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Miscibility of Poly(vinylidene fluoride) and Cellulose Acetate Blends in Dimethyl Formamide

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The miscibility of poly(vinylidene fluoride) (PVDF) and cellulose acetate blends in dimethyl formamide has been investigated by viscosity, density, refractive index and ultrasonic velocity studies. The polymer-solvent and blend-solvent interaction parameters and heat of mixing have been calculated using the viscosity, density and ultrasonic velocity data. The results indicated the existence of positive interactions in the blend polymer solutions and that they are miscible in dimethyl formamide in the entire composition range between 303-323 K. The study also revealed that the variation in the temperature does not affect the miscibility of poly(vinylidene fluoride) and cellulose acetate blends in DMF significantly. The presence of hydrogen bonding in the blends in the solid state has also been indicated by FTIR studies. SEM images also supported the miscibility of blends.

Key Words: Polymer solutions, Ultrasonic velocity, Viscosity, Interaction parameter, Polymer blends, Miscibility, Cellulose acetate, Poly(vinylidene fluoride), Dimethyl formamide.

INTRODUCTION

The study of miscibility and interactions present in polymer and solvent in a polymer blend solution system is of great significance for engineering applications of polymers. They also provide substantial information on the processes involving polymer production and their uses[1,2]. Polymer blends are physical mixtures of structurally different polymers or copolymers, which interact through secondary forces with no covalent bonding which are miscible at molecular level. The basis of polymer-polymer miscibility may arise from any specific interaction, such as hydrogen bonding, dipole-dipole forces or charge transfer interactions in the system[3,4]. Polymer blend miscibility has been studied widely with a number of techniques[5-9].

A review of literature suggested that no previous studies have been done on the miscibility of poly(vinylidene fluoride) (PVDF) and cellulose acetate (CA) in dimethyl formamide (DMF). Hence as a part of our research program on polymer blends and solutions[10,11] miscibility behaviour of PVDF and CA blends in DMF is presented in this paper. The choice of the polymers is due to their pharmaceutical, biomedical and industrial applications[12,13]. Further, it may also be noted that the polymers containing polar groups with a susceptibility to act as proton donors were found to be miscible with those having a tendency to act as proton acceptors due to a specific interaction like hydrogen bonding. The structures of PVDF and cellulose acetate are shown in Fig. 1.

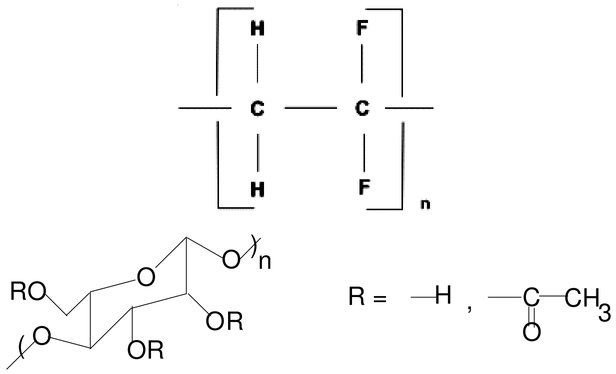

Fig. 1. Structures of poly(vinylidene fluoride) and cellulose acetate

EXPERIMENTAL

Poly(vinylidene fluoride) (molecular weight, 75000; Alfa Aesar) and cellulose acetate (molecular weight, 70000; Alfa Aesar) were used as received. DMF (Merck) was distilled before use.

Preparation of polymer solutions: Dilute solutions of 2 % (w/v) PVDF and cellulose acetate in DMF were prepared separately in different stoppered conical flasks. Solutions of lower concentrations were then prepared by appropriately diluting these stock solutions with DMF. Similarly different blend compositions of 10/90, 20/80, 30/70, 40/60, 50/50, 60/

40, 70/30, 80/20, 90/10 ratio, along with the pure polymer solutions in DMF at nine concentrations between 0.5-2.0 % (v/v) of the blends as well as pure components were prepared by mixing appropriate quantities of stock solutions of PVDF and cellulose acetate.

Preparation of the blend films: The blend solutions prepared as stated above were cast on clean Teflon dish. Films were dried initially at room temperature and were then kept in a vacuum oven at 40 ºC for 48 h to remove any residual DMF traces. The complete removal of DMF has also been confirmed by FTIR spectra of the films. The absence of N-C=O bending and C-N stretching frequencies at 600 and 1300 cm^{-1}, respectively indicate the absence of DMF in the blend film.

Solution and solid state property measurements: The densities of individual and blend polymer solutions in DMF were measured with a Mettler Toledo Digital density meter model Densito 30 PX. The temperature of the measurement was within an uncertainty of ± 0.1 ºC. The instrument was calibrated with standard density water supplied with the instrument. The estimated error in the density measurement was within ± 0.05 %. Dilute solution viscosities of PVDF, cellulose acetate and their blend solutions were measured at different temperatures using an Ubbelhode viscometer with an accuracy of ± 0.1 %. Solution viscosities at different temperatures were determined by equilibrating the viscometer tube in a thermostat maintained at a desired temperature for about 10 min before the flow time measurement. The temperature of the bath was kept constant within an accuracy of ± 0.1 ºC. Ultrasonic velocity measurements were carried out on a fixed frequency continuous wave ultrasonic interferometer (Model F81, Mittal Enterprises, New Delhi) operating at 2 MHz using the standard procedure. The error in the measurement of ultrasonic velocity was within ± 0.1 %. Measurements at different temperatures were carried out by circulating water at required temperatures from a thermostatic bath, inside the double walled jacket covering the interferometer cell. The accuracy of temperature maintenance was within ± 0.1 ºC. Measurements at different temperatures were carried out by circulating water at required temperatures from a thermostatic bath, inside the double walled jacket covering the interferometer cell. The accuracy of temperature maintenance was within ± 0.1 ºC. The refractive index values of polymer solution were measured with a Mettler Toledo Refractometer model Refracto 30 GS. The uncertainty in the values was within ± 0.0001 units at all the temperatures. At least three independent readings of all the physical properties were taken for each mixture. The average of these values was used for the data analyses.

FTIR, SEM: FTIR measurements of the polyblend films were carried out at room temperature using a Nicolet Avatar 330 FTIR spectrometer. SEM images of the blend films were recorded on a Jeol Scanning electron microscope.

RESULTS AND DISCUSSION

Solution property studies: Viscosity of the blend solutions were measured at 303, 313 and 323 K for different CA/PVDF blend compositions at ratios of 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, 90/10 along with the pure polymer solutions in DMF at seven concentrations, namely, 0.1-1.2 % (v/v) of the blends as well as pure components. Density, refractive index and ultrasonic velocity of the polymer solutions were measured at three different temperatures indicated above for all the CA/PVDF compositions at a concentration of 2 % (v/v).

From viscosity data, relative and reduced viscosities of the polymer solutions have been calculated and plotted against composition/solution concentration (Figs. 2 and 3).The plot of relative viscosity *versus* blend composition (Fig. 2) was linear for the entire composition range. This behaviour is a characteristic of a miscible blend system[14-16]. The plots of reduced viscosities of the component polymers and their blend compositions *versus* concentrations at different temperatures (Fig. 3) were also linear without any cross over indicating that the blends are completely miscible. A sharp cross over in the plots of reduced viscosity *versus* concentration is generally shown by immiscible blends.

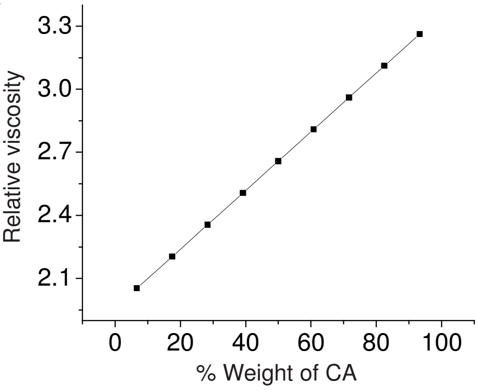

Fig. 2. Relative viscosity *versus* composition of CA/PVDF blends at 303 K

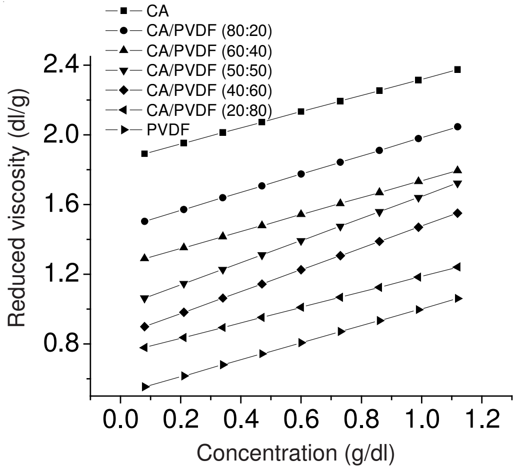

Fig. 3. Reduced Viscosity *vs.* concentration of CA/PVDF blends at 313 K

The interaction parameter of the component polymers and their blend compositions have been obtained from the plots of the reduced viscosity *versus* concentration and are given in Table-1. The slope of the curve gives the corresponding interaction parameter value, which has been evaluated on the basis of classical Huggins equation[17,18]. Krigbaum and Wall[14] interaction parameter Δb of the blends has been obtained from the difference between the experimental and theoretical values of the interaction parameters b_{12} and b_{12}^*. Polymer 1-polymer 2 interaction parameter Δb can be calculated as follows:

TABLE-1
INTRINSIC VISCOSITY AND SLOPE OF REDUCED VISCOSITY *VERSUS* CONCENTRATION PLOTS OF CELLULOSE ACETATE/ POLY(VINYLIDENE FLUORIDE) BLENDS AND INDIVIDUAL SOLUTIONS AT DIFFERENT TEMPERATURES

Cellulose acetate/ poly(vinyldine fluoride) (v/v)	Intrinsic viscosity (dl/g) at 303 K	Slope of red viscosity *vs.* concentration curve at 303 K	Intrinsic viscosity (dl/g) at 313 K	Slope of red viscosity *vs.* concentration curve at 313 K	Intrinsic viscosity (dl/g) at 323 K	Slope of red viscosity *vs.* concentration curve at 323 K
0/100	0.704	0.212	0.514	0.287	0.833	0.208
20/80	0.766	0.466	0.743	0.444	0.914	0.447
40/60	0.924	0.495	0.849	0.526	0.997	0.459
50/50	1.208	0.573	1.012	0.578	1.045	0.523
60/40	1.416	0.584	1.251	0.685	1.251	0.559
80/20	1.533	0.732	1.461	0.722	1.378	0.711
100/0	1.630	0.893	1.854	0.864	1.580	0.811

$$\frac{(\eta_{sp})_m}{C_m} = (\eta)_m + b_m C_m \tag{1}$$

where C_m = total concentration of polymers $C_1 + C_2$, $(\eta_{sp})_m$ is the specific viscosity and b_m represents the global interaction between all polymeric species defined by the equation,

$$b_m = X_1^2 b_{11} + 2X_1X_2b_{12} + X_2^2 b_{22} \tag{2}$$

where X_1 and X_2 weight fractions of polymer 1 and polymer 2, respectively, b_{12} is the interaction parameter of the blend system which can be calculated from eqn. 2 and b_{11} and b_{22} are respective individual interaction parameters. The interaction parameters b_{11}, b_{22} and b_m have been calculated from the slopes of the plot of reduced viscosity *versus* concentration[16]. The interaction parameter b_{12}^* was then calculated theoretically by using equation,

$$b_{12}^* = (b_{11}b_{22})^{1/2} \tag{3}$$

The difference (Δb) calculated from the theoretical b_{12}^* from eqn. 3 and the experimental b_{12} with eqn. 2 is given as,

$$\Delta b = (b_{12} - b_{12}^*) \tag{4}$$

If $\Delta b > 0$, blends are miscible and if $\Delta b < 0$ phase separation occurs. It has been found that Δb values are positive (Table-2) for all blend compositions and at all studied temperatures. This suggests that the blends are miscible in the studied range. If η_1 and η_2 are sufficiently apart, a more effective parameter μ, defined by Chee *et al.*[7] can be used to predict the compatibility. The relation is given by,

$$\mu = \frac{\Delta b}{(\eta_2 - \eta_1)^2} \tag{5}$$

TABLE-2
Δb AND Δk_{AB} VALUES FOR THE CELLULOSE ACETATE/ POLY(VINYLIDENE FLUORIDE) BLENDS AT DIFFERENT TEMPERATURES

Cellulose acetate/ poly(vinyldine fluoride) (w/w)	303 K		313 K		323 K	
	Δb	Δk_{AB}	Δb	Δk_{AB}	Δb	Δk_{AB}
0/100	–	–	–	–	–	–
20/80	0.48	0.16	0.27	0.59	0.50	0.49
40/60	0.13	0.14	0.15	0.06	0.09	0.16
50/50	0.15	0.13	0.14	0.02	0.12	0.11
60/40	0.04	0.30	0.25	0.11	0.32	0.34
80/20	0.04	0.04	0.05	0.37	0.16	0.19
100/0	–	–	–	–	–	–

where η_1 and η_2 are intrinsic viscosities of pure component solutions. The blend is miscible when $\mu \geq 0$ and immiscible if $\mu < 0$. The values of μ, calculated with aforementioned expression at different temperatures for the present system have been presented in Table-3. The results show that the μ values for the system under study are all positive and sufficiently high, indicating the miscibility of the blends. High value of μ may also be due to specific interaction of hydrogen bonding between the polymers.

TABLE-3
μ AND α VALUES FOR THE CELLULOSE ACETATE/ POLY(VINYLIDENE FLUORIDE) BLENDS AT DIFFERENT TEMPERATURES

Cellulose acetate/ poly(vinyldine fluoride) (w/w)	303 K		313 K		323 K	
	μ	α	μ	α	μ	α
0/100	–	–	–	–	–	–
20/80	0.55	0.13	0.15	0.18	0.89	0.69
40/60	0.15	0.64	0.08	0.84	0.16	0.20
50/50	0.17	0.32	0.07	0.47	0.21	0.43
60/40	0.04	0.17	0.13	0.20	0.57	0.29
80/20	0.04	0.19	0.02	0.15	0.28	0.16
100/0	–	–	–	–	–	–

Recently, Sun *et al.*[19] have suggested a new formula for the determination of polymer miscibility as follows:

$$\alpha = K_m - \frac{K_1[\eta_1]_2^2 W_2^2 + 2\sqrt{K_1K_2}\,[\eta]_1[\eta]_2 W_1W_2}{\{[\eta]_1 W_1 + [\eta]_2 W_2\}^2} \tag{6}$$

where, K_1, K_2 and K_m are the Huggins's constants for individual components 1 and 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving this equation. They have also suggested that a blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$. The α values for the present system at various temperatures have been listed in Table-3. The positive values at all temperatures indicate that the blends are miscible. Further, we have also carried out calculations to identify the miscibility of blends based on Huggins[17] constant. The Huggins constant is a parameter which also could be used to express the interaction between unlike polymers[20]. The k_{AB} value was concerned with b_{AB} as shown in the equations

$$b_{AB} = k_{AB}[\eta]_A[\eta]_B \tag{7}$$

and

$$k_{AB} = \frac{b_m - (b_A W_A^2 + b_B W_B^2)}{2[\eta]_A[\eta]_B W_A W_B} \tag{8}$$

The factor k_{AB}, is a theoretical value derived from the geometric means of k_A and k_B as

$$k_{AB,t} = (k_A k_B)^{0.5} \quad (9)$$

The deviation from the theoretical value also provides information about the interaction between unlike polymers as shown in

$$\Delta k_{AB} = k_{AB} - k_{AB,\,\text{theoretical}} \quad (10)$$

The positive Δk_{AB} value indicates that the polymer mixture in solution-state is miscible. Table-2 shows the Δk_{AB} values for present system, which are positive for all the compositions up to 323 K indicating the miscibility of the blends in this temperature range[29].

The heat of mixing (ΔH_m) was also used as a measure to study the blend compatibility[21-23]. According to Schneier[22], ΔH_m of the polymer blends is given by

$$\Delta H_m = \left\{ W_1 M_1 \rho_1 (\delta_1 - \delta_2)^2 \left[\frac{W_2}{(1-W_2)} M_2 \rho_2 + (1-W_1) M_1 \rho_1 \right]^2 \right\}^{1/2} \quad (11)$$

where W, M and ρ are the weight fraction of the polymer, the monomer molecular weight and the polymer density, respectively and δ represents the solubility parameter of the polymer. The δ values of poly(vinylidene fluoride) [13.6 $(\text{cal/cm}^3)^{1/2}$] and cellulose acetate [12.2 $(\text{cal/cm}^3)^{1/2}$] were taken from the literature[24] and these values were used to calculate ΔH_m with eqn. 11. Fig. 4 shows the variation of ΔH_m *versus* blend composition. It is evident from the figure that the variation follows almost a linear pattern, without any reversal (increase followed by decrease or *vice-versa*) in the trend. This behaviour further confirms that the blend solutions are miscible in the studied range of compositions and temperature. Further, the heat of mixing calculated at different temperatures did not vary significantly and in fact, as is seen in the Fig. 4, the ΔH_m values for various temperatures are almost overlapping. This behaviour shows that the effect of temperature on miscibility of the blends is not very significant.

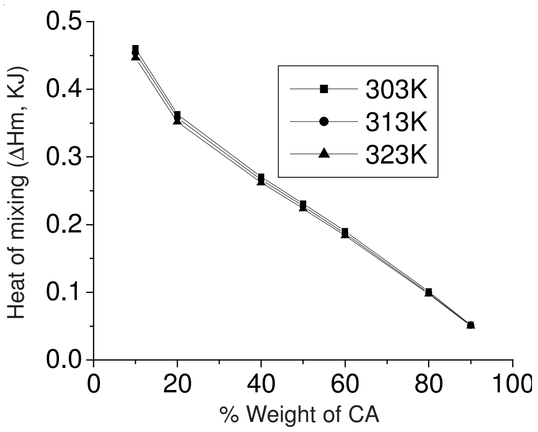

Fig. 4. Heat of mixing of CA/PVDF blends at different temperature

To confirm the miscibility behaviour of the blends further, the ultrasonic velocity, adiabatic compressibility, density and refractive index values of the blend solutions have been measured at five different temperatures. Adiabatic compressibility has been calculated by using the formula,

$$\beta_{ad} = \frac{1}{v^2 \rho} \quad (12)$$

where ν = ultrasonic velocity and ρ = density. Ultrasonic velocity, adiabatic compressibility, density and refractive index of the blend solutions have been plotted against blend compositions at different temperatures (Figs. 5-7) and they are found to be linear. For incompatible blend solutions, these plots are non-linear showing distinct phase inversion at intermediate compositions. Hence these results provide further supporting evidence for miscible nature of the studied blends in the entire composition range. The miscibility may be due to the presence of intermolecular interactions such as hydrogen bonding between the blend polymers.

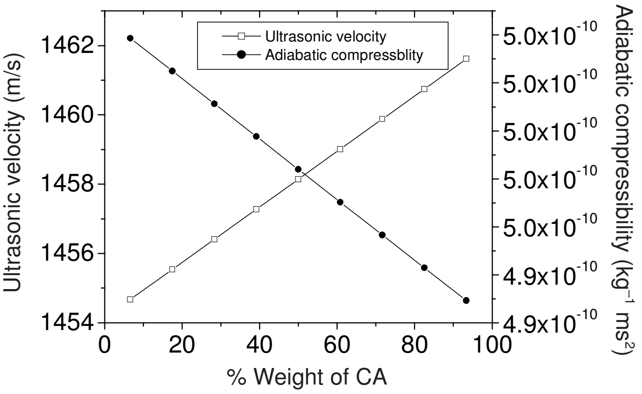

Fig. 5. Ultrasonic velocity and adiabatic compressibility *versus* composition of CA/PVDF blends at 303 K

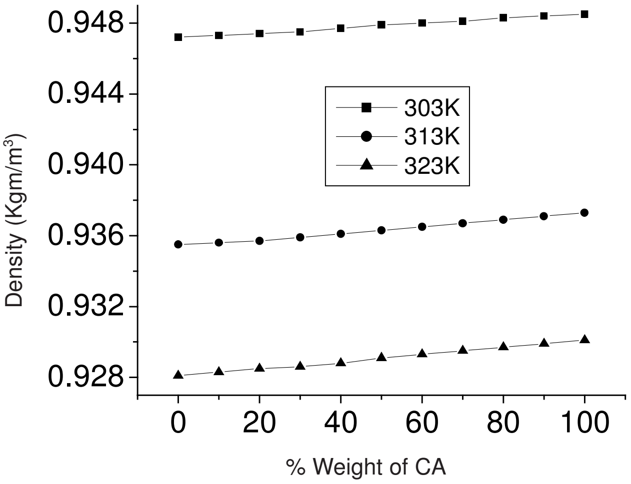

Fig. 6. Effect of temperature on the variation of density with the composition of 1 % w/v of CA/PVDF blend in solution

FTIR spectroscopy: To confirm the presence of hydrogen bonding in the blends and hence the miscibility of blends in the solid state, FTIR spectra of the individual and blend polymer films have been measured at room temperature. Although the changes in energies, bond lengths and electron densities with the formation of hydrogen bonds are actually quite small and about two to three orders of magnitude smaller than typical chemical changes, FTIR spectroscopy is very sensitive to the formation of hydrogen bond[25-27]. If the groups involved in the hydrogen bond formation in a blend system

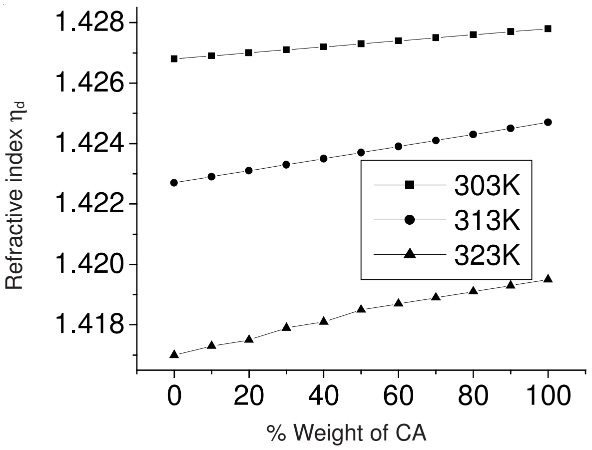

Fig. 7. Effect of temperature on the variation of refractive index with the composition of 2 % w/v of CA/PVDF blend in solution at different temperatures

are carbonyl and hydroxyl moieties, then the vibration frequencies of both the groups are expected to show a red shift due to hydrogen bond formation compared to the non-interacting group frequencies. In the present case, the carbonyl frequency of pure PVDF at 1735 cm^{-1} decreased to 1732 cm^{-1} in the 50:50 CA/PVDF blend indicating the formation of a weak hydrogen bond between component polymers, which can contribute to the miscibility of the blends. This enhancement in the -OH stretching frequencies may be attributed to the presence of intra and intermolecular hydroxyl-hydroxyl as well as hydroxyl-O-hydrogen bonding interactions in cellulose acetate which occurs at lower frequencies (3469 cm^{-1}) and the same being changed to intermolecular hydroxyl-carbonyl hydrogen bonding interactions in the blend system. Similar observations have also been reported in the case of miscible blends of polyvinyl alcohol and polyvinyl pyrrolidone. Hence the FTIR spectral results also compliment the results obtained by solution studies, ascertaining the presence of specific interactions and miscibility of the of the blend system studied[26-28].

SEM Study: Fig. 8 shows SEM images of 50:50 CA/PVDF blend. As can be seen from the images, the blend exhibits uniform morphological features without any phase separation or aggregation indicating the miscibility of the blend[25,29].

Conclusion

The miscibility behaviour of PVDF and cellulose acetate blends in DMF has been studied in the temperature range 303-323 K. The miscibility has been analyzed by solution viscosity, ultrasonic velocity and refractive index measurement of the blend solutions and calculating various interaction parameters based on these data. The results indicated that the blends are miscible in the entire composition range between 303-323 K. The FTIR study of the blend films also indicated the presence of weak specific interactions supporting the results of solution studies. The SEM images of the blend film showed uniform morphological features indicating complete blend miscibility.

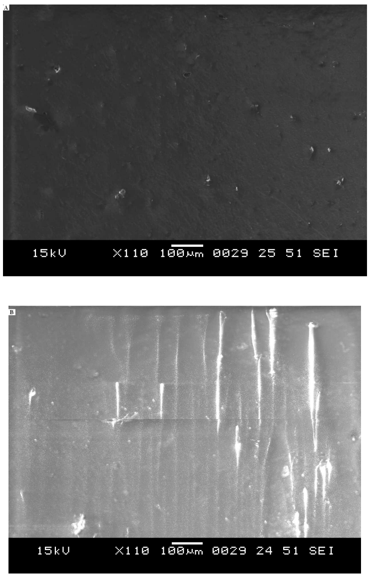

Fig. 8. SEM images of 50:50 CA/PVDF blend: (A) low magnification and (B) high magnification

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