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Research paper

Miscibility Study of Hexanoyl Chitosan/ Poly(Vinyl Chloride) Blends by Dilute Solution Viscometry and FTIR

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Abstract

Miscibility behaviour of hexanoyl chitosan and poly(vinyl chloride) (PVC) blends in different ratios was measured using dilute solution viscometry (DSV) and FTIR spectroscopy. The difference between the experimental and theoretical values of intrinsic viscosity, $\Delta[\eta]_m$ and the thermodynamic parameter, α were used to investigate the miscibility behaviour of the blends. FTIR studies suggested that there is no interaction between hexanoyl chitosan and PVC. The values of intrinsic viscosity, $\Delta[\eta]_m > 0$ and $\alpha < 0$ indicates repulsive interaction and immiscibility of polymer blend. FTIR results for hexanoyl chitosan showed no shift in frequency and no alteration in band shape as well as band inyensity with addition of PVC to the system. Both viscometric and FTIR results showed that hexanoyl chitosan and PVC are immiscible for all compositions under investigation.

Keywords: *Miscibility; hexanoyl chitosan; PVC; DSV; FTIR*

1. Introduction

Study on polymer-polymer miscibility is receiving great attention in the area of polymer science and engineering. The miscibility of polymer blends is important in the preparation of polymer blends, as the properties of polymer blends depends on the degree of miscibility of their components. There are numerous techniques to study the miscibility of polymer blends such as thermal method [1-2], morphological method [3], NMR method [4], viscometry measurement [5-6], FTIR method [7] and inverse gas chromatography [8]. Among these methods, viscometry measurement and FTIR are the simple and inexpensive techniques to study the miscibility of polymer.

The miscibility of poly(vinyl) chloride (PVC)/polyethylene oxide (PEO) blends and poly(vinyl) chloride (PVC)/ polymethylmetaclite (PMMA) blends, respectively was studied by Ramesh et al., [9]. The positive value of thermodynamic parameter, α obtained has indicates good miscibility of all investigated polymer blends. In contrast, the immiscibility of hexanoyl chitosan/polystyrene (PS) were studied by Tan winie et al., [10] using DSV method with the negative value of α indicates that the blend system were immiscible.

DSV provides information on thermodynamic interaction via changes in viscosity of blend solutions. In this work, dilute solution viscometry (DSV) and FTIR were investigated to study the miscibility of hexanoyl chitosan and PVC. The deviation between theoretical and experimental values of intrinsic viscosity, $\Delta[\eta]_m$ and the thermodynamic parameter, α are used to investigate the miscibility behaviour of hexanoyl chitosan and PVC. On the other hand, FTIR provides information on polymer-polymer interaction via changes in the intensity, shape and position of peak of the participating group.

2. Materials and methods

Hexanoyl chitosan which soluble in tetrahydrofuran (THF) was prepared by acyl modification of chitosan [11]. Poly(vinyl chloride) (PVC) with molecular weight of 2.3 x 10^5 g mol^{-1} was purchased from Aldrich. Blends of hexanoyl chitosan/PVC at (90:10), (80:20), (70:30) and (60:40) weight ratios were prepared using THF as the solvent. Viscosity measurements were carried out using Ubbelohde viscometer at 25.0± 0.1ºc. The concentration of the stock solution in THF was fixed at 0.4023 g dL^{-1}. Efflux times for each blend composition were measured by the serial dilution technique. The specific viscosities, $[\eta]_{sp}$ were then calculated from the efflux times. ATR- FTIR studies were investigated using a Thermo Fisher Scientific FTIR iS10 spectrophotometer in the range of frequency between 600 cm^{-1} and 4000 cm^{-1} at a resolution of 2 cm^{-1}.

3. Results and discussion

3.1. Dilute Solution Viscometry (DSV)

Miscibility parameters are derived from the Huggins' equation [12], which expresses the specific viscosity, η_{sp} of a single polymer solution as a function of concentration, C:

$$\frac{\eta_{sp}}{C} = [\eta] + bC \quad (1)$$

where $[\eta]$ is the intrinsic viscosity and b is related to the Huggins coefficient, k by

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$$b = k[\eta]^2 \tag{2}$$

For a polymer mixture in a common solvent, the Huggins' equation can be formulated as [12].

$$\frac{\eta_{sp.m}}{(C_{H-Chi} + C_{PVC})} = [\eta]_m + b_m(C_{H-Chi} + C_{PVC}) \tag{3}$$

where subscripts *H-Chi*, *PVC* and *m* denotes hexanoyl chitosan, PVC and their mixture, respectively. The correlation between b_m and the Huggins coefficient of the polymer mixture, k_m is given as

$$b_m = k_m[\eta]_m^2 \tag{4}$$

From the plots of η_{sp}/C vs C shown in Fig. 1, the $[\eta]_m$ are extracted by the extrapolation to infinite dilution of the plots. The values of b_m are obtained from the slope of the plots. Regression values, r^2 of the plots for blends of all compositions after equation (3) lies in the range of 0.95 to 0.99.

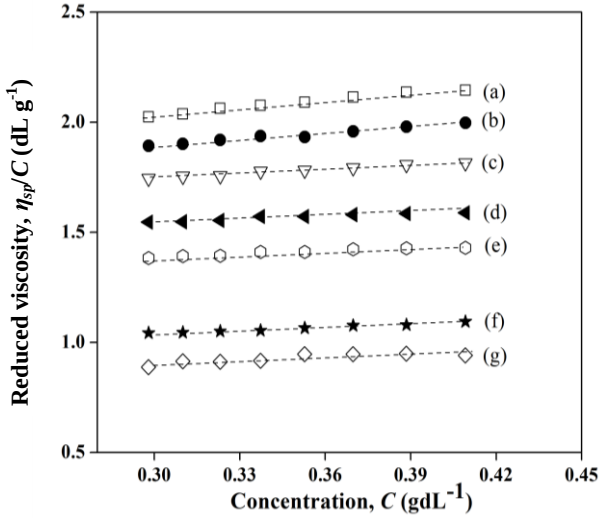

Fig. 1: The variation of reduced viscosity with concentration for hexanoyl chitosan/PVC blends at ratio of (a) 100:0, (b) 90:10, (c) 70:30, (d) 50:50, (e) 30:70, (f) 10:90 and (g) 0:100

The difference between the theoretical and experimental values of intrinsic viscosity, $\Delta[\eta]_m$ could be measured from equation (5) [13]:

$$\Delta[\eta]_m = [\eta]_m - [\eta]_m^t \tag{5}$$

The experimental values, $[\eta]_m$ are extracted from Fig. 1. The theoretical values, $[\eta]_m^t$ are:

$$[\eta]_m^t C_m = [\eta]_{H-Chi} C_{H-Chi} + [\eta]_{PVC} C_{PVC} \tag{6}$$

where,

$$C_m = C_{H-Chi} + C_{PVC} \tag{7}$$

By introducing the mass fraction of hexanoyl chitosan, $W_{H\text{-}Chi}$ and PVC, W_{PVC},

$$W_{H-Chi} = \frac{C_{H-Chi}}{C_m} \tag{8}$$

and

$$W_{PVC} = \frac{C_{PVC}}{C_m} \tag{9}$$

Hence, equation (6) can be recast as:

$$[\eta]_m^t = W_{H-Chi}[\eta]_{H-Chi} + W_{PVC}[\eta]_{PVC} \tag{10}$$

where $[\eta]_{H\text{-}Chi}$ and $[\eta]_{PVC}$ are the intrinsic viscosities of the neat polymer solutions.

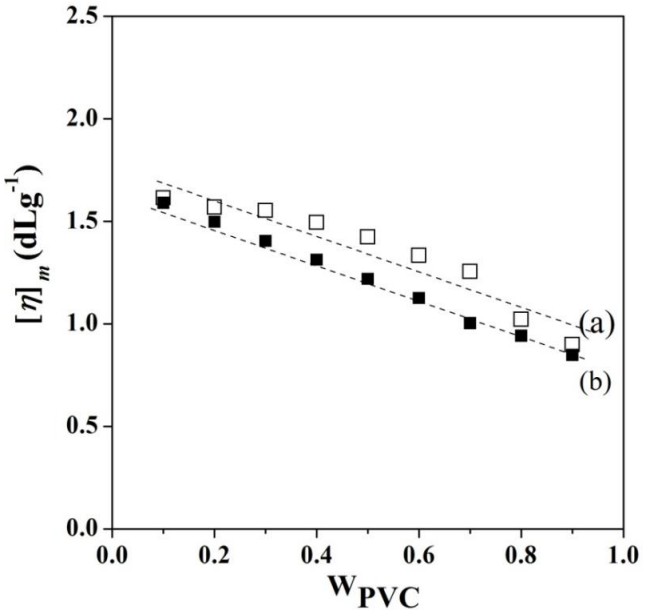

Fig. 2: The (a) intrinsic viscosity and (b) ideal viscosity dependence on weight fraction of PVC in hexanoyl chitosan-PVC blend system.

Fig. 2 shows the plot of $[\eta]_m$ as a function of mass fraction of PVC in the blends. According to Gracia et a [13], $\Delta[\eta]_m < 0$ indicates the blends is miscible and $\Delta[\eta]_m > 0$ indicates the blends is immiscible. From Fig. 2, the intrinsic viscosities for the blends of H-Chi/PVC obey linear relationship with the ideal values measured by weight additive rule using Eqn. (10). The positive deviation from additivity is observed for all compositions suggested that the immiscibility of hexanoyl chitosan and PVC blend system.

Values of $[\eta]_m$ and $[\eta]_m^t$ are tabulated in Table 1. The $[\eta]_{H\text{-}Chi}$ is higher than the $[\eta]_{PVC}$. $\Delta[\eta]_m < 0$ indicates miscible polymer blend and $\Delta[\eta]_m > 0$ indicates immiscible polymer blend. Results from Table 1 reveal the positive deviation of $\Delta[\eta]_m$ for all compositions. This suggests the immiscibility of hexanoyl chitosan and PVC.

Another miscibility criterion, the thermodynamic parameter, α was proposed by [14]. For a ternary system composed of two polymers and a solvent, three types of interaction contribute to the value of k_m.

$$k_m = k_{m1} + k_{m2} + k_{m3} \tag{11}$$

Table 1. Viscometry data for neat hexanoyl chitosan, PVC and their blends

$W_{H\text{-}Chi}$	W_{PVC}	$[\eta]_m$ (dL g^{-1})	$[\eta]_m^t$ (dL g^{-1})	b_m(dL g^{-1})^2	$\Delta[\eta]_m$	α	Remark
1.0	0.0	1.68	-	1.11	-	-	-
0.9	0.1	1.61	1.59	0.93	0.35	-0.05	immiscible
0.7	0.3	1.55	1.40	0.64	0.26	-0.18	immiscible
0.6	0.4	1.49	1.31	0.59	0.26	-0.21	immiscible
0.5	0.5	1.42	1.21	0.41	0.20	-0.31	immiscible
0.4	0.6	1.33	1.12	0.46	0.26	-0.29	immiscible
0.3	0.7	1.25	1.00	0.43	0.27	-0.32	immiscible
0.2	0.8	1.02	0.94	0.47	0.45	-0.21	immiscible
0.1	0.9	0.89	0.84	0.47	0.60	-0.16	immiscible
0.0	1.0	0.75	-	0.48	-	-	-

where k_{m1} is the long-range hydrodynamic interaction of single molecule pairs.

$$k_{m1} = \frac{\left(\sqrt{b_{H-Chi}}W_{H-Chi} + \sqrt{b_{PVC}}W_{PVC}\right)^2}{\left(W_{H-Chi}[\eta]_{H-Chi} - W_{PVC}[\eta]_{PVC}\right)^2} \quad (12)$$

k_{m2} is the formation of double molecules and aggregates. At sufficient low concentration, one may assumes no strong specific interaction forces between molecules that results in aggregation [14]. Thus, $k_{m2} = 0$. The intermolecular attraction or repulsion, $km_3 = \alpha$. Hence equation (11) can be formulated as

$$\alpha = k_m - \frac{\left(\sqrt{b_{H-Chi}}W_{H-Chi} + \sqrt{b_{PVC}}W_{PVC}\right)^2}{\left(W_{H-Chi}[\eta]_{H-Chi} - W_{PVC}[\eta]_{PVC}\right)^2} \quad (13)$$

where k_m is calculated according to Eqn. (4). $b_{H\text{-}Chi}$ and b_{PVC} are determined from the slopes of the plots of neat polymer solutions. $[\eta]_{H\text{-}Chi}$ and $[\eta]_{PVC}$ are obtained by the extrapolation to infinite dilution of the plots of neat polymer solutions.

$\alpha > 0$ indicates attractive interaction and miscibility, $\alpha < 0$ indicates immiscibility and repulsive interaction and between polymer blend. $\alpha = 0$ indicates no interaction between polymer components. Referring to Table 1, α shows negative sign for all compositions. Again, this suggests immiscibility of hexanoyl chitosan and PVC in the blends.

3.2. Fourier Transform Infra Red Spectroscopy (FTIR)

Characteristics frequencies exhibited by hexanoyl chitosan are observed at 1748 cm^{-1} (C=O of N(COR)$_2$), 1710 cm^{-1} (C=O of OCOR) and 1650 cm^{-1} (O=C-NHR) [15]. PVC exhibited the vibrational frequencies at 2967 cm^{-1} (C-H stretching of CHCl) and 2918 cm^{-1} (C-H stretching of CH$_2$) [16]. Fig. 3 shows the FTIR spectra for neat hexanoyl chitosan and blends in the wavenumber region from 1500 cm^{-1} to 2000 cm^{-1}. In the presence of PVC, the C=O of N(COR)$_2$ at 1748 cm^{-1}, C=O of OCOR at 1710 cm^{-1} and O=C-NHR at 1650 cm^{-1} for hexanoyl chitosan are observed to experience no shift in frequency and no alteration in band shape as well as band intensity.

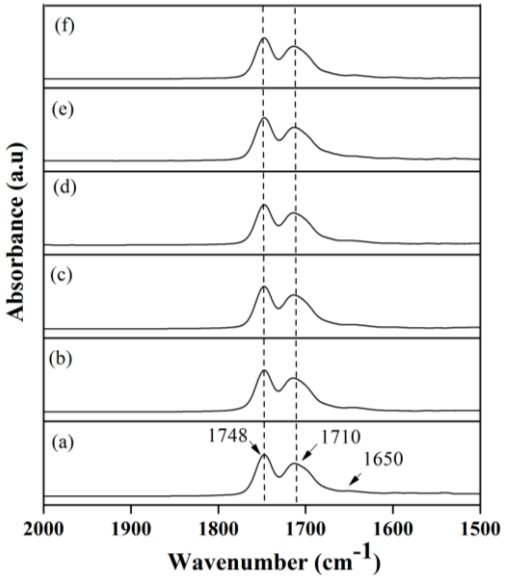

Fig. 3: Infrared spectra for hexanoyl chitosan/PVC blends at the ratio of (a) 100:0, (b) 90:10, (c) 80:20, (d) 70:30, (e) 60:40 and (f) 50:50 in the region between 1500 and 2000 cm^{-1}.

Similarly, characteristices bands of PVC remain unchanged in the presence of hexanoyl chitosan (cf. Fig. 4). This indicates the immiscibility of hexanoyl chitosan and PVC which is in good agreement with the viscometric results.

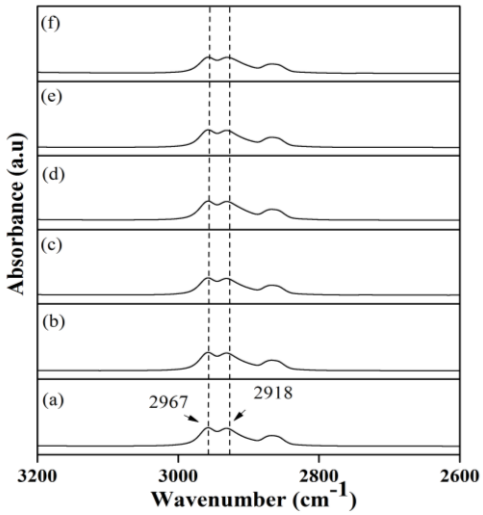

Fig. 4: Infrared spectra for hexanoyl chitosan/PVC blends at the ratio of (a) 0:100, (b) 90:10, (c) 80:20, (d) 70:30, (e) 60:40 and (f) 50:50 in the region between 2600 and 3200 cm^{-1}.

Miscibility behaviour of hexanoyl chitosan and PVC blends was investigated by DSV and FTIR. The viscometric parameter, $\Delta[\eta]_m$ and the thermodynamic parameter, α indicated that the hexanoyl chitosan/PVC blends are immiscible for all compositions of polymer blend under investigation. This is in agreement by the results from FTIR. The viscosity changes solutions are reflected in the deviation between the experimental and theoretical Huggins parameters. Thus, the difference between the experimental and theoretical values of Huggins coefficient $\Delta[\eta]_m$ and thermodynamic parameter, α are proposed to evaluate the miscibility behavior of polymer blends.

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