Asian Journal of Chemistry; Vol. 32, No. 2 (2020), 260-264

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2020.22316

# Viscosity, Miscibility Studies and Mechanical Properties of Pullulan/Poly(vinyl alcohol) Blends at 30 ºC and 40 ºC

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*Received*: 7 July 2019; *Accepted*: 3 August 2019; *Published online*: 30 December 2019; AJC-19709

The miscibility studies of pullulan and poly(vinyl alcohol) (PVA) blends by reduced viscosity measurements, refractometry, mechanical properties and SEM analysis. Viscometric measurements at 30 and 40 ºC were taken using Ubbelohde viscometer. Ultrasonic interferometric was used to measure the ultrasonic velocities of different blend compositions. Refractive indices of blend solutions with different compositions were measured directly with an Abbe′s refractometer with thermostat containing water circulated at 30 and 40 ºC. The mechanical properties, refractive index, ultrasonic velocity and density studies showed that there is an increase of all these with PVA content in the blends. But SEM studies have given an indication of immiscibility in the blend system. Overall, pullulan/PVA blends have shown good physical and mechanical properties particularly for 90/10 composition.

**Keywords: Pullulan, Poly(vinyl alcohol), Blend composition, Viscosity, Miscibility.**

## INTRODUCTION

Blended mixtures of structurally different polymers are technologically and scientifically very important [1] because they posses reduced basic cost and improved processing. They also enable to maximize valuable properties. Adhesion between the polymers is provided by the presence of chemically grafted units, in blends. Some polymers can form interacting product without a chemical graft. Hydrogen bonding which is a weaker secondary force plays a dominant role in such cases [2].

Pullulan, a polysaccharide polymer consisting of maltotriose units, also known as α-1,4-; α-1,6-glucan, generally used for producing film binders, adhesives, thickeners, viscosity improvers, coating agents and gene delivery carriers because of its oxygen impermeability, non-toxic and non-irritating properties [3]. A number of potential applications of pullulan may be improved and extended by introducing functional groups. Chemical modification of maltotriosyl unit of pullulan can be performed to procure tailored derivatives as it contains nine hydroxyl groups in a geometrically unique environment. By this way, one can synthesize products of a broad structural diversity. Several publications, particularly patents are reported about variety of pullulan derivatives [4-13]. Amphiphilic polymers undergo intramolecular microphase separation and form self assembled aggregates with ordered supramolecular architectures.

Chemically, poly(vinyl alcohol) can be classified broadly as a polyhydric alcohol with secondary hydroxyl groups on alternate carbon atoms. The changes in product properties- thus changes in application utility, which can be controlled in the manufacturing process as well as by chemical modifications or compounding at the time of use. Both completely and partially PVA have many characteristics in common which make the polymer valuable to a number of industries. PVA is also known for its solubility in water, its clean film formation, resistance to grease, oil and solvents. A high tensile strength, adhesive and binder properties and as a superior stabilizer are its specialties [14].

The tensile strength of PVA is higher than of plastics. A decrease in film tensile strength is a result of addition of plasticizer like glycerine to PVA, but it increases the elongation property of the blend. Poly(vinyl alcohol) is resistant to organic solvents, which increase with the degree of hydrolysis. Partially hydrolyzed grades are substantially unaffected by most esters, ethers, ketoses, aliphatic and aromatic hydrocarbons and the higher monohydric alcohols [15,16].

In this article, pullulan/poly(vinyl alcohol) is selected, since PVA is able to form a complex with hydroxyl group containing polymers. Therefore, viscosity, ultrasonic velocity, density and mechanical properties for the compatibility of pullulan/ poly(vinyl alcohol) blends in water at different temperatures were studied. SEM analysis of blend films and the solid state miscibility had been investigated.

## EXPERIMENTAL

Poly(vinyl alcohol) and pullulan were obtained from Neutriscience, USA. Aqueous solutions of different compositions were prepared for homopolymers PVA, pullulan and their blends (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90).

Ubbelohde suspended level viscometer (USLV) was used at constant temperature bath. Ultrasonic interferometer technique [17-20] had been applied for ultrasonic velocity measurements. The temperature was maintained at 30 and 40 ºC. A frequency of 2 MHz was maintained for the experiment and the specific gravities of different compositions were observed by conventional methods at 30 and 40 ºC.

SEM studies were carried out for the blends films and their uniformity in mixing is also investigated by using a JOEL (JSM 6380LA) analyzer. Temperature was controlled at (80 ± 2 ºC) at the time of drying the blend films. This was done to prevent any damages to the films.

**Preparation of blends:** Pullulan 2 % and PVA solutions in distilled water are used in this study. Pullulan/PVA blends of different compositions *viz*. 90/10, 80/20, 70/30, 60/40, 50/ 50, 40/60, 30/70, 20/80 and 10/90 were prepared by mixing the aqueous solutions and then the solution was poured onto the clean leveled borocil glass plate (30 cm × 20 cm) and allowed to dry overnight and the films conditioned and stored at room temperature before the various properties were studied.

## RESULTS AND DISCUSSION

**Reduced viscosity measurements:** Reduced viscosities data of different compositions (90/10, 80/20, 70/30, 60/40, 50/50, 40/60, 30/70, 20/80 and 10/90) of pullulan/PVA have been investigated at 30 and 40 ºC (Tables 1 and 2). The 90/10 pullulan/PVA blend composition having higher slope than for PVA rich compositions at 30 ºC is shown by Huggin′s plot (Fig. 1). This is due to an increase in hydrodynamic volume of the interacting macromolecules in solution [21,22]. It is found that pullulan/PVA blends are miscible only at 90/10 composition. A lowering in the slope of the above plots below this critical concentration is due to the phase separation. An increase in the miscibility of pullulan/PVA blends up to 70/30

TABLE-1
$\eta_{sp}/c$ DATA FOR PULLULAN, PVA AND THEIR BLENDS AT 30 °C

| Conc. (g/dm$^3$) | $\eta_{sp}/c$ (dl/g at 30 °C) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pullulan | PVA | Pullulan/PVA | | | | | | | | |
| | | | 90/10 | 80/20 | 70/30 | 60/40 | 50/50 | 40/60 | 30/70 | 20/80 | 10/90 |
| 0.2 | 0.825 | 1.040 | 0.842 | 0.850 | 0.866 | 0.890 | 0.915 | 0.930 | 0.952 | 0.970 | 0.990 |
| 0.4 | 0.890 | 1.170 | 0.905 | 0.930 | 0.952 | 0.970 | 1.010 | 1.020 | 1.060 | 1.083 | 1.115 |
| 0.6 | 0.958 | 1.305 | 0.990 | 1.015 | 1.030 | 1.060 | 1.093 | 1.120 | 1.150 | 1.195 | 1.235 |
| 0.8 | 1.030 | 1.440 | 1.060 | 1.090 | 1.105 | 1.150 | 1.190 | 1.220 | 1.250 | 1.300 | 1.350 |
| 1.0 | 1.100 | 1.565 | 1.130 | 1.160 | 1.200 | 1.240 | 1.276 | 1.310 | 1.362 | 1.415 | 1.470 |
| 1.2 | 1.170 | 1.705 | 1.200 | 1.240 | 1.280 | 1.330 | 1.370 | 1.402 | 1.460 | 1.525 | 1.595 |
| 1.4 | 1.245 | 1.840 | 1.280 | 1.332 | 1.370 | 1.425 | 1.460 | 1.500 | 1.557 | 1.645 | 1.710 |
| 1.6 | 1.310 | 1.980 | 1.350 | 1.405 | 1.450 | 1.505 | 1.555 | 1.603 | 1.670 | 1.750 | 1.836 |
| 1.8 | 1.380 | 2.110 | 1.420 | 1.490 | 1.540 | 1.600 | 1.650 | 1.695 | 1.760 | 1.860 | 1.953 |
| 2.0 | 1.460 | 2.250 | 1.498 | 1.560 | 1.620 | 1.685 | 1.740 | 1.790 | 1.870 | 1.970 | 2.080 |

TABLE-2
$\eta_{sp}/c$ DATA FOR PULLULAN, PVA AND THEIR BLENDS IN WATER AT 40 °C

| Conc. (g/dm$^3$) | $\eta_{sp}/c$ (dl/g at 40 °C) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Pullulan | PVA | Pullulan/PVA | | | | | | | | |
| | | | 90/10 | 80/20 | 70/30 | 60/40 | 50/50 | 40/60 | 30/70 | 20/80 | 10/90 |
| 0.2 | 0.700 | 0.980 | 0.730 | 0.754 | 0.780 | 0.822 | 0.840 | 0.860 | 0.890 | 0.910 | 0.950 |
| 0.4 | 0.770 | 1.098 | 0.805 | 0.830 | 0.860 | 0.900 | 0.930 | 0.955 | 1.000 | 1.020 | 1.050 |
| 0.6 | 0.840 | 1.213 | 0.880 | 0.910 | 0.936 | 1.980 | 1.020 | 1.060 | 1.100 | 1.130 | 1.167 |
| 0.8 | 0.910 | 1.321 | 0.950 | 0.995 | 1.027 | 1.072 | 1.130 | 1.158 | 1.205 | 1.240 | 1.280 |
| 1.0 | 0.980 | 1.432 | 1.030 | 1.080 | 1.120 | 1.160 | 1.220 | 1.260 | 1.300 | 1.350 | 1.390 |
| 1.2 | 1.040 | 1.545 | 1.100 | 1.150 | 1.200 | 1.250 | 1.310 | 1.350 | 1.414 | 1.460 | 1.500 |
| 1.4 | 1.110 | 1.655 | 1.170 | 1.219 | 1.280 | 1.345 | 1.410 | 1.463 | 1.520 | 1.570 | 1.602 |
| 1.6 | 1.180 | 1.760 | 1.240 | 1.300 | 1.374 | 1.441 | 1.511 | 1.570 | 1.620 | 1.680 | 1.720 |
| 1.8 | 1.250 | 1.879 | 1.320 | 1.374 | 1.450 | 1.520 | 1.605 | 1.666 | 1.730 | 1.785 | 1.830 |
| 2.0 | 1.320 | 1.990 | 1.390 | 1.437 | 1.530 | 1.610 | 1.700 | 1.780 | 1.830 | 1.900 | 1.950 |

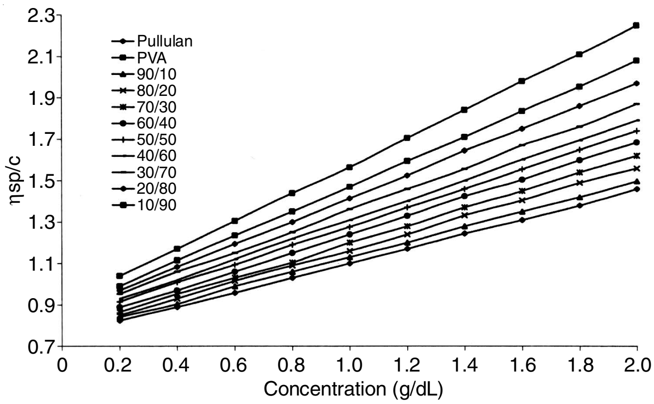


Fig. 1. Plot of ηsp/c *versus* concentration for 2 % w/v, pullulan/PVA blends at 30 °C

blend compositions at 40 ºC (Fig. 2) is also observed. This is because of the effect of temperature on the miscibility of pullulan/PVA blends.

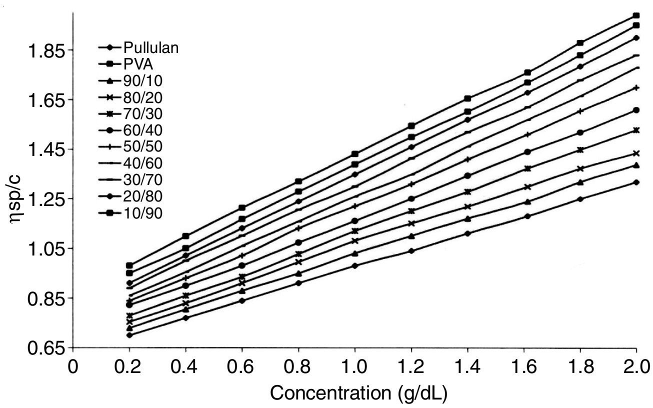


Fig. 2. Plot of ηsp/c *versus* concentration for 2% w/v, pullulan/PVA blends at 40 °C

In order to probe the miscibility of pullulan/PVA blends, Chee's [23] and Sun *et al.* [24] equations have been used.

**Chee equation:** $$\Delta B = b_{23} - \frac{1}{2}(b_{22} + b_{33})$$

**Sun *et al.* equation:** $$\mu = \frac{\Delta B}{([\eta]_3 - [\eta]_2)^2}$$

Positive values of these parameters give the conclusion that the blends are miscible. Similarly, the negative values show the immiscibility of the blends.

Using Chee [23] and Sun *et al*. [24] equations, interaction parameters μ and α values of pullulan/PVA blend compositions are calculated (Figs. 3 & 4). These computed values of interaction parameters give a valuable information towards the miscibility of blends. The values at 90/10 composition are positive, while negative for the other compositions. When the temperature is increased to 40 ºC, miscibility of blends at 70/30 compositions show the α values positive, which gave an indication that miscibility of polymers is proportional to an increase in temperature (Table-3).

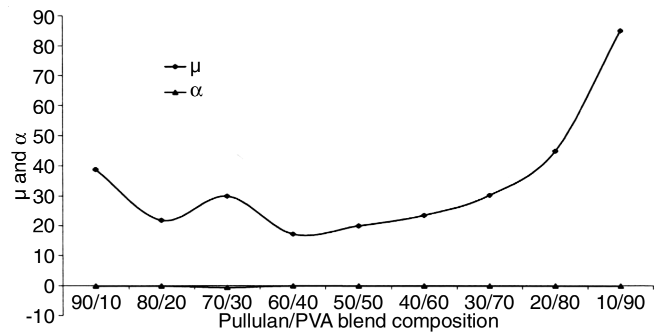


Fig. 3. Variation of μ and α with composition of pullulan/PVA at 30 °C

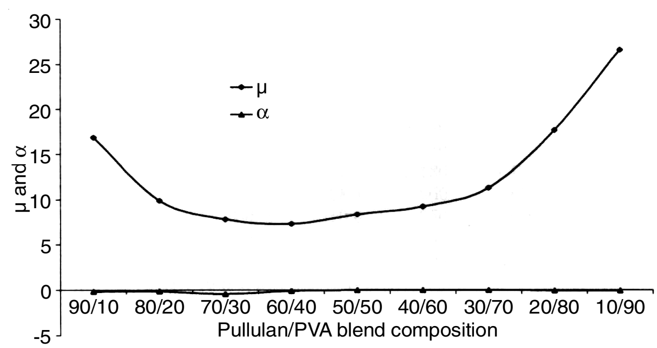


Fig. 4. Variation of μ and α with composition of pullulan/PVA at 40 °C

**Effect of temperature on reduced viscosity, refractive index and ultrasonic velocity:** Ultrasonic velocity and refractive index studies are the supportive data for viscosity data to investigate the miscibility of blends. The nature of ultrasonic velocity and refractive index against different blend compositions are plotted for pullulan/PVA blends in Figs. 5 and 6, respectively at 30 and 40 ºC. It is confirmed that the blends are immiscible because of the non-linearity curves, which is attributed due to the phase separation at 30 and 40 ºC. This is in accordance with earlier reported studies [25,26].

TABLE-3
REFRACTIVE INDEX, ULTRASONIC VELOCITY, μ AND α FOR PULLULAN PVA IN WATER AT 30 AND 40 °C

| Blend composition | Refractive index | | Ultrasonic velocity (m/s) | | μ | | α | |
|---|---|---|---|---|---|---|---|---|
| | 30 °C | 40 °C | 30 °C | 40 °C | 30 °C | 40 °C | 30 °C | 40 °C |
| 90/10 | 1.3438 | 1.3356 | 1498.4 | 1511.6 | 38.77 | 16.860 | -0.1516 | -0.171 |
| 80/20 | 1.3450 | 1.3366 | 1497.6 | 1508.8 | 21.79 | 9.900 | -0.1557 | -0.140 |
| 70/30 | 1.3430 | 1.336 | 1496.4 | 1511.6 | 29.88 | 7.805 | -0.6189 | -0.412 |
| 60/40 | 1.3472 | 1.3350 | 1498.8 | 1511.6 | 17.11 | 7.319 | -0.0568 | -0.089 |
| 50/50 | 1.3440 | 1.3290 | 1497.4 | 1509.0 | 19.86 | 8.333 | -0.1330 | -0.018 |
| 40/60 | 1.3430 | 1.3350 | 1497.2 | 1508.4 | 23.38 | 9.223 | -0.1440 | -0.027 |
| 30/70 | 1.3480 | 1.3380 | 1498.8 | 1510.0 | 30.17 | 11.290 | -0.1679 | -0.014 |
| 20/80 | 1.3410 | 1.330 | 1496.4 | 1711.6 | 44.86 | 17.640 | -0.1561 | -0.073 |
| 10/90 | 1.3450 | 1.3307 | 1496.4 | 1511.2 | 84.96 | 26.580 | -0.1223 | -0.069 |

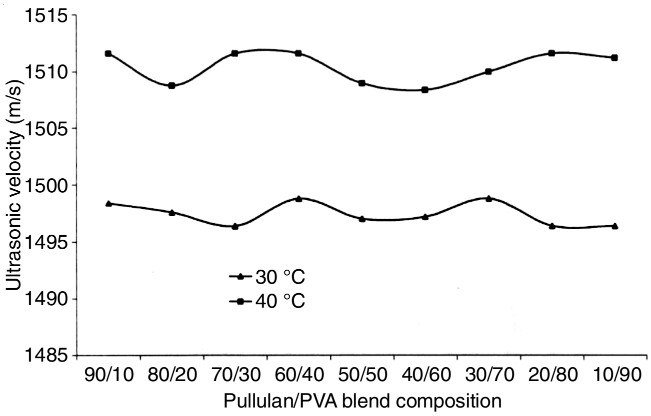


Fig. 5. Plot of ultrasonic velocity with composition of 2 % w/v of pullulan/PVA blends at 30 and 40 °C

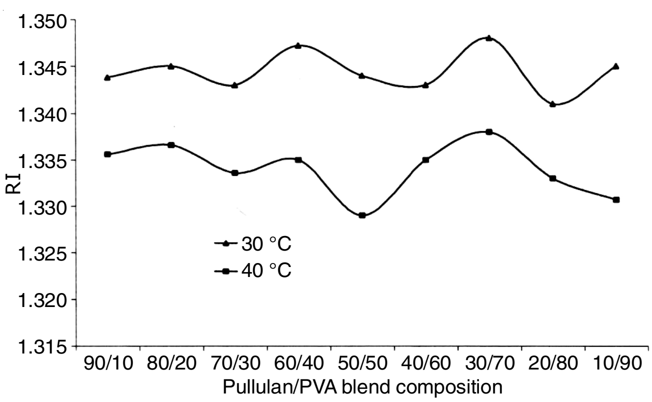


Fig. 6. Plots of RI with composition of 2 % w/v of pullulan/PVA blends at 30 and 40 °C

These studies also showed that the extent of H-bonding of OH group of PVA with pullulan is very weak. It is important to note that the above studies are parallel to Sun *et al*. [24] equation. So, pullulan/PVA blends at 30 and 40 ºC are completely immiscible over the entire compositions. Since there is no change in nature of blend of pullulan/PVA blends at different temperatures, it can be stated that there is no effect of temperature.

**Mechanical properties:** Mechanical properties like tensile strength, % elongation, burst strength and density of the prepared pullulan/PVA blends were evaluated and there values are shown in Table-4. It is observed that tensile strength and % elongation increases with the PVA content in blends. The density and burst strength of the blends also increases with PVA content, but there is not much variation in tear strength.

**SEM analysis:** From SEM analysis (Fig. 7), it can be observed that there is a phase separation. The phases of pullulan and poly(vinyl alcohol) separate into discrete phases and there is no uniformity and homogeneity.

## Conclusion

Based on the viscosity data, ultrasonic velocity and refractive index measurements, it is found that pullulan/PVA blends are immiscible over the entire composition range at 30 and 40 ºC. SEM studies also support the above conclusion. However, pullulan/PVA blends have shown good physical and mechanical properties particularly for 90/10 composition.

## CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

## ACKNOWLEDGEMENTS

The authors thank Prof. Dr. K. Sheshappa Pai, Department of Polymer Science, University of Mysore, Mandya, India for his valuable suggestions.

TABLE-4
PHYSICO-MECHANICAL PROPERTIES OF PULLULAN/PVA BLENDS

| Blend composition | Tensile strength (MPa) | Tensile modulus (MPa) | Elongation at break (%) | Tear strength (N) | Burst strength (kg/cm$^2$) | Density (g/mL) |
|---|---|---|---|---|---|---|
| Pullulan | 15.09 ± 1.04 | 32 ± 10 | 3.00 ± 0.34 | 0.56 | 0.6 | 1.12 ± 0.01 |
| PVA | 19.25 ± 2.11 | 523 ± 64 | 150 ± 24.45 | 0.88 | 2.00 ± 0.22 | 1.32 ± 0.35 |
| 90/10 | 12.34 ± 1.30 | 304.8 ± 100 | 4.125 ± 0.26 | 0.70 | 0.91 ± 0.56 | 1.16 ± 0.21 |
| 80/20 | 8.43 ± 1.90 | 210.050 ± 45 | 3.64 ± 0.58 | 0.63 | 0.99 ± 0.24 | 1.15 ± 0.32 |
| 70/30 | 9.24 ± 0.2 | 170.35 ± 108 | 6.140 ± 1.40 | 0.61 | 0.98 ± 0.26 | 1.09 ± 0.54 |
| 60/40 | 8.13 ± 1.00 | 124.45 ± 54 | 14.52 ± 2.34 | 0.58 | 1.07 ± 0.56 | 1.09 ± 0.46 |
| 50/50 | 9.95 ± 0.8 | 145.6 ± 35 | 12.43 ± 4.80 | 0.68 | 1.32 ± 0.54 | 1.23 ± 0.62 |
| 40/60 | 11.42 ± 0.47 | 89.70 ± 37 | 25.15 ± 10.0 | 0.65 | 1.36 ± 0.57 | 1.24 ± 0.55 |
| 30/70 | 15.26 ± 1.80 | 168.62 ± 12 | 38.89 ± 16.0 | 0.67 | 1.62 ± 0.35 | 1.28 ± 0.38 |
| 20/80 | 17.01 ± 3.00 | 453.45 ± 18 | 84.87 ± 8.90 | 0.77 | 1.78 ± 0.95 | 1.28 ± 0.72 |
| 10/90 | 17.16 ± 4.2 | 336.30 ± 66 | 112.4 ± 30.0 | 0.71 | 1.77 ± 0.31 | 1.30 ± 0.21 |

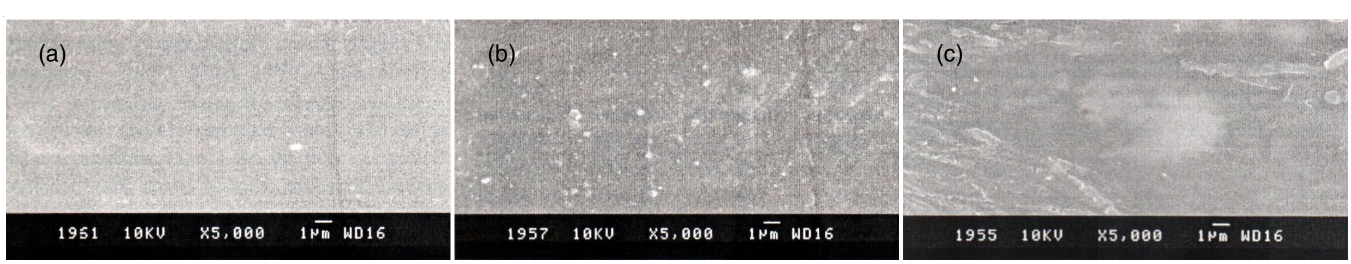


Fig. 7. SEM photographs of pullulan/PVA blends (a) (20/80), (b) (60/40) and (c) (80/20) at 5000 magnification

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