Miscibility Studies of Sodium Alginate/Poly(vinyl alcohol) Blend in Water by Viscosity, Ultrasonic, and Refractive Index Methods

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ABSTRACT: The miscibility of a sodium alginate/poly(vinyl alcohol) blend in water was studied by viscosity, ultrasonic velocity, and refractive index techniques at 30, 40, and 50°C. Using the viscosity data, interaction parameters μ and α were computed. These values revealed that the blend is miscible when the sodium alginate content is more than 50% in the blend. This was further confirmed by ultrasonic and refractive index methods. It was further observed that the temperature has only a marginal effect on the miscibility of this blend. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 90: 33–39, 2003
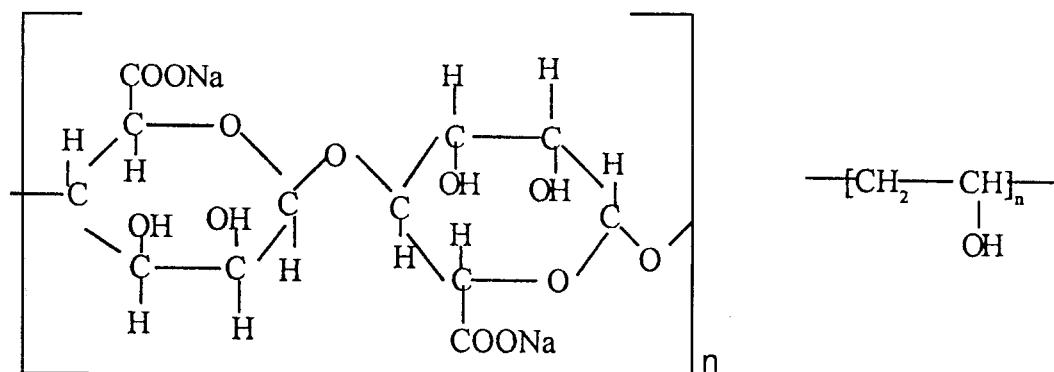
INTRODUCTION

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] There have been various techniques which are somewhat complicated, costly, and time-consuming for studying the miscibility of polymer blends.[5] Hence, simple, low-cost, and rapid techniques are of great importance in recent times to study the miscibility of polymer blends. Chee,[6] Sun et al.,[7] and Singh and Singh[8,9] suggested viscosity and ultrasonic velocity measurements for investigating polymer–polymer miscibility. Recently, Varada Rajulu et al.[10] studied polymer miscibility by ultrasonic and refreactive index methods. In this article, we studied the miscibility of sodium alginate (SA)/poly(vinyl alcohol) (PVA) blends in aqueous solutions at different temperatures by viscometric, ultrasonic velocity, and refractive index techniques.

The simplest fundamental unit of SA is related to cellulose and the structural configuration is better represented by two 1,4-linked residues of β-D-mannuronic acid. The sodium salt of this acid is water-soluble and forms a viscous liquid. The structures of both SA and PV$_A$ are represented as follows:

(a) Sodium Alginate   (b) Poly (vinyl alcohol)

EXPERIMENTAL

PVA ($\bar{M}_w \pm 14{,}000$; AR grade, Merck India Ltd., India) and SA [research grade, Thomas Baker (Chemicals) Ltd., Mumbai, India] were used for this work. A dilute polymer solution of 1% w/v was prepared for viscometric studies. Stock solutions of homopolmers and the blends of SA/PVA of different compositions, 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10, were prepared in water. Viscosity measurements at 30, 40, and 50°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.

The ultrasonic velocity measurements were made on 1% w/v SA/PVA solutions of 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10 at 30, 40, and 50°C using an ultrasonic interferometric technique.[11] The ultrasonic experimental cell has a double-walled jacket and thermostated water was circulated from a thermostat with a thermal stability of ±0.05°C. The experimental frequency was 2 MHz and the ve-

locity measurements were accurate to better than ±0.5%.

The refractive indices of the SA/PVA blend solutions were measured with an Abbe's refractometer and thermostated with a water-circulated system at 30, 40, and 50°C.[12] The accuracy of the refractive index measurement is ±0.02%.

RESULTS AND DISCUSSION

The reduced viscosity data for SA, PVA, and their blends at 30, 40, and 50°C are presented in Tables I–III, respectively. The Huggin's plots for the pure components and blends at 30, 40, and 50°C are presented in Figures 1–3, respectively. From these figures, it is clearly evident that, for the blend, the Huggin's curves are composed of two regions with varying slopes. Such an observation was also made by Haiyang et al.[13] in the case of a poly(vinyl chloride)/poly(ε-caprolactam) blend and reported that the blend was miscible.

TABLE I
Reduced Viscosity Data for SA, PVA,
and Their Blends in Water at 30°C

Concentration	SA	PVA	1% w/v SA/PVA blend solution at 30°C		
			90/10	70/30	50/50
1.0000	11.4119	1.1264	9.6531	7.6666	5.7931
0.9090	10.9060	1.0495	8.9526	7.1544	5.4526
0.8000	10.6150	1.0057	8.4482	6.8965	5.3155
0.7000	9.9417	0.9524	7.9474	6.5517	5.0082
0.6000	9.6274	0.9003	7.4563	6.3302	4.7934
0.5000	9.1058	0.8505	7.0804	5.9310	4.6666
0.4000	8.6294	0.7764	6.6379	5.6896	4.4252
0.3000	8.2353	0.7279	6.5134	5.5172	4.2528
0.2000	7.7058	0.7184	6.6666	5.8195	4.6850
0.1086	7.2581	0.6550	7.0913	6.1562	5.0803

TABLE II
Reduced Viscosity Data for SA, PVA,
and Their Blends in Water at 40°C

Concentration	SA	PVA	1% w/v SA/PVA blend solution at 40°C		
			80/20	60/40	40/60
1.0000	10.6438	1.0137	7.8219	6.3151	4.7534
0.9090	10.2777	0.9494	7.4458	5.9978	4.5210
0.8000	9.7431	0.9075	7.1575	5.7534	4.3493
0.7000	9.3542	0.8510	6.8297	5.5189	4.2074
0.6000	9.0411	0.8219	6.5068	5.3196	3.9954
0.5000	8.5205	0.7671	6.2465	5.0137	3.8630
0.4000	8.0822	0.7191	5.9246	4.8287	3.6643
0.3000	7.7169	0.6849	5.8447	4.7611	3.7443
0.2000	7.2603	0.6164	5.9589	4.9315	3.9041
0.1086	6.8114	0.5045	6.1808	5.1716	4.1625

TABLE III
Reduced Viscosity Data for SA, PVA,
and Their Blends in Water at 50°C

Concentration	SA	PVA	1% w/v SA/PVA blend solution at 50°C		
			80/20	60/40	40/60
1.0000	9.6513	0.9193	7.4645	5.2749	4.2903
0.9090	9.2267	0.8517	7.1329	5.0392	4.086
0.8000	8.8048	0.8266	6.7358	4.9195	3.9314
0.7000	8.5253	0.7834	6.4055	4.7235	3.8479
0.6000	8.1451	0.7526	6.2365	4.5699	3.629
0.5000	7.7419	0.7096	5.8709	4.3548	3.4581
0.4000	7.4193	0.6854	5.5645	4.1532	3.3483
0.3000	7.0968	0.5914	5.6451	4.2473	3.4946
0.2000	6.6935	0.5645	5.7258	4.4354	3.629
0.1086	6.3862	0.5198	5.8089	4.6041	3.8614

To quantify the miscibility of the polymer blends, Chee[6] 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 $\bar{b} = w_1 b_1 + w_{22}$, 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

$$b = w_t^2 b_{11}^2 + w_2^2 b_{22}^2 + 2w_1 w_2 b_{12} \tag{3}$$
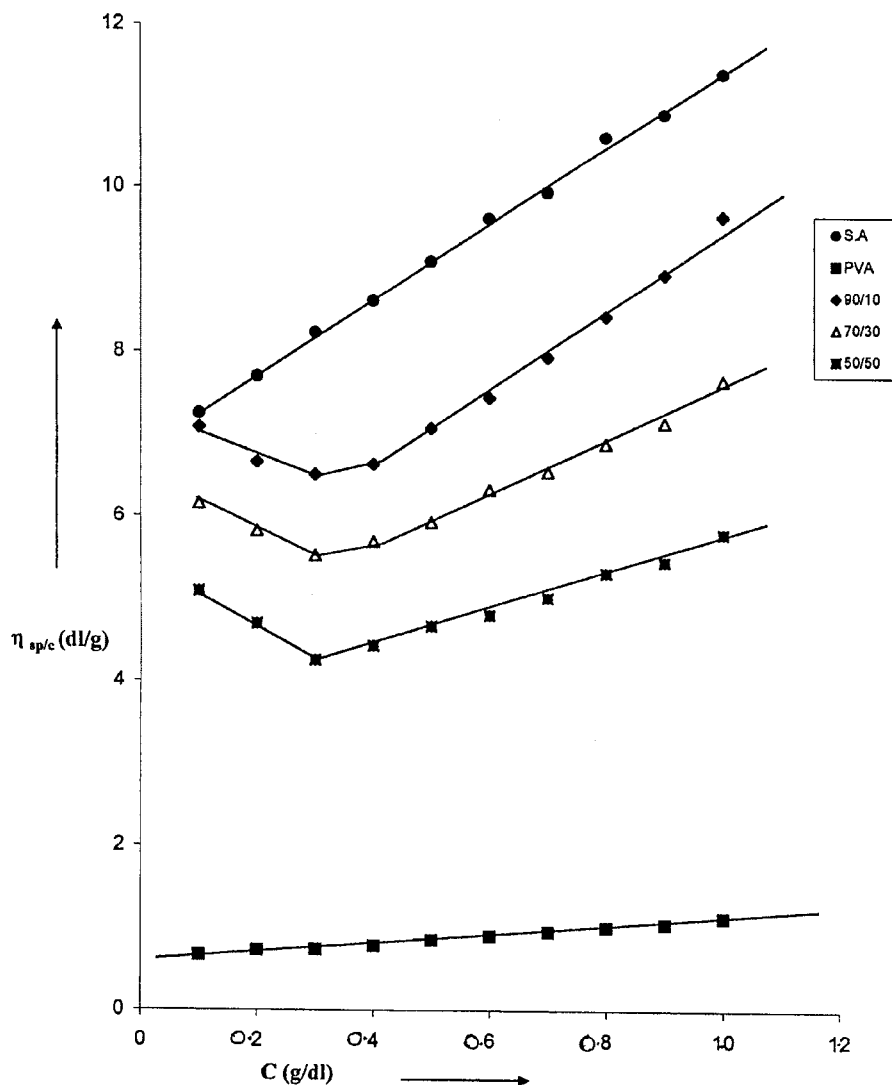
where b_{12} is slope for the blend solution.

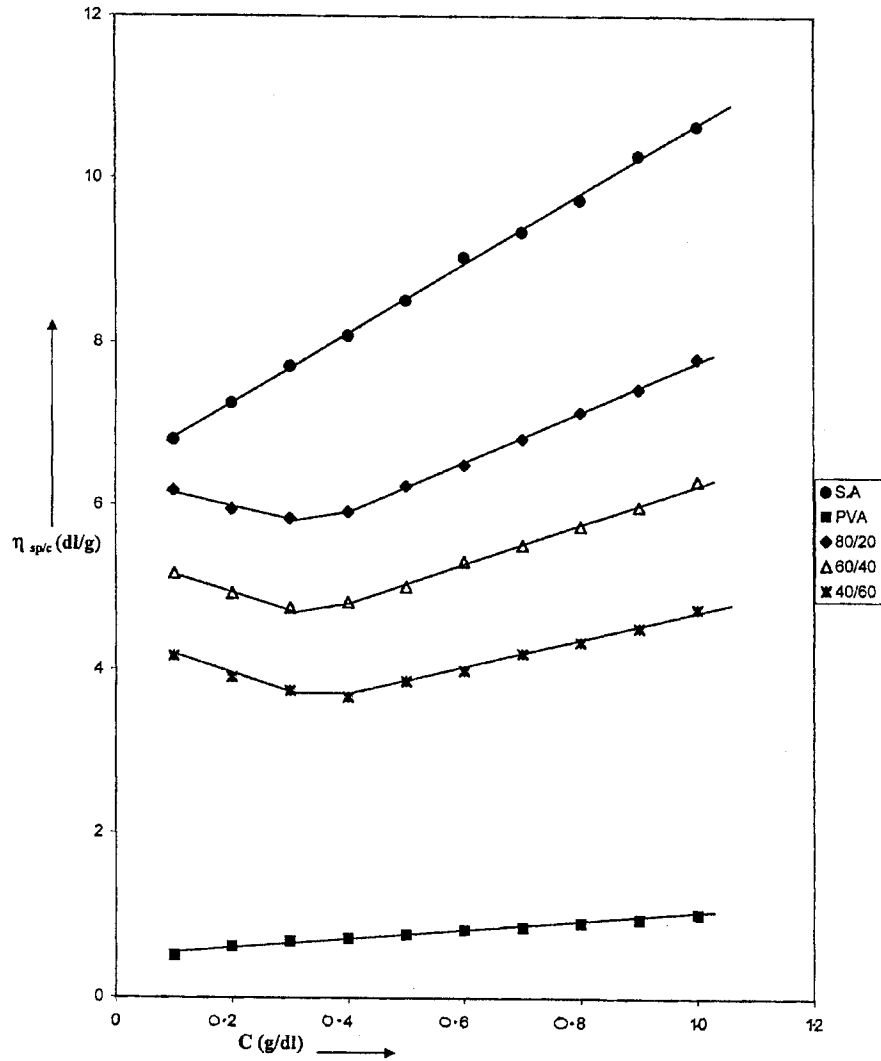**Figure 1** Huggin's plot for 1% w/v SA/PVA blend in water at 30°C.

Figure 2   Huggin's plot for 1% w/v SA/PVA blend in water at 40°C.

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

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

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.[7] suggested a most satisfactory new equation for the determination of polymer miscibility as

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

$$(5)$$

where K_1, K_2, and Km 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 $\alpha < 0$.

The computed values of the μ values are negative when the alginate content is to 60% and then positive beyond this value. However, α is found to be positive when the SA content is more than 50% at 30°C and more than 40% at 40 and 50°C, (Table IV). As the secondary interactions are considered in the equation for α, eq. (5) is more accurate than is eq. (4). Hence, it can be stated that the blend of SA/ PVA is miscible when the SA content is more than 50%. The reduced viscosity data for a 50/50% wt composition of the SA/PVA blend at different temperatures are presented in Table V. Figure 4 shows
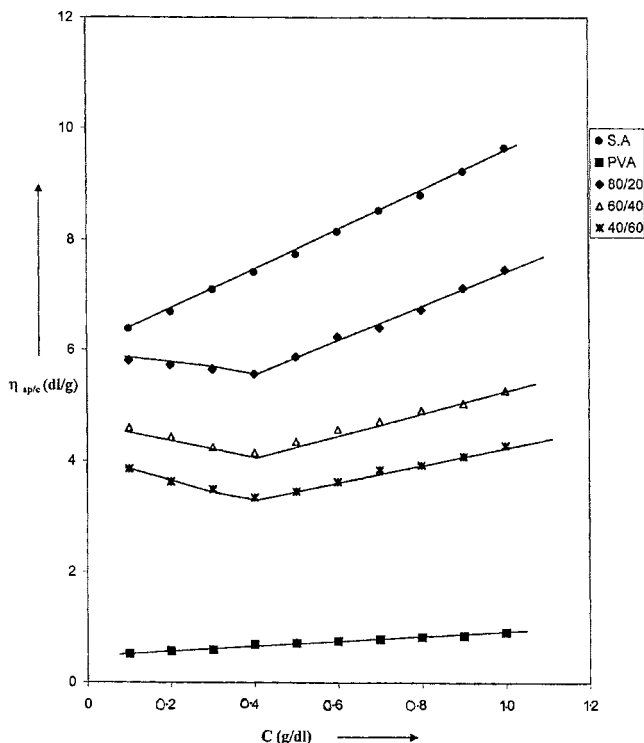
Figure 3 Huggin's plot for 1% w/v SA/PVA blend in water at 50°C.

the variation of the reduced viscosity with the concentration at different temperatures and it is evident that the reduced viscosity decreases as the temperature increases.

To confirm this further, the authors measured the ultrasonic velocity and refractive index of the blend under consideration at various compositions at 30, 40, and 50°C. These values are presented in Table VI. The variation of the ultrasonic velocity and refractive index with the blend composition is shown

TABLE V
Reduced Viscosity Data for 50/50 % wt SA/PVA Blend in Water at Different Temperatures

Concentration	SA/PVA blend in aqueous solution of 50/50 composition		
	At 30°C	At 40°C	At 50°C
1.0000	5.7931	5.3598	4.8019
0.9090	5.4526	5.1388	4.6161
0.8000	5.3155	4.9315	4.4556
0.7000	5.0082	4.7553	4.2067
0.6000	4.7934	4.5205	4.1398
0.5000	4.6666	4.3013	3.9677
0.4000	4.4252	4.1096	3.7096
0.3000	4.2528	4.0634	3.8709
0.2000	4.6850	4.4521	4.1129
0.1086	5.0803	4.7932	4.3070

in Figures 5 and 6, respectively. The graphs show both linear and nonlinear regions. It was already established[14,15] that the variation is linear for miscible and nonlinear for immiscible blends. In the present case, the variation is found to be linear when the SA content is more than 50% at 30°C and 40% at 40 and 50°C. This observation is in conformity with the μ and α values. So, the present study indicates the existence of miscibility windows when the SA content is more than 50%. It may be due to some specific interaction like H-bonding to some extent between SA and PVA.

CONCLUSIONS

Using viscosity, ultrasonic velocity, and refractive index methods, it is concluded that the polymer blend of SA/PVA is found to be miscible when the SA content is more than 50% at 30°C and the temperature effect is only marginal at 40 and 50°C. Below this critical SA concentration, the blends were found to be immiscible.

TABLE IV
Interaction Parameters μ and α of SA/PVA Blend in Water of Different Composition at 30, 40, and 50°C

| Composition SA/PVA	At 30°C		At 40°C		At 50°C	
	μ	α	μ	α	μ	α
10/90	−0.0474	−0.3128	−0.0517	−0.4116	−0.0514	−0.6699
20/80	−0.0497	−0.2070	−0.0487	−0.1904	−0.0457	−0.2554
30/70	−0.0412	−0.0619	−0.0374	−0.0439	−0.0417	−0.0540
40/60	−0.0273	−0.0312	−0.0188	0.0056	−0.0146	0.0059
50/50	−0.0140	0.0053	−0.0083	0.0296	−0.0096	0.0134
60/40	−0.0010	0.0125	0.0010	0.0233	−0.0059	0.0148
70/30	0.0128	0.0351	0.0119	0.0301	0.0102	0.0178
80/20	0.0069	0.0021	0.0220	0.0219	0.0292	0.0250
90/10	0.0380	0.0513	0.0476	0.0580	0.0480	0.0449
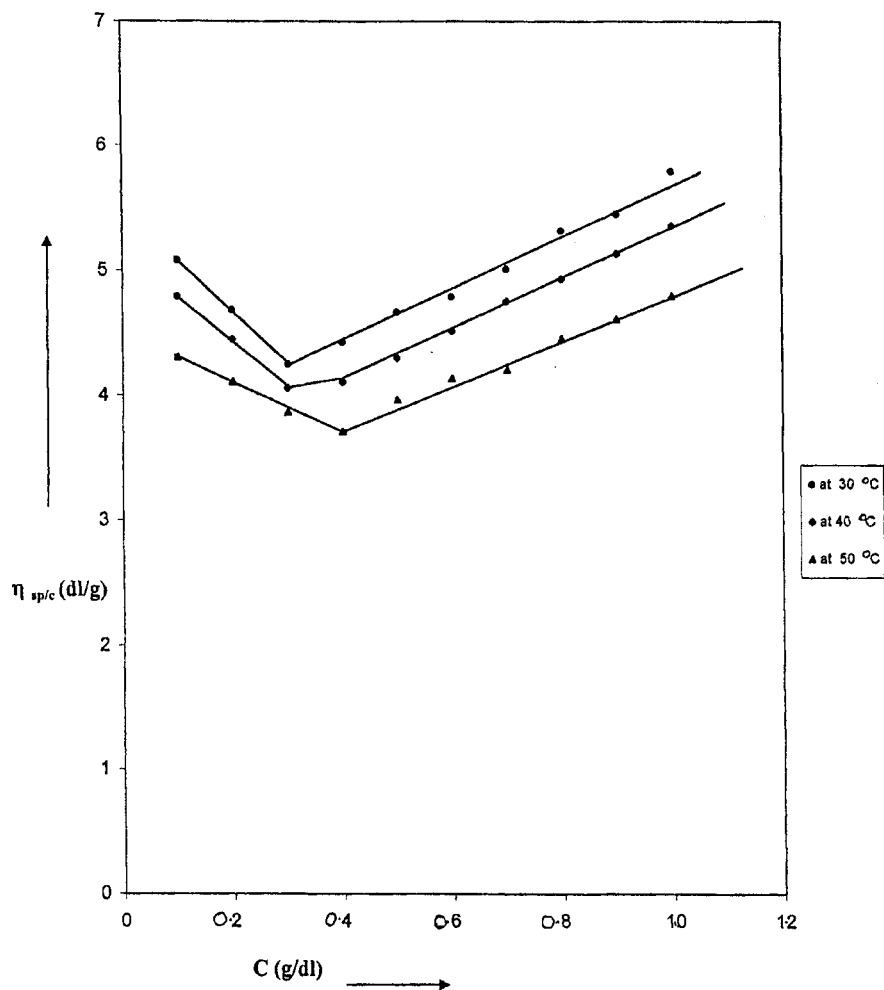
Figure 4 Effect of temperature on the reduced viscosity with concentration for 50/50 % wt composition of 1% w/v SA/PVA blend solution.

TABLE VI
Ultrasonic Velocity and Refractive Index Data for SA/PVA Blend in Water at Different Temperatures

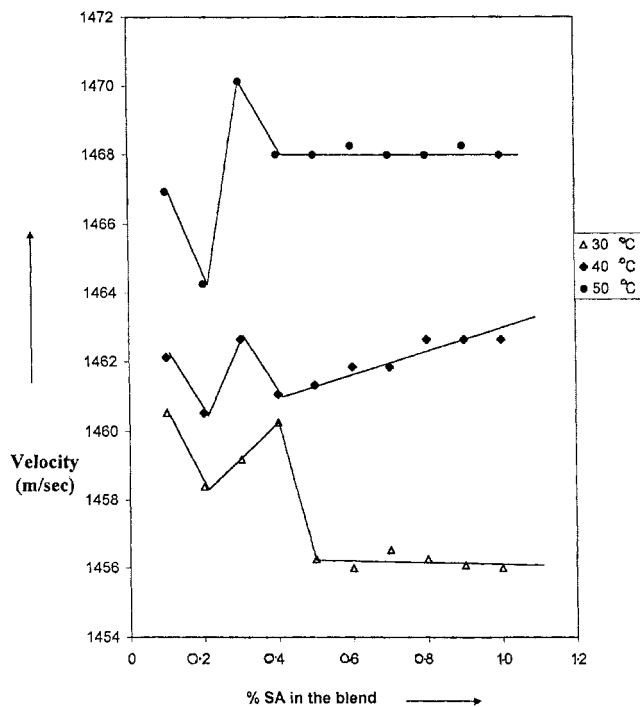| % Wt composition SA/PVA	Ultrasonic velocity (m/s)			Refractive index		
	30°C	40°C	50°C	30°C	40°C	50°C
10/90	1460.53	1462.13	1466.93	1.3410	1.3405	1.3400
20/80	1458.40	1460.53	1464.26	1.3405	1.3400	1.3390
30/70	1459.20	1462.66	1470.13	1.3410	1.3405	1.3395
40/60	1460.26	1461.06	1468.00	1.3415	1.3410	1.3400
50/50	1456.26	1461.33	1468.00	1.3420	1.3410	1.3400
60/40	1456.00	1461.86	1468.26	1.3420	1.3410	1.3400
70/30	1456.53	1461.86	1468.00	1.3420	1.3410	1.3400
80/20	1456.26	1462.66	1468.00	1.3420	1.3410	1.3400
90/10	1456.08	1462.66	1468.26	1.3420	1.3410	1.3400
100/0	1456.00	1462.66	1468.00	1.3420	1.3410	1.3400

Figure 5 Effect of temperature on the variation of ultrasonic velocity with composition of 1% w/v SA/PVA blend solution.
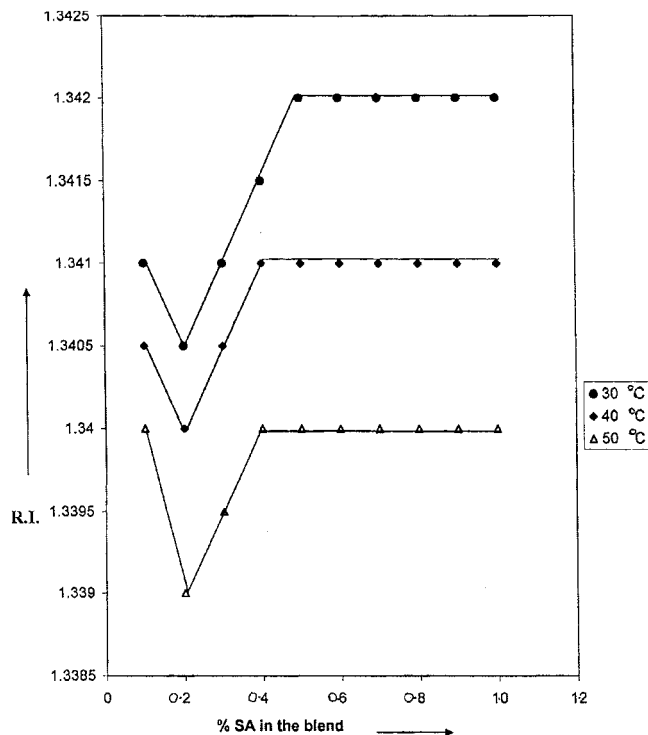

Figure 6 Effect of temperature on the variation of refractive index with composition of 1% w/v SA/PVA blend solution.

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