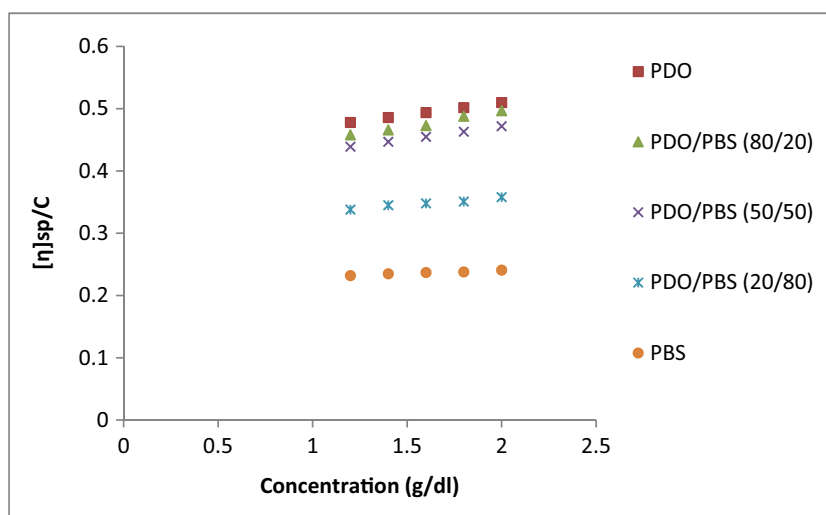
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Experimental

Material

Poly (1,4-butylene succinate) ($T_m = 120$ °C and density = 1.3 g/cm^3) extended with 1,6-diisocyanatohexane and poly

Fig. 1 Reduced viscosity vs total concentration of polymers at 25 °C



(dioxanone) ($T_m = 110$ °C and density = 1.38 g/cm³) were purchased from Sigma-Aldrich. PBS and PDO were dried in vacuum oven at 60 °C for 6 h before use. Analytical grade and high purity 1-methyl-2-pyrrolidone (NMP) was supplied from Merck and was used as the solvent.

Methods

Viscosity Measurement

Both homopolymers and polymer blends of PBS/PDO were studied by dilute solution viscometry in NMP at 25, 30 and 40 °C. Stock solutions of each binary and ternary system were prepared at room temperature by stirring the mixture for 60 min. The concentration of the stock solution of PBS/PDO was (2% w/v). Blend samples with composition of PBS/PDO (100/0, 80/20, 50/50, 20/80 and 0/100) were prepared with an initial concentration of 2% w/v. Viscosity measurements of

dilute polymer solution were carried out in a controlled thermostatic bath using an Ubbelohde capillary viscometer with a nominal viscometer constant of 0.003 mm²/s². Temperature was fixed in a thermostatic bath with thermal stability of ± 0.05 at 25, 30, 40 °C. The flow times were recorded with an accuracy of ± 0.01 s. The flow time of each solution was determined as the average of several readings.

Film Preparation

Aqueous solution of 2% (w/v) polymers was cast on a petri dish at room temperature. The solvent was allowed to evaporate in a controlled air stream for one day and the resulting thin films were further dried in vacuum at 60 °C for two days. In this way, blends were prepared with various compositions ranging from 80/20 to 20/80 in weight ratio for preparing for FTIR spectra and SEM analysis.

Fig. 2 Reduced viscosity vs total concentration of polymers at 30 °C

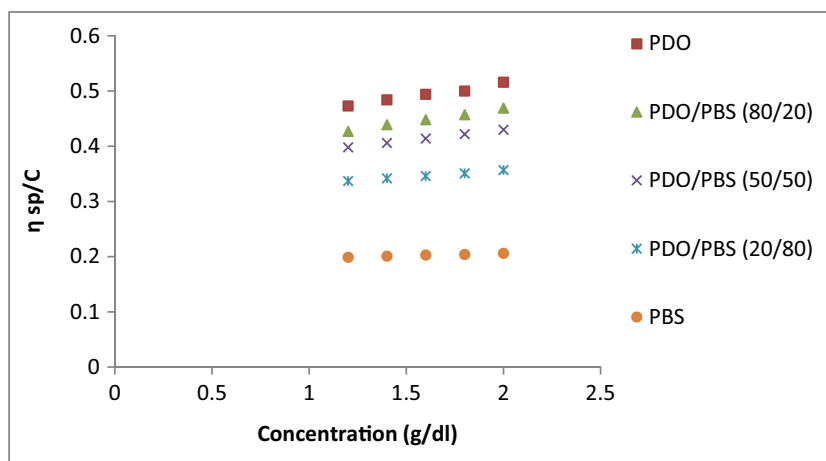
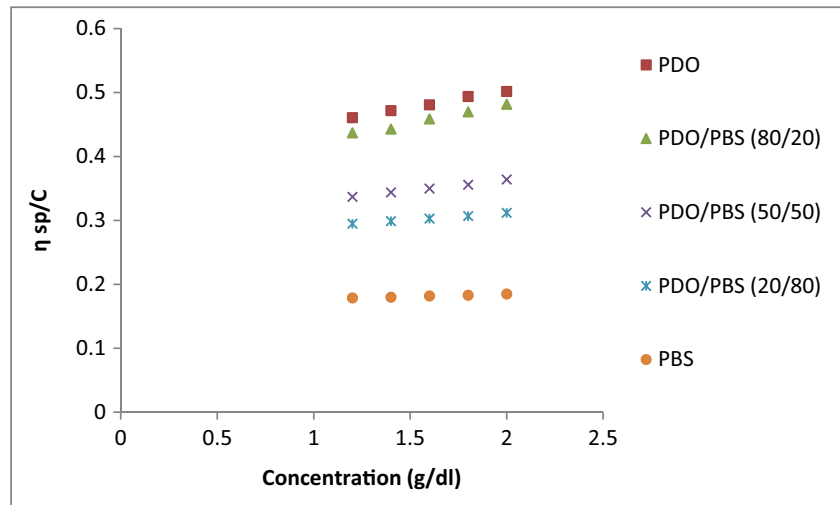


Fig. 3 Reduced viscosity vs total concentration of polymers at 40 °C



Intrinsic Viscosity and Huggins Coefficient Calculations

A classical procedure to measure concentration of the solution viscosity can be formed as Taylor expansion [14]:

$$\eta_r - 1 = \eta_{sp} = A_0 c + A_1 C^2 + A_2 C^2 + \dots \quad (1)$$

Where the coefficient $A_0 = [\eta]$, indicate intrinsic viscosity which dividing by concentration (η_{sp}/c) gives Huggins eq. A plot of (η_{sp}/C) versus concentration shows straight line and is measured by extrapolation of (η_{sp}/C) to zero concentration. The Huggins equation written by Eq. (2) [15]:

$$\frac{\eta_{sp}}{C} = [\eta] + K_H [\eta]^2 C \quad (2)$$

Where K_H is Huggins constant, dimensionless, generally ranges between 0.35 in good solvent.

and 0.5 in poor solvent. Thus $[\eta]$ obtained as intercept of linear plot.

The compatibility of polymers in solution can be analyzed accurately by viscosity techniques. Compatibility of a polymer-polymer-solvent ternary system can be estimated by measuring the intrinsic viscosity values. According to Huggins equation, η_{sp} is specific viscosity as single-solute in this equation, the plot of η_{sp}/C versus C yields linear plot

with intercept $[\eta]$ and also the slope is binary interaction between polymer segment, b , which is related to Huggins constant K_H by equation $b = k_H [\eta]^2$.

With substituting b in in Huggins equation, Eq.(3) can be obtained:

$$\frac{\eta_{sp}}{C} = [\eta] + bC \quad (3)$$

Values of b and $[\eta]$ can indicate miscibility of the polymer 1 and polymer 2. In order to estimate the miscibility or immiscibility of polymer blends, Chee proposed an ideal expression for interaction parameter ΔB and μ , when polymers are mixed in weight fractions of component w_1 and w_2 as [16]:

$$\Delta B = b - b^- / 2 \quad w_1 w_2 \quad (4)$$

According to this equation, the coefficient b and b^- given by:

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2w_1 w_2 b_{12} \quad (5)$$

$$b^- = w_1 b_{11} + w_2 b_{22} \quad (6)$$

Using these values, a more effective parameter μ can be defined as follows:

$$\mu = \frac{\Delta B}{([\eta]_1 - [\eta]_2)^2} \quad (7)$$

Table 1 Viscosity Data for PDO, PBS and PBS/PDO Blends at 25 °C

| Sample | W_{PDO} | $[\eta](dL/g)$ | b | K_H | R |
|----------------|-----------|----------------|--------|-------|------|
| PDO | 0.403 | 0.43 | 0.04 | 0.22 | 0.99 |
| PBS/PDO(20/80) | 0.302 | 0.39 | 0.05 | 0.33 | 0.98 |
| PBS/PDO(50/50) | 0.212 | 0.38 | 0.0401 | 0.28 | 0.99 |
| PBS/PDO(80/20) | 0.101 | 0.31 | 0.023 | 0.23 | 0.98 |
| PBS | 0 | 0.22 | 0.01 | 0.2 | 0.99 |

Table 2 Viscosity Data for PDO, PBS and PBS/PDO Blends at 30 °C

| Sample | W_{PDO} | $[\eta](dL/g)$ | b | K_H | R |
|----------------|-----------|----------------|-------|-------|------|
| PDO | 0.401 | 0.41 | 0.053 | 0.32 | 0.98 |
| PBS/PDO(20/80) | 0.300 | 0.36 | 0.051 | 0.39 | 0.99 |
| PBS/PDO(50/50) | 0.211 | 0.35 | 0.04 | 0.33 | 0.99 |
| PBS/PDO(80/20) | 0.10 | 0.30 | 0.024 | 0.24 | 0.99 |
| PBS | 0 | 0.18 | 0.008 | 0.23 | 0.98 |

Table 3 Viscosity Data for PDO, PBS and PBS/PDO Blends at 40 °C

| Sample | W_{PDO} | $[\eta](\text{dL/g})$ | b | K_H | R |
|----------------|------------------|-----------------------|-------|-------|------|
| PDO | 0.402 | 0.39 | 0.052 | 0.33 | 0.99 |
| PBS/PDO(20/80) | 0.303 | 0.36 | 0.058 | 0.44 | 0.98 |
| PBS/PDO(50/50) | 0.201 | 0.29 | 0.033 | 0.37 | 0.99 |
| PBS/PDO(80/20) | 0.12 | 0.27 | 0.021 | 0.28 | 0.98 |
| PBS | 0 | 0.17 | 0.007 | 0.25 | 0.98 |

Where μ is Chee's interaction parameter, $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The polymer blend is miscible while $\mu \geq 0$ and $\mu < 0$ indicate phase separation.

Sun et al. has proposed another miscibility criterion, α , for determination of polymer-polymer miscibility in the absence of strong specific interaction between

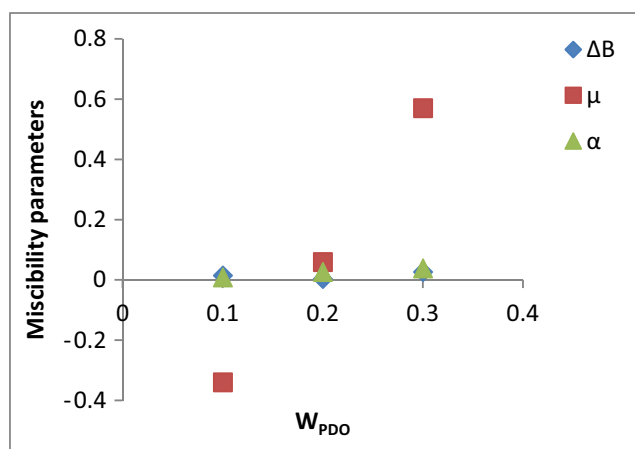
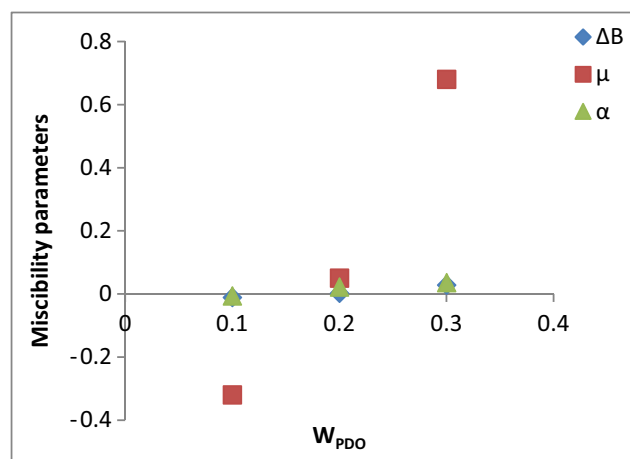
$$\alpha = K_m - \left(K_1 w_1^2 [\eta]_1^2 + K_2 w_2^2 [\eta]_2^2 + 2(K_1 K_2)^{\frac{1}{2}} [\eta]_1 [\eta]_2 w_1 w_2 \right) / ([\eta]_1 w_1 + [\eta]_2 w_2)^2 \quad (8)$$

Where K_m , K_1 and K_2 are Huggin's constant for mixture, component 1 and component 2 and α is the Sun interaction parameter, for ternary mixture (polymer 1-polymer 2-solvent).

The sign of parameter α predicts miscibility of polymer blends, when $\alpha \geq 0$ miscible. For values of $\alpha < 0$ the blend is regarded as immiscible.

For ternary systems, three types of interaction contribute to evaluation of K_m [18].

In general, if ΔB , μ , and α are positive for any polymer blend it indicates miscibility, whereas if these values are negative phase separation is presume. For coefficient α , if there

**Fig. 4** Miscibility parameter (ΔB , μ , α) vs weight fraction of PDO at 25 °C**Fig. 5** Miscibility parameter (ΔB , μ , α) vs weight fraction of PDO at 30 °C

macromolecules that cause aggregation and also in low concentration as [17]:

are attractive interaction among molecules stronger than hydrodynamic one $\alpha > 0$, on the other hand if the interactions are repulsive $\alpha < 0$ and while $\alpha = 0$ exhibit the miscibility region [16, 17].

Film characterization

Scanning electron microscopy (SEM) was used to study the morphology of prepared films. SEM images were made with a KYKY EM3200 instrument with an accelerating voltage of 26

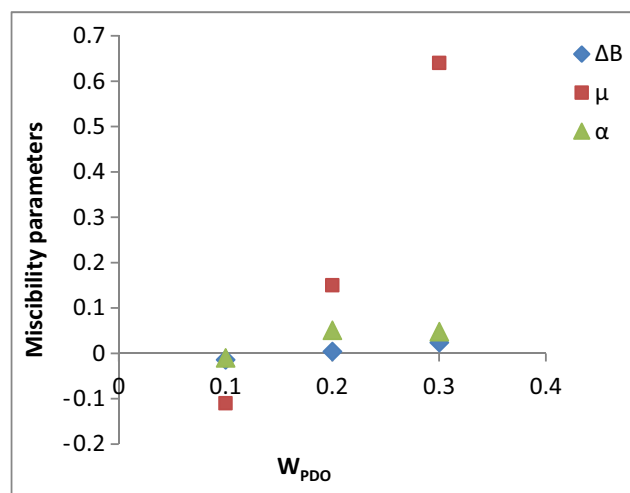
**Fig. 6** Miscibility parameter (ΔB , μ , α) vs weight fraction of PDO at 40 °C

Table 4 Miscibility Parameter for PBS/PDO Blends at 25 °C

| Blend | W_{PDO} | $\Delta B \left(\frac{\text{dl}}{\text{g}} \right)^2$ | μ | α |
|----------------|------------------|--|-------|----------|
| PBS/PDO(20/80) | 0.3 | 0.026 | 0.57 | 0.038 |
| PBS/PDO(50/50) | 0.2 | 0.003 | 0.059 | 0.026 |
| PBS/PDO(80/20) | 0.1 | -0.0145 | -0.34 | -0.0082 |

kv. The structural changes were assessed by Fourier transform infrared spectroscopy (FTIR) using a Thermo Scientific Nicolet 6700 FTIR spectrometer.

Results and discussion

The Viscosity Studies of samples

Dilute solution viscometry was carried out to find out the miscibility window for different blends of PBS/PDO of compositions (100/0, 80/20, 50/50, 20/80 and 0/100) at 25, 30 and 40 °C. Figures 1, 2 and 3 show the reduced viscosity versus total concentration at 25, 30 and 40 °C. The viscosity data for PBS, PDO and PBS/PDO blends are given in Tables 1, 2 and 3 respectively. The Huggins coefficient K_H and interaction parameter b as slope for each polymer have been calculated using the Huggins plots (η_{sp}/C) shown in Figs. 1, 2 and 3. Linear relationships are observed for pure PBS, pure PDO and for all compositions of blends. The intrinsic viscosity of PDO is greater than intrinsic viscosity of PBS. In addition, the intrinsic viscosities of both polymers and their blends decrease with increasing temperature because with increasing the temperature the resistance to flow is reduced.

As the fraction of PBS is increased in the mixture the intrinsic viscosity takes lower values. The conformations of polymers could be predicted from the Huggins coefficient K_H . The Huggins coefficient can take values in the range 0.2–0.8 for flexible polymer chains. At all temperatures studied the Huggins coefficient values of all samples have been found to be in the range 0.2–0.4 so the polymer systems studied have random coil conformations¹⁴.

As can be observed in Figs. 1, 2 and 3 reduced viscosity against concentration plots for polymer blends samples are

linear plots and the correlation coefficient, R , values are near to unity as given in tables.

It is possible to obtain useful information about polymer-solvent interactions by analyzing the data which is obtained from viscosity measurement. Usually when two polymers are mixed together their blend becomes immiscible because thermodynamically the entropy of mixing is small for macromolecules. If specific interactions between components are strong, the polymer blends depend on concentration of polymer component ratio and temperature and become miscible. When data given in Table 1, 2 and 3 are examined, it can be observed that the K_H values at all temperatures studied are around 0.2–0.3 for both PDO and PBS indicating that NMP is a good solvent for both components. PBS/PDO blends with a composition of 20/80 and 50/50 have higher K_H values at all temperatures than PDO or PBS alone in the solvent at the same temperature. These results show that there are attractive interactions between PDO and PBS at PBS/PDO (20/80) and (50/50) compositions, while at higher fractions of PBS the mixture does not exhibit any proof of favorable interactions in solution.

Miscibility of PBS/PDO Blends

Based on the experimentally observed intrinsic viscosity $[\eta]$ for ternary system, the miscibility criteria (ΔB (dl/g)², μ , α) were studied at 25, 30, 40 °C in a composition of (0.3, 0.2 and 0.1) with respect to PDO. These parameters were calculated in Figs. 4, 5 and 6 and tabulated in Tables 4, 5 and 6.

While Tables 4, 5 and 6 studied based on Figs. 4, 5 and 6, it can be observed that the miscibility parameters ΔB , α and μ reduce as the weight fraction of PBS (W_{PBS}) increases in polymer blends. When the fraction of PDO is higher in the mixture, PDO chains may act as a pseudo solvent for shorter

Table 5 Miscibility Parameter for PBS/PDO Blends at 30 °C

| Blend | W_{PDO} | $\Delta B \left(\frac{\text{dl}}{\text{g}} \right)^2$ | μ | α |
|----------------|------------------|--|-------|----------|
| PBS/PDO(20/80) | 0.303 | 0.028 | 0.68 | 0.036 |
| PBS/PDO(50/50) | 0.208 | 0.0024 | 0.056 | 0.022 |
| PBS/PDO(80/20) | 0.101 | -0.011 | -0.32 | -0.0062 |

Table 6 Miscibility Parameter for PBS/PDO Blends at 40 °C

| Blend | W_{PDO} | $\Delta B \left(\frac{dl}{g} \right)^2$ | μ | α |
|----------------|------------------|--|-------|----------|
| PBS/PDO(20/80) | 0.305 | 0.024 | 0.64 | 0.048 |
| PBS/PDO(50/50) | 0.202 | 0.004 | 0.15 | 0.051 |
| PBS/PDO(80/20) | 0.106 | -0.014 | -0.11 | -0.01 |

PBS chains since it is possible for PDO chains to entangle around PBS chains and move together in solution. However, when PBS chains have a higher fraction in the blend than PDO chains, this mechanism becomes less probable. Instead, PDO and PBS chains act independently in solution. As a result, the sign of these parameters based on Chee and Sun et al. [16, 17] method indicates the miscibility of blends, so the positive values of ΔB , μ and α in blend composition (PBS/PDO (20/80 and 50/

50)) at all temperature show us the miscibility between two polymers. However PBS/PDO (80/20) blend composition was found negative values which indicate phase separation in mixture at all temperatures. Therefore miscibility parameters show that, interactions between PDO and PBS are favored at lower weight fraction of PBS. It can also be concluded that changing the temperature has no significant effect on miscibility between PDO and PBS chains.

Fig. 7 Surface morphology of (a) neat PBS film, (b) neat PDO film, (c) PBS/PDO (20/80) blend film, (d) PBS/PDO (50/50) blend film, (e) PBS/PDO (80/20) blend film.

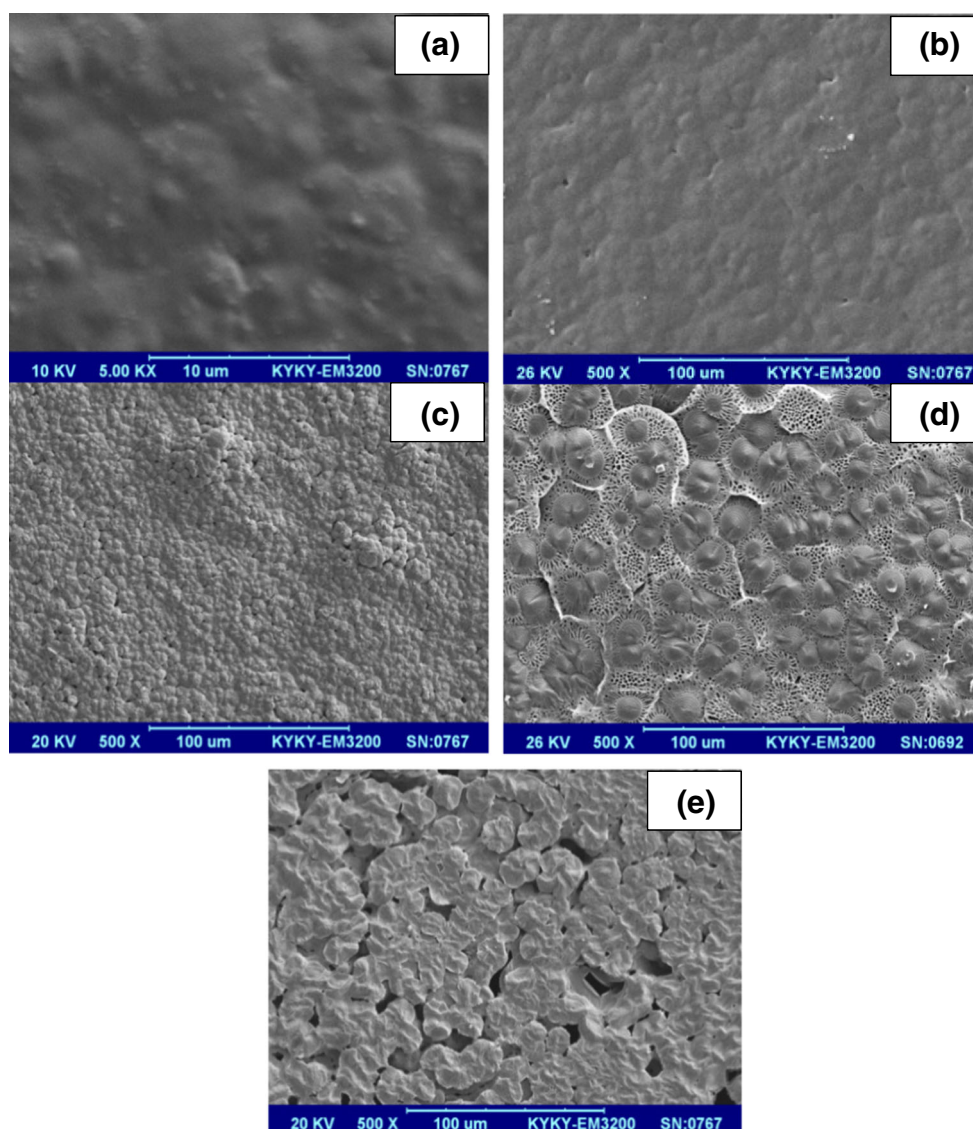
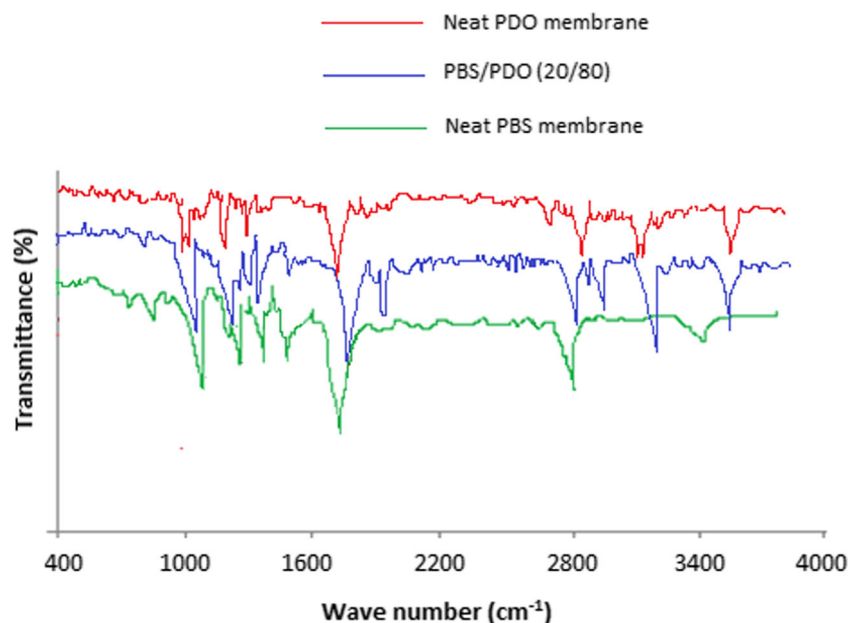


Fig. 8 FTIR spectra of the films of PBS, PDO and their blend



Film characterization

Solution-cast films of 100/0, 80/20, 50/50, 20/80 and 0/100 PBS/PDO were prepared to check the morphology of blends with scanning electron microscope (SEM). The results are given in Fig. 7.

SEM pictures show that the surfaces of pure PDO and PBS films are totally homogenous. The PBS/PDO (20/80) composition blend shows homogeneity and it can be observed that PBS was well distributed in PDO matrix, whereas (80/20) blend indicated clear phase separation; it reveals that immiscibility. It can be concluded from the SEM pictures analysis that (50/50) blend is semi-miscible due to some phase separation observed. So it can be concluded that PBS/PDO (20/80) composition blend has a good interaction between PDO and PBS.

The identification of PBS, PDO and blend (PBS/PDO (20/80)) films comes from the FTIR spectrum, as shown in Fig. 8. For miscible blends, frequency shifts usually indicate specific interactions between the characteristic groups of the pure polymers [5]. For the neat PBS film the peaks at 1750 cm^{-1} , 1156 cm^{-1} and 2925 cm^{-1} correspond on carbonyl, $\text{C}-\text{O}-\text{C}$ stretching in ester linkage and CH_2 stretching vibration, respectively. In the spectrum of PDO, the peaks at $2800\text{--}3000\text{ cm}^{-1}$ were ascribed to the C-H stretching vibration. The small peak at $3000\text{--}3600\text{ cm}^{-1}$ was observed, indicating existence of end OH from PDO macromolecular chains. Moreover, the band at 1054 cm^{-1} is due to C-O-C stretching vibration in ether linkage in PDO.

According to the spectrum of PBS/PDO (20/80) blend film, the shifts from 1750 to 1761 cm^{-1} are observed for the PBS characteristic bands. Furthermore, the shift from 1054 to 1150 cm^{-1} can be seen for the symmetric

stretching of C-O-C. These results confirm compatible of the PBS/PDO (20/80) blend film.

Conclusion

The miscibility of PBS/ PDO blends in NMP has been investigated by dilute solution viscometry and other techniques such as SEM and FTIR in the solid state. The values of miscibility parameters revealed compatibility of the system with increasing PDO fraction. PBS/PDO blend with 20/80 and 50/50 composition are miscible in solution according to positive miscibility parameter values obtained. On the other hand, PBS/ PDO (80/20) sample is immiscible according to negative values of ΔB , μ and α . It is also observed that temperature has no significant effect on the miscibility of PBS/ PDO system within the temperature range studied. Furthermore, morphology studies also reveal homogeneity in dispersion when PDO content is more than 50% in the blend. The sample with (20/80) PBS/PDO fraction is miscible while (50/50) PBS/PDO sample is semi-miscible.

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