

## Investigation on Polyacrylonitrile/Cellulose Acetate Blends

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**Abstract:** The molecular interactions of polyacrylonitrile (PAN) and cellulose acetate (CA) were investigated thoroughly via dilute solution viscometry in dimethylformamide (DMF) as a common solvent at 30 °C. The intrinsic viscosities and viscometric interaction parameters were experimentally determined for both binary (polymer/dimethylformamide) and ternary (PAN/CA/dimethylformamide) systems. As all investigated PAN/CA ternaries evidenced negative viscometric interaction parameter values ( $\Delta b$  &  $\Delta k < 0$ ), the existence of repulsive intermolecular interactions was deduced, and PAN/CA blends were assigned as immiscible. Moreover, the results of microscopy photograph analysis indicated that pure PAN film evidences a homophasic structure, and the size of the phase domain increases gradually with increases in CA. In DSC analysis, it was determined that the glass transition temperature of the blend film increased slightly with increases in the CA content of the blend film.

**Keywords:** viscometry, film, polyacrylonitrile, cellulose acetate.

### Introduction

Polymer blends are simple but the constituent polymers are intimately physical with negligible covalent bonds occurring between them. Polymers may be miscible or immiscible, depending on the thermodynamics of polymer-polymer interactions and the kinetics of the mixing process.<sup>1-4</sup> Compatible polymer pairs are generally described as polymer mixtures that have desirable properties when blended. Compatibility is the term used to cover a wide range of situations to describe good adhesion, useful and improved properties. All those are dependent on the extent of polymer miscibility interest. The mixing exhibited at the molecular scale is expressed as 'miscibility'.<sup>5,6</sup>

There is a great need to quantify miscibility or interaction parameters by experimental means for a blend system, so that the structure property relationships can be developed more completely. There are various experimental methods for measuring miscibility either quantitatively or qualitatively.

Several works on polymer-polymer miscibility have been developed recently. For such investigations, the techniques most commonly and widely used are electronic microscopy, spectroscopy, thermal analysis and viscometry.<sup>7,8</sup> Because of its simplicity, viscometry becomes an attractive method for studying the compatibility of polymers in solution. The

basis for using dilute solution viscosity as a parameter for determination of compatibility of polymer blends lies in the fact that while in solution the repulsive interaction may cause shrinkage of the polymer coils resulting in a viscosity of polymer mixture that is lower than the value calculated from viscosities of the pure component on the assumption of the additivity law.<sup>9</sup>

Cellulose secondary acetate (CA) is one of the well known polymers produced from naturally available plant substance. Cellulose acetate finds application in fibers as well as in moulding. Miscibility and properties of cellulose acetate and nylon 6 blends has been investigated by Shashidhara and his group using viscometry method.<sup>10</sup>

In this present work, we focus on polymer-polymer interaction of cellulose acetate (CA) and polyacrylonitrile (PAN) resulting from the viscosities of blend solutions using dimethylformamide (DMF) as a cosolvent. The obtained viscosity data are compared with DSC results and microscopy photographs. The main objective, as mentioned above, is the evaluation of the miscibility in blends of CA and PAN, in terms of viscosity data, DSC thermograph and microscopy photograph.

**Theoretical Background.** A ternary system contains a solvent (component 1) and two polymers (component 2 and 3), which can be set in this equation:<sup>11,12</sup>

$$b_m C^2 = b_{22} C_2^2 + b_{33} C_3^2 + 2b_{23} C_2 C_3 \quad (1)$$

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$C_2$  and  $C_3$  are the concentrations of component 2 and 3 in mixed polymer solutions;  $b_{22}$  and  $b_{33}$  are the interaction coefficients of the binary components in solution; and  $b_{23}$  is the interaction coefficient for the mixture of components.  $b$  is obtained experimentally by plotting  $\eta_{sp}/c$  of polymer solution versus solution concentrations ( $C$ ).

Krigbaum and Wall suggested<sup>13</sup> that information about the interaction between two polymers should be obtained from  $\Delta b$  expressed as:

$$\Delta b = b_{23} - \sqrt{b_{22}b_{33}} \quad (2)$$

Where  $b_{23}$  is obtained by substituting terms in eq. (1).  $\Delta b \geq 0$  signifies there are attractive interactions between different components and the blend is miscible, whereas  $\Delta b < 0$  indicates phase separation.

Another criterion is proposed for ternary system according to Huggin's equation

$$\eta_{sp} = [\eta]c + K[\eta]^2c^2 \quad (3)$$

$$K_m[\eta]_{m,id}^2c_m^2 = K_3[\eta]_3^2c_3^2 + K_2[\eta]_2^2c_2^2 + 2K_{23}[\eta]_2[\eta]_3c_2c_3 \quad (4)$$

Where,  $\eta_{sp}$  is the specific viscosity and  $\eta$  is the intrinsic viscosity of polymer solutions. Subscript  $m$  refers to polymer blend solution.  $C$  is the concentrations of polymer in the solution and  $K$  is Huggins coefficient which is introduced as follow;

$$K_m = K_{id} + \Delta K \quad (5)$$

Where,  $K_{id}$  is the ideal Huggins coefficient and  $\Delta K$  shows deviation behavior of polymer blend solutions from ideal solution. The value of  $K_1$ ,  $K_2$ , and  $K_m$  can be obtained from eq. (3) by determining the specific viscosity and intrinsic viscosity of polymer solutions.

Information about the interaction between two polymers should be obtained from the difference of experimental  $K_{23}$  and its theoretical amount that can be shown as  $\Delta K$ :

$$\Delta K = K_{23} - \sqrt{K_2K_3} \quad (6)$$

$$\Delta K = \left\{ (K_m[\eta]_{m,id}^2c_m^2 - K_2[\eta]_2^2c_2^2 - K_3[\eta]_3^2c_3^2) / (2[\eta]_2[\eta]_3c_2c_3) - ((\eta_{sp,2} - [\eta]_2c_2)(\eta_{sp,3} - [\eta]_3c_3)) / ([\eta]_2^2[\eta]_3^2c_2^2c_3^2)^{1/2} \right\} \quad (7)$$

Hence positive deviations from ideal behavior are indicative of attractions between the different polymer species, whereas negative deviations result from repulsions. We can express these findings in terms of coefficient  $\Delta K$ , as follows:

$$\begin{aligned} \Delta K > 0 & \text{ Miscibility} \\ \Delta K < 0 & \text{ Immiscibility} \end{aligned}$$

## Experimental

**Materials.** The PAN sample was synthesized by aqueous

**Table I. Characteristic of Solutions that Used to Casting Films**

Sample	PAN/CA Ratio	Total Solid Concentration	Casting Temperature (°C)
1	100/0	10	25
2	90/10	10	25
3	80/20	10	25
4	60/40	10	25
5	50/50	10	25

solution polymerization system using AIBN as an initiator.<sup>14</sup> Its viscosity average molecular weight ( $M_v$ ) was measured to be  $0.93 \times 10^5$ . CA was purchased from Aldrich with a degree of polymerization and substitution of 160 and 2.4 respectively, while DMF was purchased from Fluka Chemika.

**Preparation of Blend Solutions and Film.** The original binary solutions were prepared by dissolving in dimethylformamide (DMF).<sup>15</sup> The dissolution of PAN was facilitated by slight heating and string. The ternary solution of PAN and CA prepared by dissolving mixtures had different weight ratios in DMF at 50°C. The solutions were filtered and diluted to the designated volume at room temperature.

The solution was cast on to a dry and smooth glass plate by employing a laboratory caster to form a homogeneous liquid layer. The solutions which listed in Table I were cast and dried at room condition.

**Viscometry Method.** Viscometric measurements were carried out at 30°C, using the viscometer (Cannon-Fenske 50 K 919 Capillary) immersed in a water bath with a thermoregulator, which was used to keep temperature constant. Relative viscosities of polymer solutions were calculated by dividing the flow times of solutions by that of the pure solvent ( $t_0 = 216.4S$ ).

**Microscopy.** In order to study the film structural, a piece of the film was placed on a microscope slide, surrounded with paraffin oil and covered with cover glass. This was observed through a low magnification microscope (Amplivl Interphako) which was equipped with a camera.

**Differential Scanning Calorimetry.** A Perkin-Elmer differential scanning calorimeter (Model DSC 2010, USA) was used to record differential scanning calorimetry (DSC) curves, by heating from 20 to 140°C in nitrogen atmosphere at a heating rate of 10°C min<sup>-1</sup>. Powdered samples (10 mg each) were weighed and encapsulated in pans.

## Results and Discussion

**Viscosities Analysis.** The plots of specific viscosity blend concentration,  $\eta_{sp}/c$  vs  $C$ , for PAN/CA blend solutions and each polymer is shown in Figure 1. The graphs are linear and the points fit in straight lines very well. The interception of these lines with the Y axis gives the intrinsic viscosities,  $[\eta]$ , of the corresponding polymer solutions. PAN solution

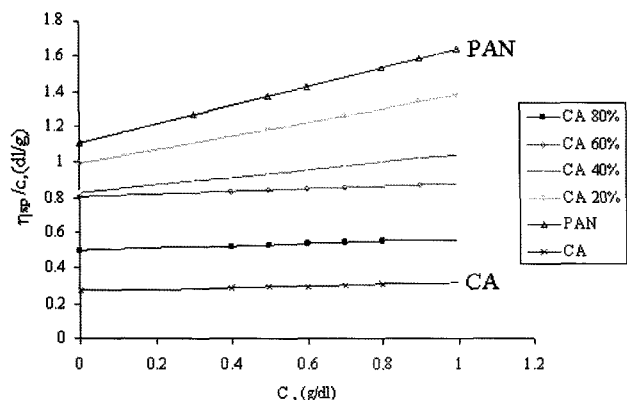


Figure 1.  $\eta_{sp}/c$  versus  $C$  for PAN/CA blend solutions.

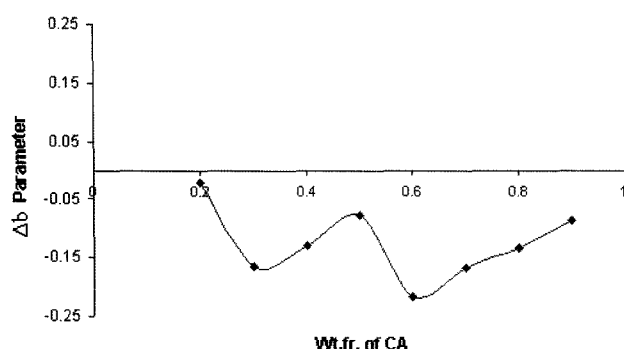


Figure 2. Plot of interaction parameters versus CA concentration in PAN/CA blends.

is the highest intrinsic viscosity and pure CA solution is the lowest one and it is reduced by increment of CA in polymer blends solution. Results for intrinsic viscosities can be obtained by substituting terms in eq. (3).

**Effect of Blend Compositions on  $\Delta b$ .**  $\Delta b$  Values of blends with different compositions as a function of the CA concentrations are shown in Figure 2. The  $\Delta b$  values of the PAN/CA decrease with increasing concentrations of each

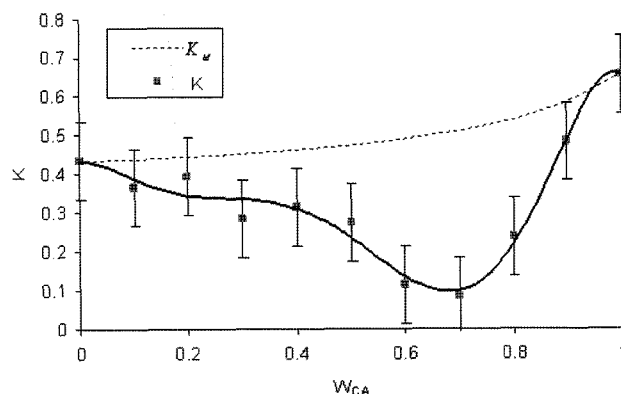


Figure 3. Plot of Huggins coefficient versus CA concentrations in blend.

component. When the concentrations of CA is more than 20 wt%, the slope of the line is sharp. However, when the concentration of PAN is increased beyond 20% the slope of the line is sharp too. In other words, with the increasing in CA concentration the  $\Delta b$  value keeps on decreasing and beyond about 60% concentration it rises and is always negative. The lowest amount of  $\Delta b$  occurred at 30% and 60% of CA content, so it agrees with the previous results.<sup>16-18</sup> All the  $\Delta b$  values listed in Table II are negative, which indicate that these blends are not miscible<sup>19</sup> and prove that  $\Delta b$  can be a good criterion for this blend solution.

**Huggins Coefficient.** Experimental values of the Huggins coefficient for pure components,  $K_2$  (PAN), and  $K_3$  (CA), and for blends,  $K_m$ , were determined according to eq. (3) from the slope of each line presented in Figure 1. Results are listed in Table II. Values of  $K_{id}$  were calculated from eq. (5). The amounts of  $K_m$  are less than  $K_{id}$  that indicates the amounts of  $\Delta K$  should be negative according to eq. (5). These results indicate immiscibility of two constituents in blend solutions. This can be seen more clearly in Figure 3 where experimental values of  $K_m$  are depicted versus blend

Table II. Viscometric Data for Ternaries Blends Containing PAN and CA

System	$w_{PAN}^*$	$b$ (dL/g) <sup>2</sup>	$b_{23}$ (dL/g) <sup>2</sup>	$\Delta b$	$K$	$K_{id}$
PAN		0.5324			0.4339	
CA		0.048			0.6565	
PAN/CA	0.898		0.4507	-0.0459	0.3664	0.4392
PAN/CA	0.801		0.3879	-0.0206	0.3944	0.4455
PAN/CA	0.699		0.2623	-0.1650	0.2838	0.4530
PAN/CA	0.601		0.2148	-0.1289	0.3128	0.4623
PAN/CA	0.499		0.1852	-0.0787	0.3411	0.4740
PAN/CA	0.399		0.075	-0.2164	0.1151	0.4891
PAN/CA	0.302		0.0691	-0.1666	0.0819	0.5909
PAN/CA	0.200		0.0606	-0.1330	0.2394	0.5381
PAN/CA	0.100		0.0572	-0.0877	0.4811	0.5819

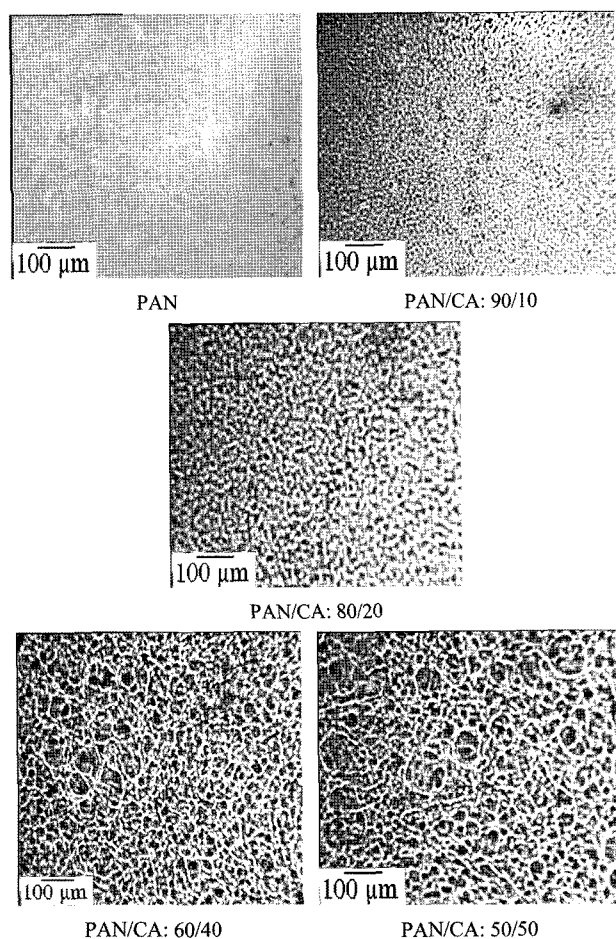


Figure 4. Surface micrograph of films.

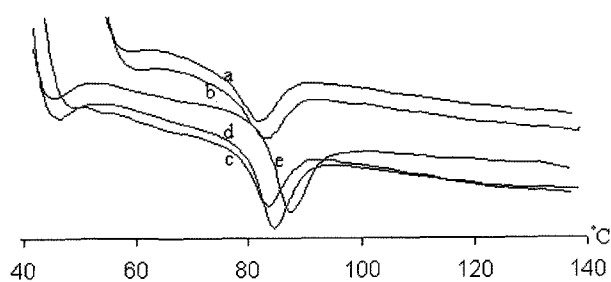


Figure 5. DSC thermograms of (a) PAN, (b) PAN/CA: 90/10, (c) PAN/CA: 80/20, (d) PAN/CA: 60/40, and (e) PAN/CA: 50/50.

composition. Negative deviations from ideal behavior become evident. The deviations are clearer with increasing concentrations of each component, especially, when weight fractions of CA and PAN reach more than 40 and 10 wt%, respectively. It is obvious that the greatest deviation happened when the weight fraction of CA is 70 wt% in the blend solution.

**Microscopy Analysis.** Figure 4 presents surface micrographs of PAN and CA blend films. PAN film shows

Table III. Glass Transition Temperature of the Films

Sample	PAN/CA Ratio	$T_g$ (°C)
1	100/0	77.2
2	90/10	78.4
3	80/20	80.3
4	60/40	82.6
5	50/50	84.7

homophase structure. With increasing CA content, the blend film tends to present a multiphase structure, and appears domains and the dominant morphology is a Particle-in-Matrix structure. The structure of the film transform from fine to rough. The domain is formed due to the high interfacial energy barrier, the low intermolecular adhesive force, phase separation and immiscibility of two polymers.

**DSC Analysis.** Polymer blends are commonly characterized by dependence of  $T_g$  on the composition of miscible systems. DSC curves of all films are shown in Figure 5. The  $T_g$  of blend films are shifted partially to higher temperature, as result of as increase in CA content (Table III). For highly miscible system, a single  $T_g$ , intermediate between those of the pure polymers is observed. The glass transition temperature ( $T_g$ ) is directly associated with mixing at molecular level in a polyblend. The glass transition temperature of polyblend films increased a little, so there was partially mixing at molecular level in the amorphous regions of PAN and CA polyblend.

## Conclusions

Viscometric studies on polyblend solutions of PAN/CA in DMF show that the Huggin's equation is valid to an excellent approximation in the range of polyblend solution studies. The values of  $\Delta b$  and  $\Delta K$  are negative and it indicates PAN/CA blend solutions are immiscible. The immiscibility is more obvious when the amount of each component is more than 20 wt% in the blends; and the deviation from ideal solution is the highest at 70 wt% of CA content. Microscopy photographs show that a pure PAN film has a homophase structure. Its structure changes by increment of CA in films and creates some domains in polyblend films. The glass transition of blend film partially increased, which shows that polyblend films mixed partially in amorphous regions.

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