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Miscibility Behavior of Pectin-Poly (vinyl alcohol) Blends in Water at 35°C

V. Naga Maheswara Reddy[1], K.S.V. Krishna Rao[2], M.C.S. Subha[3], K. Madhusudhan Rao[3], K. Chowdoji Rao[1]*

[1]Department of Polymer Science & Tech, Sri Krishnadevaraya University, Anantapur, Andhra Pradesh, India, [2]Department of Chemistry, Yogi Vemana University, Kadapa-516 003, Andhra Pradesh, India, [3]Department of Chemistry, Sri Krishnadevaraya University, Anantapur, Andhra Pradesh, India.

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ABSTRACT
Pectine, a polysaccharide, has many industrial applications, and its miscibility studies are most useful. Synthetic poly (vinyl alcohol) (PVA) is a subject of current research interest. Hence, miscibility of pectin and PVA in water is carried out in different percentages of the blend compositions. Ultrasonic velocity, viscosity, density, and refractive index are measured for these blends in water at 35°C. The interactions in binary blend systems were analyzed from the viscosity data. The blend compatibility is studied from interaction parameters obtained from viscosity data. The compatibility of pectin/PVA is also confirmed from the ultrasonic, density, and refractive index data.

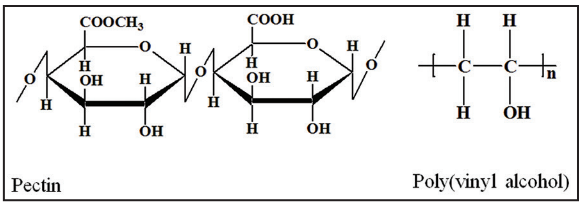
Key words: *Polymer blends, Miscibility, Polysaccharide, Poly(vinyl alcohol).*

1. INTRODUCTION

The importance of polymer blending has been increased in recent years because of the preparation of the polymeric materials with desired properties, low basic cost, and improved processability. Polymer blends are physical mixtures of structurally different polymers or copolymers which interact with secondary forces with no covalent bonding [1] such as hydrogen bonding, dipole-dipole forces, and charge-transfer complexes for homopolymer mixtures [2-4]. A number of fundamental studies of blends have been carried out in parallel with investigations on their practical applications. Among them, microscopic hybridization of natural polymers including polysaccharides may be of great significance, in view of the wider utilization and new functionalization of abundant biomass. There are various techniques to study the miscibility of blends [5] but some are time-consuming and are complicated and overall costly. Singh and Singh have suggested the use of ultrasonic velocity and viscosity measurements for finding the miscibility [6,7]. Chee and Sun *et al.* [8,9] have suggested a viscometric method for the study of the polymer miscibility. Paladhi and Singh [10,11] have revealed that variation of viscosity with polymer blend compositions is linear for miscible blends. Recently Rajulu *et al.* [12] have studied the ultrasonic, refractometric and viscosity studies of some polymer blends in solution. Hence blending of pectin, and poly (vinyl alcohol) (PVA) would provide a produce biodegradable and newer polymer blend. In order to find a solution for polymer degradable the synthetic polymer are being blended with the natural polymer to prepare a natural, which will be degradable without causing polymer pollution. In this way, the present work will give insight to prepare polymer blend of pectin/PVA. The results are presented in this paper. Pectin is a polysaccharide that acts as a cementing material in the cell walls of all plant tissues. The white portion of the rind of lemons and oranges contains approximately 30% pectin (different sources of pectin are displayed in the following pages). Pectin is the methylated ester of polygalacturonic acid, which consists of chains of 300-1000 galacturonic acid units, joined with 1α→4 linkages. The degree of esterification (DE) affects the gelling properties of pectin. The structure shown here has three methyl ester forms (−$COOCH_3$) for every two carboxyl groups (−COOH); hence it is has a 60% DE, normally called a DE-60 pectin.

In this article, we studied the miscibility of pectin/PVA blends in aqueous solutions at different temperatures by viscometric, ultrasonic velocity, and refractive index techniques. The structures of both pectin and PVA are represented as follows:

*Corresponding Author:
E-mail:chowdojirao@gmail.com



2. EXPERIMENTAL

2.1. Materials

Analytical grade pectin (mol wt 2,50,000), and PVA (mol wt 1,25,000) (Sd. fine, Bombay) were used as supplied without any further purification.

2.2. Preparation of Blend Solutions

1 weight % pectin and PVA solutions were prepared with water. Stock solutions of homopolymers and the blends of pectin/PVA of different compositions 0/100, 20/80, 40/60, 50/50, 60/40, 80/20, and 100/0 were prepared in water.

Viscosity measurements at 35°C were made using an ubbelohde viscometer and the different temperatures were maintained in a thermostat bath with a themal stability of ±0.05°C. From these blend solutions, 0.1-1.0 g/dl solutions were prepared volumetrically. Ultrasonic velocities were measured using Mittal enterprises. Ultrasonic interferometer operating at 3 MHz, with an accuracy of 0.2%. The temperature was maintained constant by circulating water from a thermostat with a double-walled jacket of the Interferometer cell with a thermal stability of ±0.05°C.

2.3. Density Measurements

Densities of the blend solutions were measured with a high precision vibrating tube digital density meter, Anton Paar, DMA model 4500/5000, (Graz, Austria). Temperature of the measuring cell was automatically controlled within an uncertainty of ±0.01 K by an inbuilt integrated Pt 100 measuring sensor. The instrument was calibrated with air, double distilled and freshly degassed water at the temperature of the measurement during every session. Densities of all the solutions belonging to a given system (including pure components) were measured during one session. Experimental uncertainty (i.e., reproducibility of the measured densities) was up to five units in the second decimal place.

Before injecting the sample, adjustments were made if deviations between the displayed values and reference values of the density standards exceeded specifications of the instrument. Air and double distilled freshly degassed water were used for calibration. Density values of water and dry air at the specific atmospheric pressure are stored in the memory of the instrument for the complete temperature range investigated. If the compared values agreed within ±0.05 kg m^{-3}, measurements were started after drying the measuring cell.

2.4. Refractive Index

Refractive indices, n_D for sodium D-line were measured using a thermostatically controlled Abbe Refractometer, Atago, model 3T (Tokyo, Japan). The uncertainty in refractive index is ±0.0001 units. At least three independent readings of all the physical properties (ρ, η, and n_D) were taken for each mole fraction of the mixture, and the average of these values are reported in Table 1.

3. RESULTS AND DISCUSSION

To quantify the miscibility of the polymer blends, Chee 12 suggested the general expression for the interaction parameter when the polymers are mixed in weight fractions w_1 and w_2 as

$$\Delta B = \frac{b - \bar{b}}{2w_1 w_2} \tag{1}$$

Where $b = w_1 b_1 + w_{22}$, b_{11} and b_{22} are the slopes of the viscosity curves for the components, and b is related to Huggin's coefficient K_H as

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

for a ternary system. It is also given by

$$b = w_t^2 b_{11}^2 + w_2^2 2b_{22}^2 + 2w_1 w_2 b_{12} \tag{3}$$

Where, b_{12} is the slope for the blend solution.

However, Chee's theory fails because experimental data are in conflict with the theoretical predictions 12. Using these values, Chee 6 defined a more effective parameter:

$$\mu = \frac{\Delta B}{[(\eta)_2 - (\eta)_1]^2} \tag{4}$$

Where, $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The polymer blend is miscible if $\mu \geq 0$ and immiscible when $\mu < 0$.

Recently, Sun *et al.* [13] suggested a most satisfactory new equation for the determination of the polymer miscibility as

$$\alpha = Km - \frac{K_1[\eta]_1^2 w_1^2 + K_2[\eta]_2^2 w_2^2 + 2\sqrt{K_1 K_2 [\eta]_1 [\eta]_2 w_1 w_2}}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2} \tag{5}$$

Where, K_1, K_2, and K_m are the Huggin's constants for individual components 1 and 2 and the blend, respectively. The long-range hydrodynamic interactions are considered while deriving the equation. The polymer blend is miscible if $\alpha \geq 0$ and immiscible when $\alpha < 0$.

Table 1: The values of density (ρ), absolute viscosity (η), relative viscosity (η_{rel}) and reduced viscosity (η_{rel}/C) for different composition of 1% (w/v) (pectin/PVA) blends in water at 35°C.

Concentration (C) g/dl	Density (ρ)	Reduced viscosity (η_{rel}/C)×10^{-2} (dl/g)	Ultrasonic velocity u×10^{-2} (cm/sec)	Refractive index (n)
0/100 (pectin/PVA)				
0.1	0.9955	0.6120	1488.7	1.4089
0.2	0.9957	0.7019	1505.2	1.3502
0.3	0.9959	0.7917	1526.1	1.3522
0.4	0.9962	0.8395	1520.1	1.3798
0.5	0.9965	0.8873	1509.1	1.3553
0.6	0.9967	0.9325	1508.0	1.3559
0.7	0.9969	0.9776	1517.6	1.3834
0.9	0.9973	1.1194	1515.2	1.3854
1.0	0.9975	1.0704	1499.6	1.3470
20/80 (pectin/PVA)				
0.1	0.9884	0.2335	1463.8	1.2903
0.2	0.9890	0.3660	1489.8	1.3117
0.3	0.9888	0.5455	1520.4	1.3241
0.4	0.9882	0.6609	1549.0	1.3302
0.5	0.9889	0.8572	1557.9	1.3302
0.6	0.9899	1.0208	1573.3	1.3365
0.7	0.9910	1.2699	1584.8	1.3526
0.9	0.9910	1.7856	1597.1	1.3672
1.0	0.9915	2.1834	1602.6	1.3834
40/60 (pectin/PVA)				
0.1	0.9877	0.2257	1456.9	1.3719
0.2	0.9876	0.5795	1471.8	1.3602
0.3	0.9877	0.6806	1500.1	1.3550
0.4	0.9882	0.8190	1518.9	1.3587
0.5	0.9899	1.1038	1531.2	1.3589
0.6	0.9911	1.4083	1536.3	1.3685
0.7	0.9919	1.6298	1551.2	1.3694
0.9	0.9919	2.3171	1543.2	1.3589
1.0	0.9927	2.6443	1541.8	1.3470
50/50 (pectin/PVA)				
0.1	0.9866	0.3507	1462.2	1.3670
0.2	0.9875	0.4469	1458.7	1.3478
0.3	0.9881	0.4948	1469.8	1.3322
0.4	0.9884	0.5225	1465.9	1.3358
0.5	0.9899	0.6609	1469.0	1.3288
0.6	0.9900	0.7993	1460.0	1.3334
0.7	0.9910	0.9931	1452.5	1.3442
0.9	0.9918	1.4360	1450.4	1.3397
1.0	0.9919	1.7405	1460.0	1.3434
60/40 (pectin/PVA)				
0.1	0.9863	0.3264	1464.9	1.3755
0.2	0.9869	0.5913	1459.0	1.3539

(Contd...)

Tables 1: Countiuned

0.3	0.9877	0.7831	1462.8	1.3418
0.4	0.9885	0.9654	1470.6	1.3442
0.5	0.9888	1.3806	1463.3	1.3454
0.6	0.9894	1.6851	1464.4	1.3635
0.7	0.9899	2.0173	1471.7	1.3840
0.9	0.9903	3.1246	1463.2	1.3907
1.0	0.9816	3.6857	1465.2	1.3699
80/20 (pectin/PVA)				
0.1	0.9883	4.6076	1436.0	1.3651
0.2	0.9863	2.8270	1450.4	1.3731
0.3	0.9885	2.9873	1460.8	1.3645
0.4	0.9886	2.8997	1458.7	1.3714
0.5	0.9890	3.2595	1447.4	1.3837
0.6	0.9899	3.4544	1446.3	1.3969
0.7	0.9897	3.5146	1456.8	1.4049
0.9	0.9898	4.1252	1473.1	1.4067
1.0	0.9993	4.2872	1476.2	1.3934
100/0 (pectin/PVA)				
0.1	0.9959	0.3581	1540.6	1.3761
0.2	0.9952	0.6542	1533.2	1.4149
0.3	0.9870	1.0214	1544.1	1.4255
0.4	0.9949	1.3193	1532.0	1.4192
0.5	0.9957	1.8604	1535.2	1.4344
0.6	0.9975	2.3305	1518.8	1.4228
0.7	0.9986	3.0272	1528.6	1.4082
0.9	0.9989	4.5967	1521.2	1.4255
1.0	0.9987	5.6305	1508.0	1.4212

PVA: Poly (vinyl alcohol)

The measured values of densities (ρ), calculated values of reduced viscosities (η_{red}), ultrasonic velocities (v), refractive indices (n) over the wide range of concentrations of blend solutions for different compositions 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 of 1% (w/v) (pectin/PVA) blends in water at 35°C are presented in Table 1.

From Figure 1 it is also observed that as the concentration of pectin increases in the blend the absolute viscosity also increases. With the increasing percentage of pectin in the (pectin/PVA) blend, PVA can interact with several chains of pectin and can form highly cross-linked structure, which causes high solution viscosity. Further, with the increase in proportion of pectin in the blend along with cross-linking effect, the effect of hydrogen bonding between the hydroxyl groups of pectin and PVA also increases. These effects at higher contents of Pectin of these blends enhance the cross-linking effect as well as hydrogen bond effect leading to high viscosity of the blends as obtained in Table 1 and Figure 1.

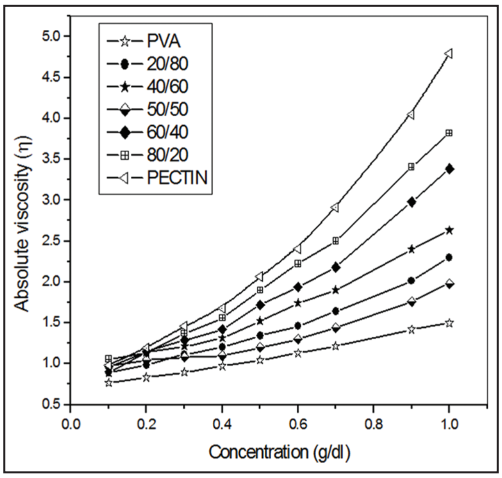
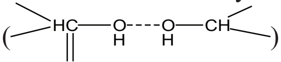


Figure 1: Variation of absolute viscosity with concentration of different compositions of (pectin/poly (vinyl alcohol) blend in water 35°C.

The Huggins plots of reduced viscosity against concentration for different compositions of 1% (w/v) (pectin/PVA) blends in water at 35°C are shown in the Figure 2. On extrapolating to zero concentration the intrinsic viscosities are determined (Figure 2) and the values of pectin, PVA and (pectin/PVA) blends of different compositions (20/80, 40/60, 50/50, 60/40, 80/20) are 2.7238, 0.7174, 1.6982, 1.7960, 1.1050, 1.9508 and 2.5591 dl/g, respectively. These values indicate that the intrinsic viscosity values of (pectin/PVA) blends for different compositions are in between the pure polymer values. The reasonable interpretation may be that the attractive interactions between pectin and PVA existed in water. These attractive interactions may lead to decrease the intermolecular excluded volume effect and decrease the hydrodynamic volume. As a consequence, the (pectin/PVA) blend coils expand, which causes an increase of the intrinsic viscosity of (pectin/PVA) blends in water compared to intrinsic viscosity values of pure polymers.

From these graphs, it is clearly evident that the Huggins curves linear in nature for all composition; this indicates mutual attraction of micromolecules in solution, which favors the polymer miscibility. Similar observation was also made by Heiyang *et al*., [13] in case of (PVC/PCL) blend and reported that the blend is miscible. In the present study Figure, 2 indicates that the (pectin/PVA) blend shows miscibility for all the (pectin/PVA) blend compositions. This may be due to the formation of H-bond between the hydroxyl groups (−OH) of D-galacturonic acid and hydroxyl groups (−OH) of PVA ( $\underset{\underset{O}{\|}}{>HC}-\underset{H}{O}{-}{-}{-}{-}\underset{H}{O}-CH<$) or corboxy groups of D-galacturonic acid and hydroxyl groups of PVA (>HC-OH---HOOC). The occurrence of proton donating and proton accepting groups in these polymers governs the nature of the intermolecular bonds responsible for the formation of associates between macromolecules of these polymers of the different nature. The change in the slope of the curve may be attributed to the mutual attraction of macromolecules in solution, which favors the polymer miscibility.

In order to quantify the miscibility and immiscibility nature of the present polymer blend system, the interaction parameters ΔB and μ suggested by Chee, and 'α' suggested by Sun *et al.* are calculated with the help of the equations 1-4 for the (pectin/PVA) blend systems in water at 35°C and are presented in the Table 2.

In general if ΔB and μ are positive for any poly blend system, it is a miscible one, where as if these values are negative the poly blends are considered as immiscible one. It is concluded from the present study basing on the values given in the Table 2 that the values ΔB and μ are positive for the systems under study and this indicates that (pectin/PVA) blend shows miscibility.

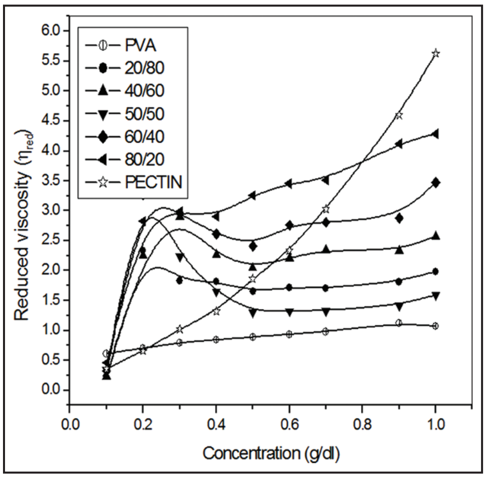


Figure 2: Variation of reduced viscosity with concentration of different compositions of (pectin/poly (vinyl alcohol) blend in water 35°C.

Table 2: Chee and Sun's interaction parameters for different compositions of 1% (w/v) (Pectin/PVA) blend in water at 35°C.

Blend composition (pectin/PVA)	**Chee's differential interaction parameters**		**Sun's miscibility parameter**
	ΔB	**μ**	**α**
20/80	0.03157	1.0242	0.7067
40/60	0.01578	0.6343	0.2463
50/50	0.00106	0.4216	0.7748
60/40	0.00472	0.3618	0.1377
80/20	0.00545	1.0528	0.3384

PVA: Poly (vinyl alcohol)

Sun *et al.*[9] has suggested new parameter 'α' for the determination of miscibility of polymer blends. The values of 'α' calculated for the present system are presented in Table 3. According to his theory a blend will be miscible if α is ≥0, and immiscible if α is <0. In the present study, the values of 'α' are found to be positive for all (pectin/PVA) blend compositions indicating that (pectin/PVA) blend are having miscible nature and conducted that the blend is miscible for all the blend composition.

Relaxation strength, r_s, was calculated as [14]:

$$r_s = 1-(u/u_\infty)^2 \quad (6)$$

where u_∞ is a constant whose, value is taken as 1600 m. s^{-1} [14], and u is experimental speed of sound.

From the density and speed of sound data, adiabatic compressibility, β_{ad}, molar compressibility, β_M, and

Table 3: The values of adiabatic compressibility (β_{ad}), acoustic impedance (Z), relaxation strength (γ_s), and rao's number (R) for different compositions of 1% (w/v) of (pectin/PVA) blends in water at 35°C.

Concentration (C) (g/dl)	Adiabatic compressibility $\beta_{ad}\times10^{11}$ (cm^2/dyne)	Acoustic impedance $Z\times10^{-2}$ (g/cm^2 sec)	Relaxation strength γ_s	Rao number (R) (cm$^{10/3}$/s$^{1/3}$ mole)
80/20 (pectin/PVA)				
0.1	4.8549	1437.03	0.1666	8988.05
0.2	4.7619	1449.40	0.1440	9101.54
0.3	4.7722	1449.40	0.1497	9163.82
0.4	4.8586	1441.04	0.1647	9039.25
0.5	4.9991	1429.78	0.1799	8977.82
0.6	5.0299	1430.80	0.1903	8926.62
0.7	5.0188	1441.79	0.1922	9050.34
0.9	4.7824	1465.87	0.1799	9156.25
1.0	4.6689	1484.47	0.1724	9175.88
60/40 (pectin/PVA)				
0.1	4.7245	1444.86	0.1617	8911.68
0.2	4.7601	1439.89	0.1685	8875.13
0.3	4.7315	1444.81	0.1641	8891.04
0.4	4.6779	1453.65	0.1553	8930.99
0.5	4.7230	1446.91	0.1636	8884.18
0.6	4.7131	1448.88	0.1623	8885.47
0.7	4.6643	1456.81	0.1540	8930.04
0.9	4.7165	1449.01	0.1637	8875.04
1.0	4.7453	1438.24	0.1614	8970.92
80/20 (pectin/PVA)				
0.1	4.8549	1437.03	0.1666	8988.05
0.2	4.7619	1449.40	0.1440	9101.54
0.3	4.7722	1449.40	0.1497	9163.82
0.4	4.8586	1441.04	0.1647	9039.25
0.5	4.9991	1429.78	0.1799	8977.82
0.6	5.0299	1430.80	0.1903	8926.62
0.7	5.0188	1441.79	0.1922	9050.34
0.9	4.7824	1465.87	0.1799	9156.25
1.0	4.6689	1484.47	0.1724	9175.88

PVA: Poly (vinyl alcohol)

specific acoustic impedance, *Z,* [14] were calculated using Equations 8, 9 and 10, respectively:

$$\beta_{ad} = 1/(u^2\rho) \tag{7}$$

$$Z = \rho u \tag{8}$$

Rao's constant, *R* of the isotropic solids was calculated as [15,16]:

$$R = \frac{Mu^{1/3}}{\rho}\left[\frac{1+v}{3(1-v)}\right]^{1/6} \tag{9}$$

Where, *M* and *v* are, respectively, molecular mass and Poisson's ratio for isotropic solids [17,18];

Calculated parameters of adiabatic compressibility, molar adiabatic compressibility and acoustic impedance at 35°C are presented in Table 3.

For further confirmation of the compatibility of these systems the acoustical derived properties such as adiabatic compressibility (β_{ad}), acoustic impedance (Z), relaxation strength (γs) and Rao Number (R) are calculated from the experimental data on density (ρ) and ultrasonic velocity (v),the data obtained are included in Table 3.

4. CONCLUSIONS

Using viscosity, density, ultrasonic velocity, and refractive index methods, it is concluded that the polymer blend of Pectin/PVA is found to be miscible when the Pextrin content is more than 50% at 35°C. Below this critical Pectin concentration, the blends were found to be immiscible. Hence from the above studies of Viscosity, ultrasonic velocity and Refractive index studies it is concluded that pectin/PVA blend is a miscible one.

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