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Viscosity, Ultrasonic, Refractometric and Morphological Studies of Pullulan/Gelatin Blends

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ABSTRACT

Measurements of Viscosity, Ultrasonic velocity, Refractive Index and SEM Studies of Pullulan/Gelatin blends in water were carried out for different blend compositions at 30^{0}C and 40^{0}C. The properties like Thermal degradation, Biodegradability, Drug releasing capacity and Durability of polymers can be enhanced by blending a polymer with another polymer. The Miscibility and Compatibility are the two important parameters for the polymer blend studies. Using the viscosity data, interaction parameters μ and α were computed to determine miscibility. These values revealed that Pullulan/Gelatin blends were immiscible over the entire composition range studied at 30^{o}C and 40^{o}C. SEM analysis also supported the same. The results were further confirmed by ultrasonic velocity, Refractive index measurements, and Morphological Studies. Physico mechanical properties of Pullulan / Gelatin blend films show poorer qualities.

Keywords: Pullulan, Gelatin, Miscibility, Blends Compositions, SEM and other measurements.

INTRODUCTION

The name "pullulan" was proposed by Bender, who was the first to describe the formation of this extracellular polysaccharide by Aureobasidium pullulans (syn. Pullularia pullulans). It is essentially a linear polymer of repeating maltotriose units linked by α -1,6 glycosidic bonds. Depending upon the culture conditions (duration, pH, phosphate concentration, etc.) under which this extra-cellular glucan is elaborated by Aureobasidium pullulans, the molecular weight varies from about 10 to 3000 kDa. The commercially available pullulan (Pullulan PI-20) has a purity of more than 90 %. Its average molecular weight (at peak of a gel permeation chromatogram) is about 200 kDa. The main impurities are mono-, di- and oligosaccharides, which are carried over from the raw material hydrolysed starch) into the final product. The specifications for pullulan include standard parameters for identification and for chemical and microbiological purity.

The film-forming properties of pullulan are the basis for its proposed use as a substitute for gelatin in the production of capsule shells (for dietary supplements), as an ingredient of coated tablets (dietary

supplements), and as an ingredient of edible flavoured films (breath fresheners). It has been used as an additive and as a food ingredient in Japan since 1976. Polymer blends are physical mixtures of structurally different polymers that interact through secondary forces with no covalent bonding. The importance of blending is because of its tailor made properties from those of the constituent polymers [1, 2]. Blending of polymers may result in reducing their basic cost, improving their processing and maximizing their important properties. The improvement in properties of the blend depends on the degree of compatibility or miscibility of the polymers at the molecular level. Depending upon the degree of molecular mixing, blends can be compatible, semi compatible or incompatible. There have been various techniques of studying the miscibility of polymer blends. Chee and Sun [3, 4] et al. suggested the viscometric methods for the study of miscibility of polymer blends. VaradaRajalu et al [5, 6]. Studied the variation of ultrasonic velocity, Refractive index and viscosity measurements. They have shown that the variation of ultrasonic velocity, viscosity and refractive index with blend composition is linear for miscible blends and non linear for immiscible blends. In the present work, the blend solutions were studied using the above techniques as they are of low cost, simple and rapid. Pullulan, an extracellular polysaccharide produced by certain strains of the polymorphic fungus Aureobasidium pullulan [7] and Gelatin were selected for the present study in view of their applications in food industry, pharmaceuticals and cosmetics [8-10]. Using viscosity data, the interaction parameters μ and α based on Chee and Sun et al. approaches were determined. Further, ultrasonic velocity, Refractive index and SEM for the above blends have also been studied.

MATERIALS AND METHODS

Pullulan [research grade, Nutriscience Innovations, USA], PVA [Mw = 14, 00; AR grade Merck (India], Gelatin research grade Merck grade were used in present study.

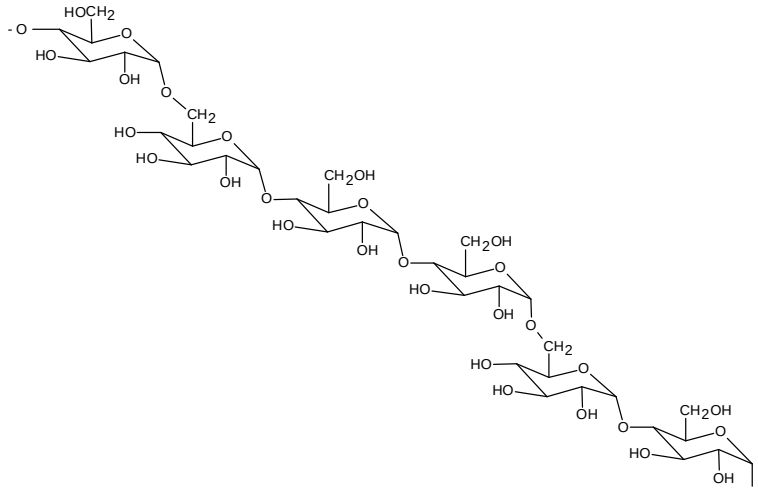


Figure-1: Chemical structure of a representative portion of Pullulan.

A dilute solution of 2%w/v of homopolymers were prepared and blended in different compositions like 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90.Viscosity at 30^0C and 40^0C were determined using Ubbelohde suspended level Viscometer [11-13]. The required temperature was maintained in thermostat bath with thermal stability of ±0.5 degree centigrade. Ultrasonic experimental cell has doubled-walled jacket and thermostated water circulated in it [14]. The experimental frequency was 2 MHz and the velocity measurements were accurate to better than ±0.5%. Refractive indices of the blend solutions were measured with an Abbe's Refractometer [15-16] and the accuracy of the refractive index measurements is ±0.02%. Mechanical properties like tensile strength, % elongation, burst strength and density of the prepared films were studied for Pullulan / Gelatin blends.

RESULTS AND DISCUSSION

The miscibility of Pullulan / Gelatin blends was studied in detail by using the equations suggested by Chee[3] and Sun[4] et al. The computed interaction parameter μ and α value for Pullulan / Gelatin blend are presented in the Table-3. Based on the variation of slope of Huggin's curves and more accurate parameter α, the conclusions were taken for the blends miscibility.

To quantify the miscibility of the polymer blends Chee suggested a general expression for the interaction parameter when polymers are mixed in weight fractions w1 and w2 as

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

Where $\bar{b}=w_1 b_{11}+w_2 b_{22}$, in which b_{11} and b_{22} are slope of the viscosity curves for the pure components. The coefficient b is related to Huggins's coefficient k_H as

$$b = k_H[\eta]^2$$

For ternary systems, the coefficient b is also given by

$$b = w_1^2 b_{11} + w_2^2 b_{22} + 2w_1 w_2 b_{12}$$

Where b_{12} is slope of the blend solution. Does it mean: Using the above expressions, Chee *et al* derived a more effective interaction parameter, defined as

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

Where $[\eta]_1$ and $[\eta]_2$ are the intrinsic viscosities for the pure component solutions. The blend is miscible when $\mu \geq 0$ and immiscible when $\mu < 0$ .The values of μ are calculated with the preceding expression at 30^0C and 40^0C are represented in the table-3.

Recently Sun et al. suggested a new formula for the determination of polymer miscibility as follows

$$k_m^1 = \frac{k_1[\eta]_1^2 w_1^2 + k_2[\eta]_2^2 w_2^2 + 2\sqrt{k_1 k_2[\eta]_1[\eta]_2 w_1 w_2}}{\{[\eta]_1 w_1 + [\eta]_2 w_2\}^2}$$

$$k_m = \frac{slope\ of\ concentration\ \text{v/s}\ reduced\ viscosity\ curve\ for\ the\ blend\ solution}{intrinsic\ viscosity\ of\ the\ polymer\ blend\ solution}$$

$$\alpha = k_m - k_m^1$$

Where k1, k2 and km are the Huggin's constants for individual components 1, 2, and the blend respectively. The long-range hydrodynamic interactions were considered while deriving this equation. Sun et al. suggested that a blend will be miscible when $\alpha \geq 0$ and immiscible when $\alpha < 0$.

Table-1: Reduced viscosity data for Pullulan/Gelatin and their blends in water at 30^0C.

Concentration in g/dm^3	$\eta_{sp/C}$ (dL/g at 30°C)										
	Pullulan	Gelatin	Pullulan / Gelatin								
			90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.2	0.859	0.550	0.805	0.78	0.75	0.72	0.67	0.63	0.62	0.60	0.590
0.4	0.903	0.561	0.860	0.84	0.78	0.75	0.70	0.65	0.63	0.61	0.590
0.6	0.958	0.561	0.920	0.88	0.82	0.77	0.73	0.66	0.65	0.61	0.600
0.8	1.016	0.563	0.980	0.93	0.86	0.80	0.75	0.68	0.66	0.62	0.600
1.0	1.100	0.563	1.050	0.99	0.89	0.83	0.78	0.70	0.68	0.62	0.610
1.2	1.197	0.560	1.110	1.03	0.93	0.86	0.82	0.72	0.69	0.63	0.610
1.4	1.250	0.570	1.160	1.08	0.96	0.89	0.85	0.73	0.70	0.63	0.615
1.6	1.320	0.570	1.230	1.14	1.00	0.92	0.88	0.75	0.72	0.64	0.620
1.8	1.390	0.570	1.300	1.19	1.04	0.95	0.91	0.77	0.74	0.64	0.625
2.0	1.450	0.580	1.360	1.24	1.08	0.98	0.94	0.79	0.75	0.65	0.630

Table-2: Reduced viscosity data for Pullulan/Gelatin and their blends in water at 40^0C.

Concentration (g/dm^3)	$\eta_{sp/C}$ (dL/g at 40^oC)										
	Pullulan	Gelatin	Pullulan / Gelatin								
			90/10	80/20	70/30	60/40	50/50	40/60	30/70	20/80	10/90
0.2	0.70	0.380	0.65	0.60	0.58	0.53	0.50	0.470	0.44	0.41	0.400
0.4	0.77	0.390	0.72	0.66	0.62	0.57	0.54	0.490	0.46	0.42	0.410
0.6	0.84	0.400	0.79	0.72	0.67	0.615	0.58	0.525	0.485	0.44	0.420
0.8	0.91	0.410	0.85	0.78	0.73	0.66	0.61	0.535	0.50	0.45	0.430
1.0	0.98	0.415	0.91	0.84	0.78	0.70	0.66	0.560	0.52	0.46	0.435
1.2	1.04	0.425	0.98	0.96	0.84	0.74	0.69	0.580	0.54	0.48	0.440
1.4	1.11	0.430	1.04	1.02	0.90	0.79	0.74	0.600	0.56	0.49	0.450
1.6	1.18	0.440	1.11	1.14	0.95	0.84	0.77	0.620	0.58	0.50	0.465
1.8	1.25	0.450	1.17	1.08	1.01	0.88	0.81	0.640	0.60	0.52	0.475
2.0	1.32	0.455	1.24	1.14	1.06	0.92	0.85	0.607	0.62	0.53	0.490

Table-3: Refractive index, Ultrasonic velocity, μ and α for Pullulan/Gelatin blend in water at 30^oC and 40^oC

Blend composition	Refractive index		Ultrasonic velocity (m/s)		μ		A	
	At 30^oC	At 40^oC	At 30^oC	At 40^oC	At 30^oC	At 40^oC	At 30^oC	At 40^oC
90/10	1.340	1.334	1497.2	1505.5	18.880	20.860	-0.046	-0.263
80/20	1.345	1.339	1499.6	1505.7	13.930	17.620	-0.045	-0.280
70/30	1.343	1.339	1496.4	1511.6	8.130	5.606	-0.104	-0.037
60/40	1.340	1.335	1498.8	1509.0	5.030	3.870	-0.442	-2.111
50/50	1.344	1.329	1495.2	1506.7	8.180	4.491	-0.182	-0.725
40/60	1.343	1.335	1497.2	1508.4	1.860	1.873	-0.060	-1.133
30/70	1.345	1.338	1498.8	1510.0	0.950	1.850	-0.067	-1.374
20/80	1.341	1.336	1496.4	1707.7	0.330	3.147	-0.196	-1.396
10/90	1.345	1.333	1499.9	1511.2	0.398	7.185	-0.147	-1.555

Table- 4: Physico-Mechanical properties of pullulan, gelatin and pullulan/gelatin blends.

Blend Composition	Tensile Strength (MPa)	% Elongation at break	Tear Strength (N)	Burst Strength (kg/cm^2)	Density (g/ml)
Pullulan	15.09±1.04	3.00±0.34	0.0093	0.6	1.32±0.01
90/10	12.73±0.98	3.03±0.67	0.0092	0.5	1.27±0.02
80/20	10.00±0.74	3.00±0.58	0.0085	0.4	1.32±0.01
70/30	7.32±1.50	2.43±1.20	0.0034	0.45	1.28±0.09
60/40	8.45±1.40	2.50±1.00	0.0028	0.4	1.25±0.08
50/50	7.00±1.00	2.00±0.45	0.0029	0.31	1.26±0.06
40/60	8.10±0.78	1.78±0.38	0.0035	0.28	1.26±0.04
30/70	8.30±0.56	1.70±0.52	0.0051	0.32	1.23±0.02
20/80	8.29±0.37	1.23±0.51	0.0047	0.30	1.216±0.04
10/90	8.74±0.23	1.22±0.21	0.0048	0.29	1.19±0.01
Gelatin	9.08±0.25	1.09±0.006	0.0051	0.34	1.28±0.009

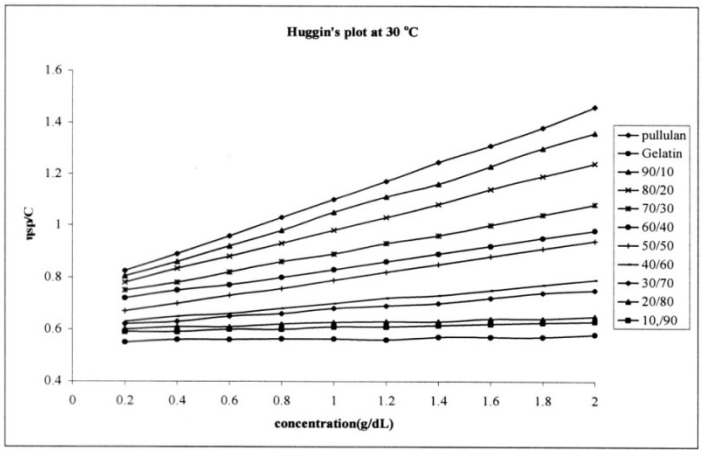


Figure1. Huggin's plot for Pullulan / Gelatin 2%(w/v) blend at 30^0C.

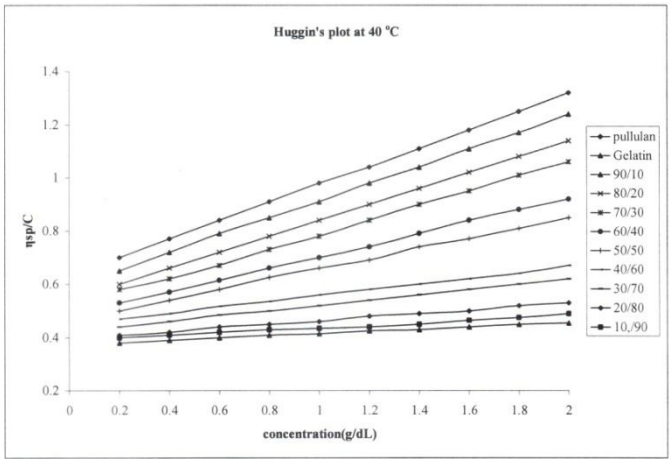


Figure 2. Huggin's plot for Pullulan / Gelatin 2%(w/v) blend at 40^0C.

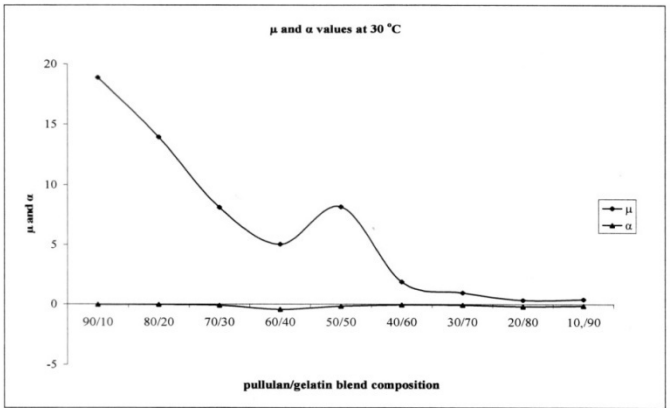


Figure 3. Variation of μ and α with composition of Pullulan/Gelatin in water at 30^oC.

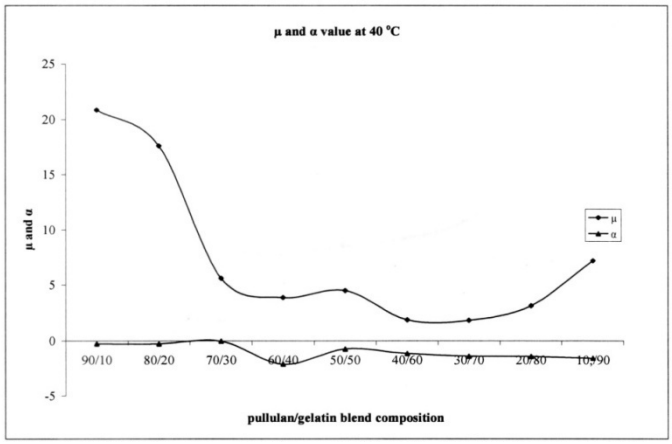


Figure 4. Variation of μ and α with composition of Pullulan/Gelatin in water at 40°C.

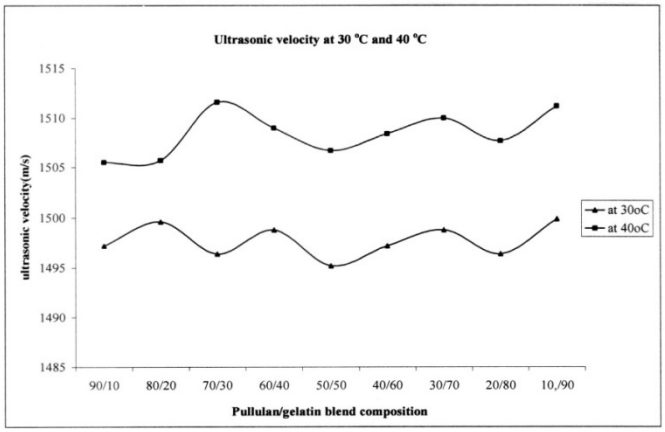


Figure 5. Variation of ultrasonic velocity with composition of 2% w/v of Pullulan/Gelatin blend in water at 30°C & 40°C.

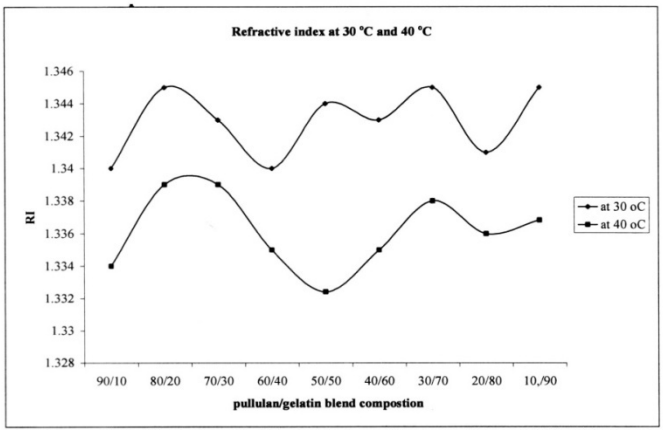
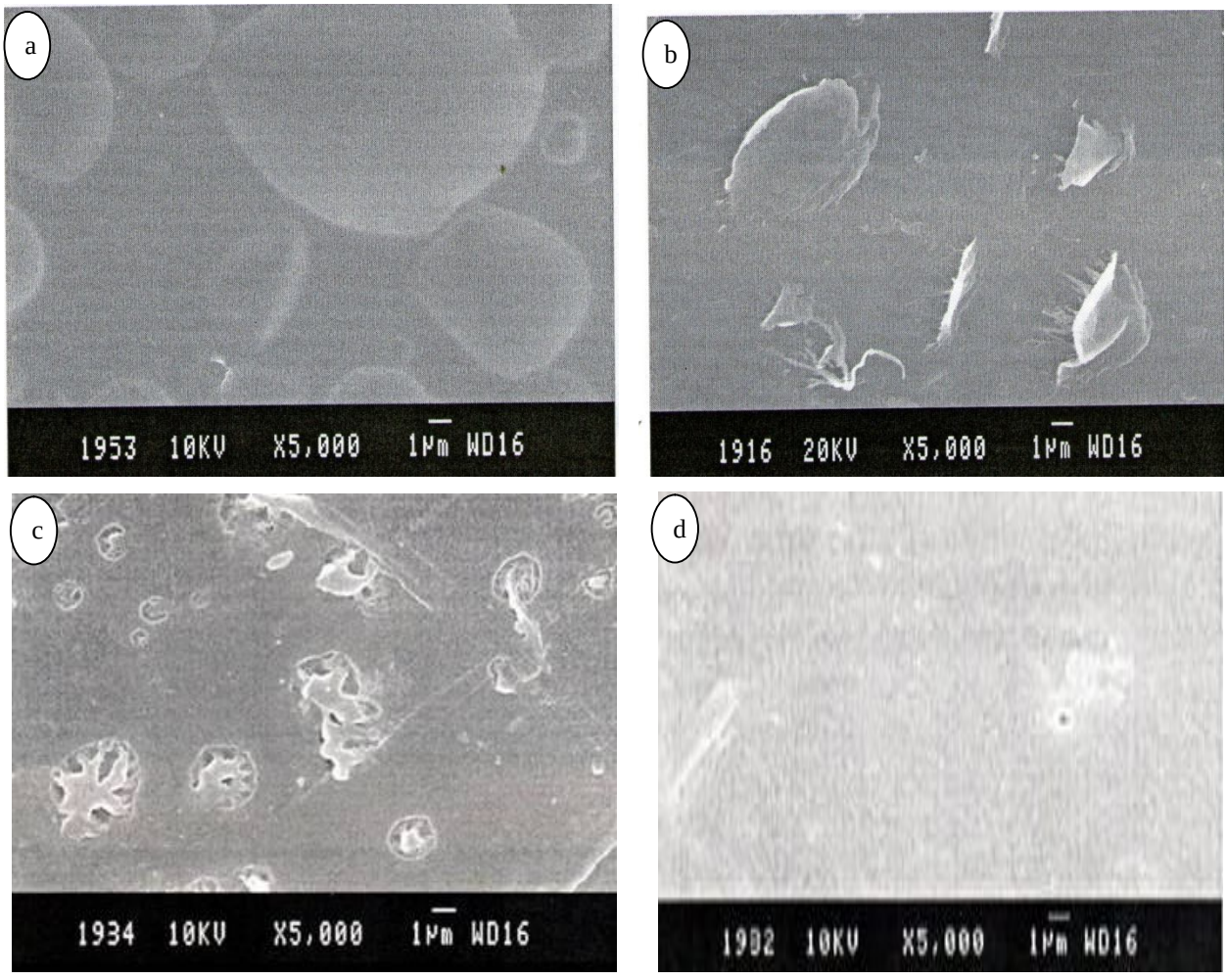


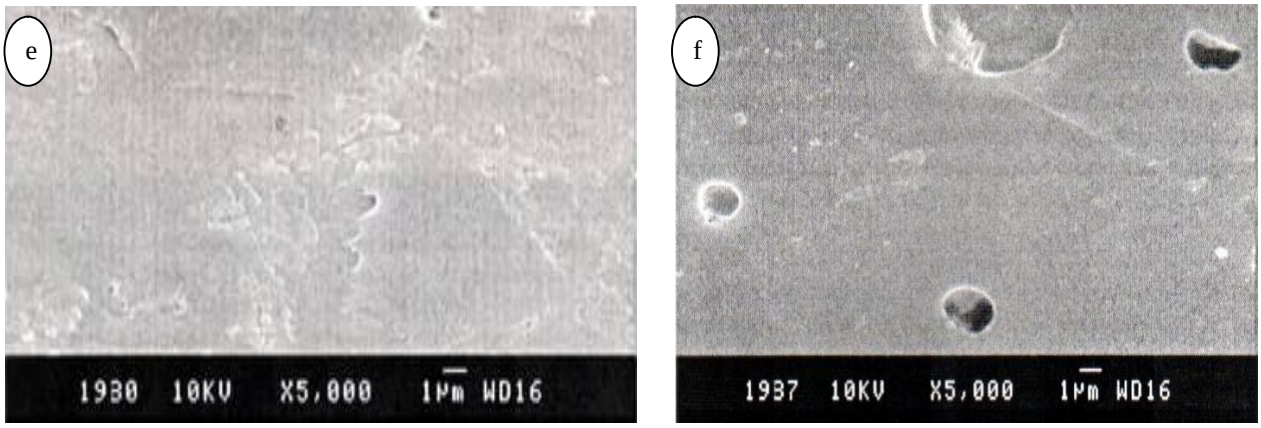
Figure 6. Variation of refractive index with composition of 2% w/v of Pullulan/Gelatin blend in water at 30°C & 40°C.

The μ values for Pullulan/Gelatin blends are positive for all the compositions [17]. But α value are found to be negative for every composition range. Hence μ and α give contradictory information, the Pullulan/Gelatin blends are immiscible over the entire composition range. From the tables 1 and 2, it is evident that the reduced viscosity decreases as the temperature increases. The reason may be due to the

progressive decrease in viscosity caused by a partial depolymerisation of the polymer chain at higher temperature for extended periods. The variation evaluated interaction parameters μ and α, at different temperatures also shows that there is no effect of temperature to the miscibility of the polymer blends. It is shown in figures 3 and 4. Hence Pullulan/Gelatin blends are semi-compatible at different temperatures. These conclusions are confirmed by ultrasonic velocity, refractive index, density studies which are presented in table 3 and figures 5 and 6.

Ultrasonic velocity and refractive index studies are used as supporting analytical data for viscosity studies in order to confirm exact nature of blends [18-20]. The ultrasonic velocity and refractive index were determined. The values are presented in the table 3 and figures 5 and 6 for Pullulan / Gelatin. These graphs show only non-linear regions over all the composition range and it is already established that the variation is linear for miscible and non-linear for immiscible blends. In the present investigation, the non-linearity in the graphs indicates the immiscibility of both the blends due to the phase separation at 30^{o}C as well as 40^{o}C. The non-linearity in the graphs may be due to the absence/insufficient H – bonding of Gelatin with pullulan. These observations are in conformity with α values based on Sun et al method. Hence, present investigation indicates that the Pullulan / Gelatin blends at 30^{o}C and 40^{o}C are completely immiscible over the entire composition range. Since there is no change in nature of blend of Pullulan/ Gelatin at different temperature [21], it can be stated that there is no effect of temperature.





Figures 7(a-f): SEM Photographs of Pullulan /Gelatin blends at 5000 magnification.
a) PVA b) Pullulan c) Pullulan/Gilatine (30/70) d) Pullulan/Gilatine (70/30)
e) Pullulan/Gilatine (20/80) and f) Pullulan/Gilatine (80/20)

Pullulan (2% w/v), Gelatin (2% w/v) solutions were prepared in distilled water. Pullulan / Gelatin blend films of different compositions - 90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90 were prepared by mixing the aqueous solutions and then the solution was poured onto the clean leveled glass plate (30x20 cm) and allowed to dry over night at room temperature. Later the film was peeled off from the plate and conditioned and stored at room temperature before the various properties were studied [22-24]. Mechanical properties like tensile strength, % elongation, burst strength and density of the prepared films were evaluated and are presented in the table 4 for Pullulan / Gelatin. From the table 4, it is evident that the tensile strength and % elongation increases with the pullulan content in the blend [25]. Density, tear strength and burst strength of the blend films increases slightly with pullulan content, but there is no much variation.

For further confirmation SEM(scanning electron microscopy) were also carried out for 70/30,30/70,20/80 and 80/20 compositions of the blend.SEM photomicrographs of pure Pullulan / Gelatin along with their blends at 5000 magnification is given in figure-7. Pullulan / Gelatin 20/80 blend photomicrograph revealed the improper distribution of the monomers [26-28]. Hence SEM studies also support the results obtained by viscosity, ultrasonic and refractive index studies. That is Pullulan / Gelatin blend is immiscible.

APPLICATIONS

The properties like Thermal degradation, Biodegradability, Drug releasing capacity and Durability of polymers can be enhanced by blending a polymer with another polymer. The Miscibility and Compatibility are the two important parameters for the polymer blend studies. The results are useful from Physico mechanical properties to know the blending qualities.

CONCLUSIONS

During the studies of Pullulan / Gelatin based on the viscosity, ultrasonic viscosity and refractive index measurements, it is concluded that the blends - Pullulan / Gelatin at different concentrations are found to be immiscible at 30^{o}C and 40^{o}C. SEM analysis also supports the same. Physico mechanical properties of Pullulan / Gelatin blend films show poorer qualities. The above study reveals that the Pullulan / Gelatin blends are immiscible and are non-compatible.

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