STUDIES ON MISCIBILITY AND THERMAL PROPERTIES OF BIOCOMPATIBLE POLYMER BLENDS OF PVP/GUAR GUM

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ABSTRACT

Miscibility of Guar gum (GG) and Poly(vinyl pyrrolidone) (PVP) polymer blends were analysed in solution and solid state using various techniques and thermal properties of the prepared blends were analysed by TGA analysis. Different composition ratios of GG/PVP blend were prepared using water as common solvent. Solution state miscibility were characterised by density, ultrasonic velocity and viscosity measurements. The density and ultrasonic velocity measurement showed that GG/PVP blends are semi-miscible. Using reduced viscosity data Chee's and Sun's interaction parameters (μ and α) were calculated. These values confirmed that GG/PVP blends are miscible when guar gum content in the blend is more than 50%. Blend films of GG/PVP were prepared by solution casting method and analysed by FTIR, SEM and DSC techniques. The SEM and DSC analysis confirmed semi-miscible nature of the blend. Hydrogen bonding interaction between polymer components is evidenced in FTIR analysis. Thermal properties of the blends are analysed by TGA analysis.

Key words: Guar gum, FTIR, Miscible, Polymer blends, PVP.

I. INTRODUCTION

Nowadays biodegradable polymers gained considerable interest in biomedical applications such as targeted drug delivery, controlled drug release system etc. due to its excellent biocompatibility. However in many cases single polymer alone cannot meet the divergent demands of biomaterials in terms of both properties and performance [1,2]. Therefore blending of two or more polymers may a suitable alternate to obtain new polymeric material, with tailor made, improved properties, at a reasonably low cost. However advancement in properties of blends depends upon the miscibility of polymers in molecular level. Generally two polymers are immiscible due to thermodynamic factor, but miscibility of polymers may achieve by introducing certain specific interactions between polymer components such as hydrogen bonding, dipole-dipole interactions, charge transfer complex formation etc [3,4].

Poly (vinyl pyrrolidone) is a synthetic water soluble polymer extensively used in pharmaceutical applications due to its biodegradability, non-toxicity, good complexing ability and good adhesive property [5]. Poly (vinyl pyrrolidone) is relatively a new polymer among the commercial water-soluble polymers. PVP is a homopolymer of N –vinyl-2-pyrrolidone, chemically named as poly-[1-(2-oxo-1-pyrrolidinyl)-ethylene] [6]. Commercial usefulness of PVP is inherent in the following properties like, wide solubility and compatibility range, complexing and detoxifying ability, physiological acceptability, protective-colloid action, film forming ability and adhesive qualities. Guar gum or guron is a naturally occurring polysaccharide extracted from the endosperm of cyanopsis tetragonolobus. Structurally it is a galactomannon with a galactose to mannose ratio of approximately 1:2. It has a chain (1-4) linked ß-D mannopyranosyl units with single α-D galactopyranosyl units connected by (1-6) linkages to on the average every second main chain unit [6-8]. Guar gum is a natural polysaccharide widely used in food and pharmaceutical industries as thickener, emulsion stabilizer and drug carrier etc. In the present study PVP blended with Guar gum in its aqueous solution and miscibility of the resulting blend was characterized by various techniques both in solution and solid state. The thermal properties of prepared blend films also studied.

II. EXPERIMENTAL PROCEDURE

The polymers employed in the present study are guar gum (Merck limited, Mumbai, India) and PVP (Hi media, Mumbai, molecular weight: 4000kD).

2.1 Ultrasonic Velocity and Density Measurements

Blends of Guar gum/PVP of different composition (0.5% w/v) were prepared by mixing aqueous polymer solutions. Ultrasonic velocity of the blend solution were measured at 30 and 40˚C temperature by using an interferometric technique; employing an ultrasonic interferometer and densities of the blend solution were measured at 30 and 40˚C using a specific gravity bottle.

2.2 Reduced Viscosity Measurements

Stock solution of Guar gum and PVP were prepared (0.5%w/v) using distilled water. Then different blend stock solutions of Guar gum/PVP (80/20, 60/40, 50/50, 40/60 and 20/80 w/v) were prepared by stirring the mixture at room temperature for about 45 minutes. Using the above polymeric solutions, different concentration of solutions (0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45 and 0.5 g/dl) were prepared and viscosity measurements were made at 30˚C and 40˚C temperatures using an Ubbelohde suspended level viscometer. Constant temperature was maintained using a thermostat bath with a thermal stability of ±0.05 ˚C.

2.3 Solid State Studies

Thin films of the polymers and their blends were prepared by solution casting method. Separate aqueous solution of Guar gum and PVP of 1% w/v were prepared. Then a solution of Guar gum was added to that of PVP with constant stirring. Prepared solution of Guar gum, PVP and their different blend compositions were then casted on Teflon coated clean glass plate and dried using IR lamp in a dust free atmosphere. The dried thin films were then peeled off from the glass plate and stored in desiccators until further study. Thin films of polymers and its blends were analyzed by FTIR, SEM and differential scanning calorimetric techniques in order to ascertain its miscibility. Thermal and mechanical properties of the blend films also studied.

FTIR spectra were recorded using NICOLET AVATAR 530 spectrophotometer. SEM photographs are recorded using a JOEL (JSM 6380 LA) analyser. DSC thermo grams were produced with a TA Q200 differential scanning calorimeter, under nitrogen environment. The first temperature cycle heated the sample to 100°C, Where it remained isothermal for about 20 minutes to remove the remaining water content present in the samples. It is the cooled to 20°C and immediately reheated to 250°C. The heating and cooling rate was set at 10°C/min. TGA analysis of the blend films were performed using TGA analyser (TGA Q50 V20.2 Build 27) under nitrogen environment at a san rate of 10 °C. Mechanical properties of blend films were measured under tensile strain. Tensile stress at maximum load, tensile strain at break and tensile modulus were determined with an Instron 5900 UTM according to ASTM D882, the test was run at 5mm/min and at room temperature.

III. RESULTS AND DISCUSSION

3.1Ultrasonic Velocity and Density Measurements

The ultrasonic velocity (υ) and density (ρ) measurements are useful techniques to investigate the miscibility of polymer blends in solution. The ultrasonic velocity and densities of the blend solutions (0.5% w/v) were measured at 30˚C and 40˚C by using an ultrasonic interferometer and specific gravity bottle respectively. In order to quantify miscibility or otherwise separate plots of ultrasonic velocity and densities versus % composition of Guar gum in the blend solution were plotted at 30 and 40˚C and the plots are shown in Figure 1 and Figure 2.

The variation of ultrasonic velocity and density versus % composition of Guar gum at 30˚ C showed both linear and non linear region [9]. The linearity in the graph observed when Guar gum concentration in the blend 60% and above. These indicated that Guar gum/PVP blends are semi-miscible in nature at 30 °C temperature. However, at 40°C temperature, both graphs were found to be non linear. Therefore blends are completely immiscible at higher temperature.

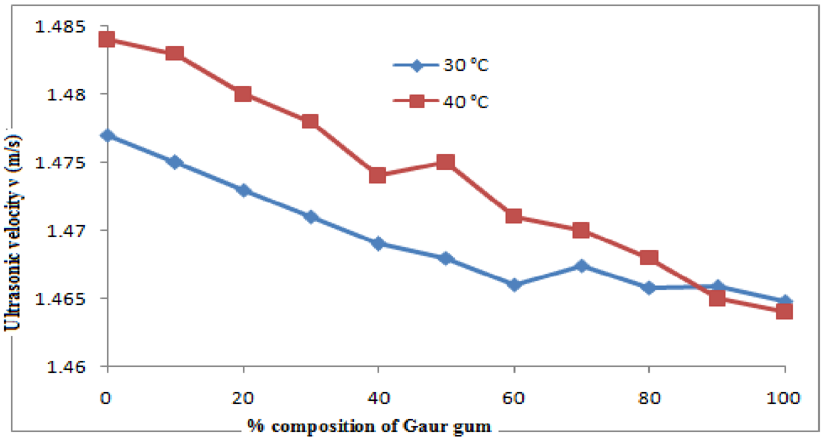

Fig 1: Variation of ultrasonic velocity versus % composition of Guar gum in the blend at 30°C & 40°C

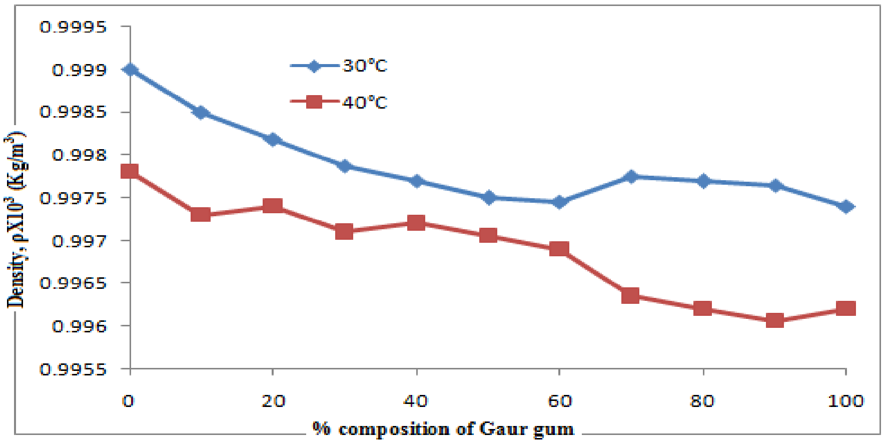

Fig 2: Variation of density versus % composition of Guar gum in the blend at 30 & 40°C

3.2 Reduced Viscosity Measurements

Reduced viscosity of homopolymer Guar gum, PVP and their different blend composition (80/20, 60/40, 50/50, 40/60 and 20/80) were measured at 30˚C and 40˚C. Huggins plots of reduced viscosity of pure polymers and their blend compositions against concentrations plotted and are shown in Figure 3 and Figure 4 respectively.

The intercept of reduced viscosity versus concentration plots gives the intrinsic viscosity of the corresponding polymers and their blends, which are given in Table 1 and Table 2 respectively. The experimental intrinsic viscosity values thus obtained were compared with their weighed average values. The 80/20, 60/40 and 50/50 compositions experimental intrinsic viscosities almost equal to the theoretically calculated values where as much deviation is observed for other concentrations. This indicated the blends may miscible in these concentrations at 30 °C temperature [10].

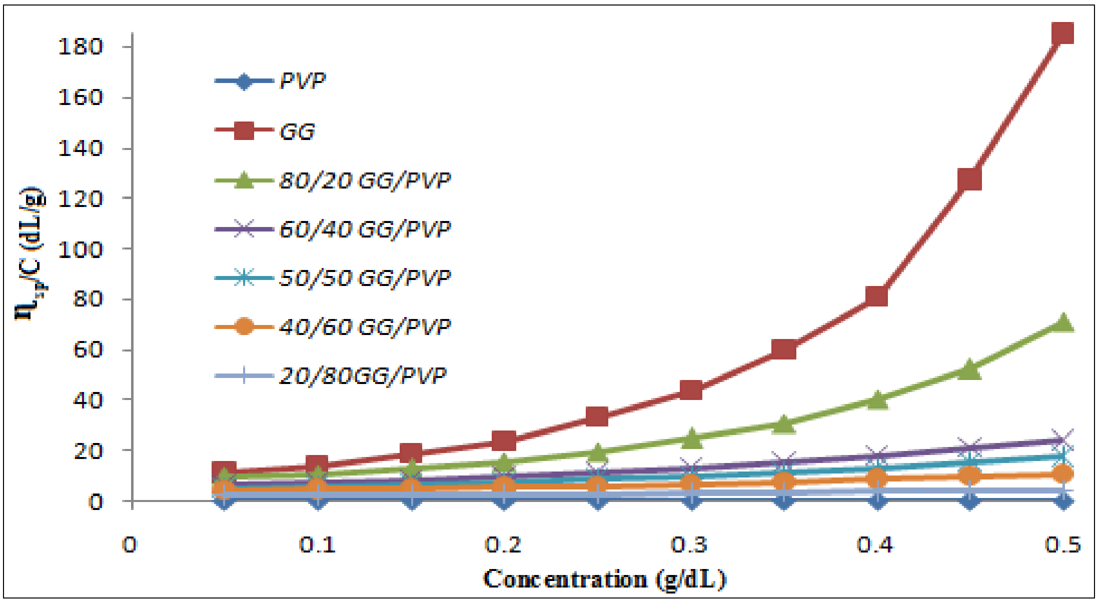

Fig 3: Huggin's plot for 0.5 % w/v GG/PVP blend at 30 °C

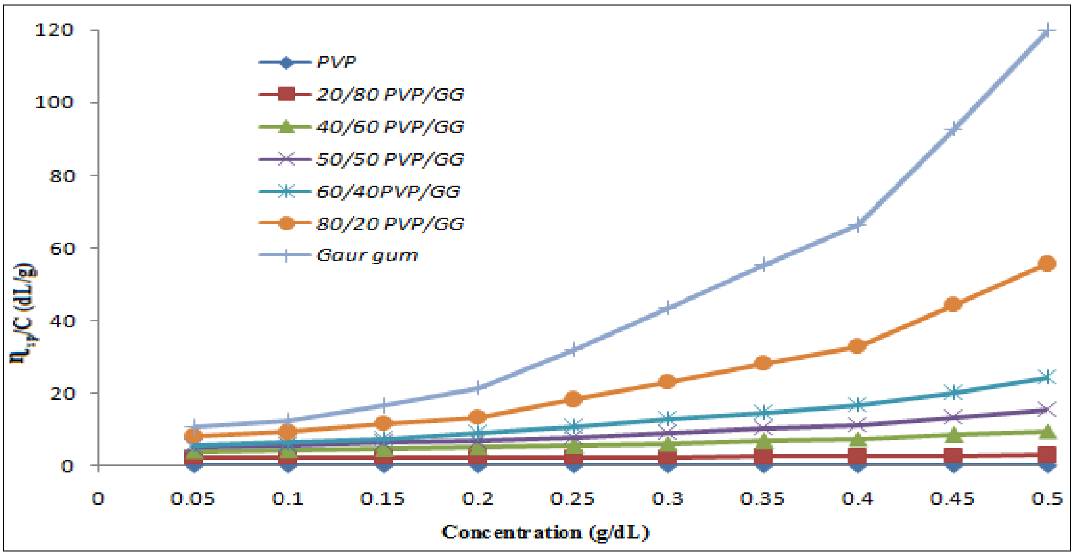

Fig 4: Huggin's plot for 0.5 % w/v GG/PVP blend at 40 °C.

Using slope and intercept from Huggin’s plot, interaction parameters ‘µ’ and ‘α’ were calculated at 30 and 40°C temperature with usual methods [11, 12] and computed values are given in Table 1 and Table 2 respectively. At

30 °C (Table 3) temperature, Chee's [11] interaction parameter 'µ'were +ve for 80/20 composition and Sun's [12] interaction parameter 'α' found to be positive for 80/20, 60/40 and 50/50 GG/PVP compositions. Secondary bonding interactions are considered while deriving interaction parameter 'α' hence it is more accurate than interaction parameter'µ'[9]. Therefore it confirmed that the Guar gum/PVP blends are miscible when Guar gum content in the blend is more than 50%. Below this critical concentration blends are found to be immiscible. However at 40 °C temperature, both interaction parameters found to be negative for all concentrations (Table 4). Hence blends are completely immiscible at higher temperature.

Table 1: Intrinsic viscosity and interaction parameter of GG/PVP blend at 30° C

Blend composition of GG/PVP	$[\eta]_{expt}$ (dL/g)	$[\eta]_{cal}$ (dL/g)	µ	α
0/100	0.170	-	-	-
20/80	2.050	1.349	-0.931	-0.923
40/60	3.060	2.533	-0.841	-0.852
50/50	3.131	3.125	-0.507	+0.271
60/40	3.716	3.536	-0.195	+1.229
80/20	4.900	4.719	+0.464	+0.396
100/0	6.084	-	-	-

Table 2: Intrinsic viscosity and interaction parameter of GG/PVP blend at 40° C

Blend composition of GG/PVP	$[\eta]_{expt}$ (dL/g)	$[\eta]_{cal}$ (dL/g)	µ	α
0/100	0.166	-	-	-
20/80	1.762	1.452	-0.408	-0.731
40/60	3.203	2.739	-0.448	-0.665
50/50	3.898	3.383	-0.513	-0.487
60/40	4.605	4.026	-0.626	-0.593
80/20	5.992	5.313	-0.779	-0.582
100/0	6.600	-	-	-

3.3 FTIR Analysis

In order to quantify hydrogen bonding interaction between the polymers, FTIR spectra of Guar gum, PVP and their blend films (100/0, 80/20, 60/40, 50/50 , 40/60 & 0/100) were recorded and spectra are given in Figure 5. Characteristic absorption bands of Guar gum obtained at 3347.3 cm^{-1} and 1012.7 cm^{-1} corresponds to –OH and C-O-C group respectively [13]. PVP readily absorbed moisture and a strong absorption band corresponds to hydroxyl group of water observed at 3392.34 cm^{-1}. Characteristic absorption of PVP observed at 1621.79 cm^{-1} corresponds to N-C=O group and absorption at 1285.61 cm^{-1} corresponds to –N-C group of pyrrolidone ring [14].

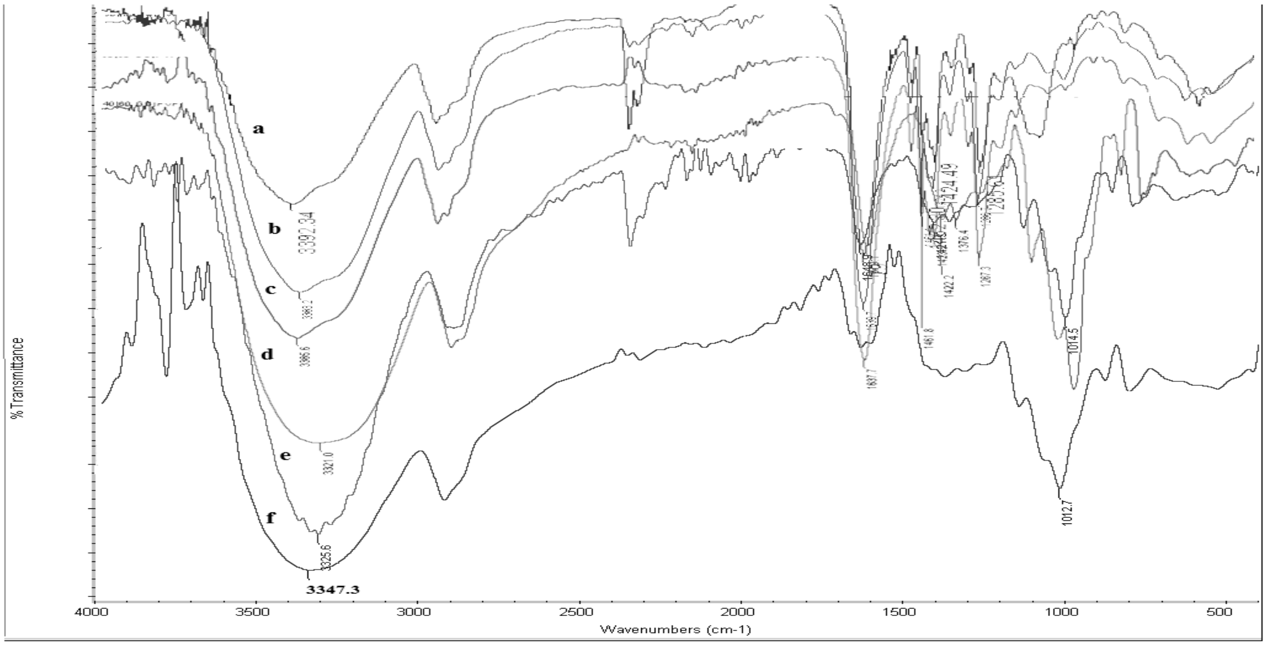

Fig 5: FTIR spectra of (a) PVP (b) 40/60 GG/PVP, (c) 50/50 GG/PVP, (d) 60/40 GG/PVP, (e) 80/20 GG/PVP, and (e) Guar gum

GG/PVP blends showed characteristic absorption corresponding to its pure components. However 80/20, and 60/40 composition showed a down shift in hydroxyl group absorption by ≈ 30 cm^{-1} to lower frequency region with respect to absorption patterns of Guar gum, and also intensity of carbonyl groups absorption decreased significantly. These may attribute to the hydrogen bonding interaction occurred between carbonyl group of PVP and hydroxyl group of Guar gum. No such observation occurred for 50/50 and 40/60 composition, hence GG/PVP blends are miscible when and only Guar gum concentration in the blend is 60% and above. Below this concentration range blends are immiscible.

3.4 Morphology Studies

In order to check the morphology of the blends, solution cast films of Guar gum, PVP and its blends (100/0, 80/20, 60/40, 50/50, and 0/100) was examined through SEM analysis and resulted SEM images are shown in Figure 6. The images showed clear homogeneity in the dispersion for 80/20, and 60/40 blend composition, where as 50/50 composition showed phase separation. Hence the Guar gum/PVP blends are semi-miscible.

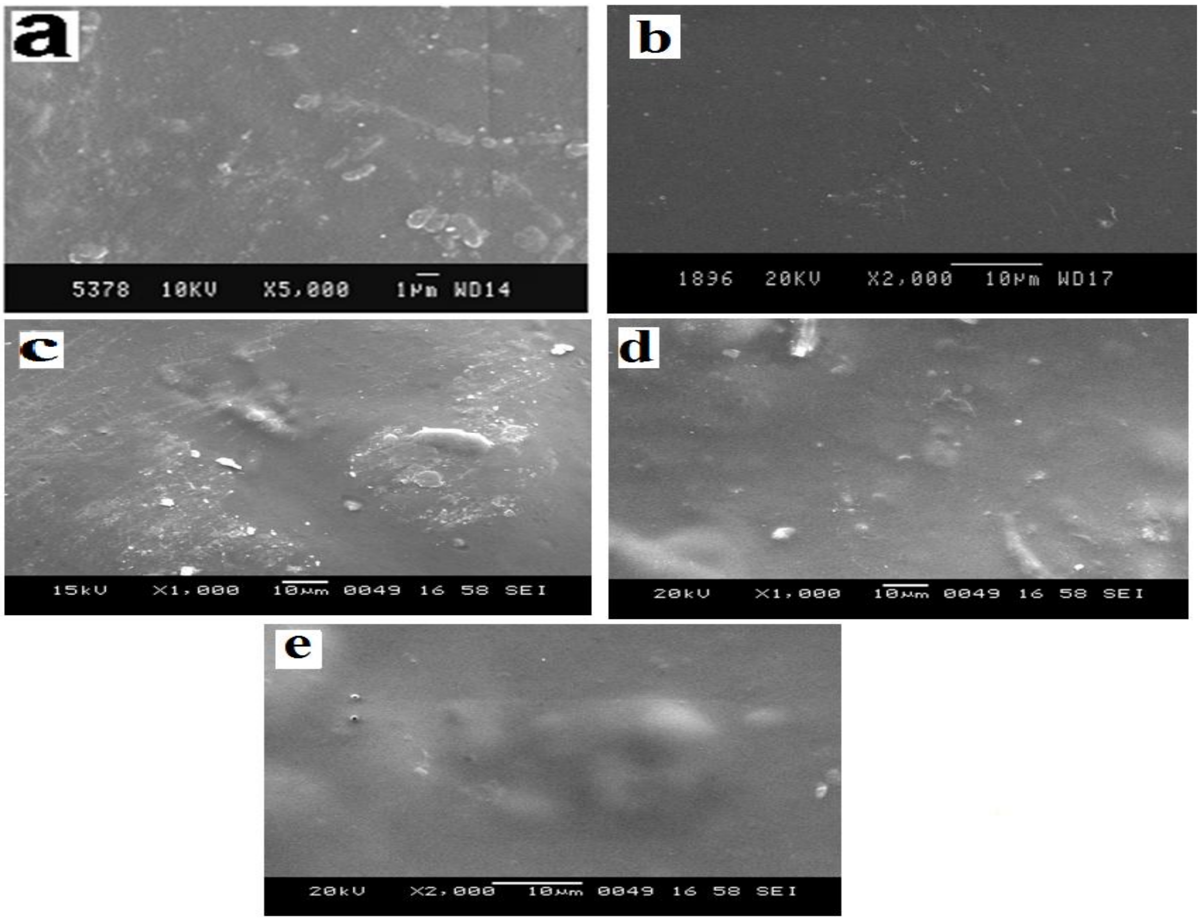

Fig 6: SEM images of (a) Guar gum, (b) PVP, (c) 50/50 GG/PVP, (d) 60/40 GG/PVP (e) 80/20 GG/PVP

3.5 Glass Transition Temperature Measurements

Glass transition temperature of homopolymer and its blend compositions (40/60, 60/40 and 80/20) were recorded by DSC-T_g measurement technique and resultant thermograms are given in Figure 7. Glass transition temperature was taken as midpoint of the change in slope of respective traces [10]. It is observed that 60/40 and 80/20 GG/PVP blends gives composition depended single glass transition temperature T_g between the T_g's of Guar gum and that of the PVP, which can be attribute to hydrogen bonding interaction between Guar gum and PVP, leads to miscibility. Whereas the thermogram of 40/60 composition showed two T_g's, corresponds to T_g's of pure Guar gum and PVP respectively, implies blend is immiscible. Therefore results confirmed semi-miscible nature of the blends.

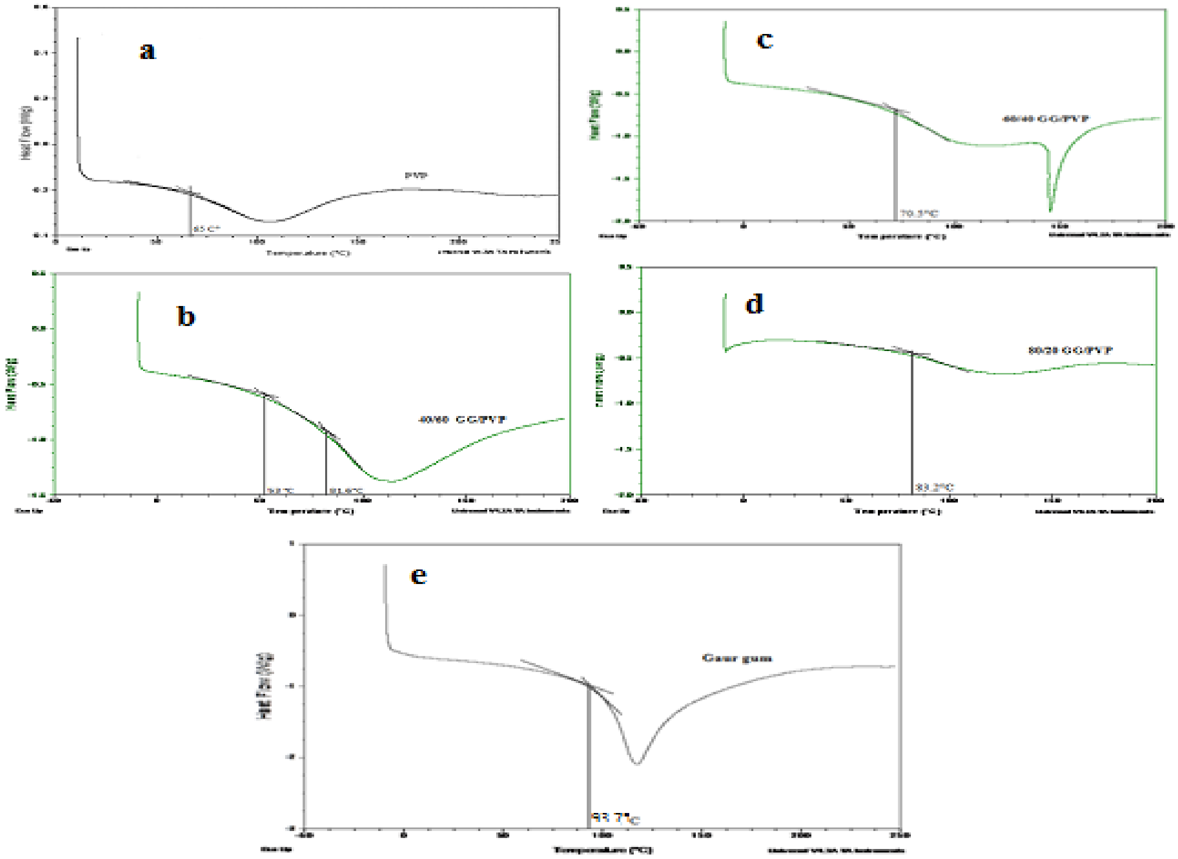

Fig 7: DSC spectra of (a) PVP, (b) 40/60 GG/PVP, (c) 60/40 GG/PVP, (d) 80/20 GG/PVP, (e) Guar gum

3.6 Thermo-Gravimetric Analysis

Thermal stability of Guar gum, PVP and their blend films (60/40 and 80/20) were analyzed using thermogravimetric analyzer under nitrogen atmosphere, the TG curves are given in Figure 8**.** In order to determine the thermal stability trend, the temperature characteristics such as T_0, T_{20} (temperature of 20% mass loss), T_{40} (temperature of 40% mass loss), T_{60} (temperature of 60% mass lose), T_{80}(temperature of 80% mass lose) and T_{max} (temperature of maximum mass loss) were calculated and presented in Table 3.

The Guar gum showed single step on set thermal degradation, begins at 231°C and ended at 595°C. PVP showed two stage thermal degradations initiated at 68 °C and ends at 126°C, this may be due the evaporation of water content present in the film. Second stage on set thermal degradation begins at 215°C and ends at 467 °C. The polymer blend films showed two stage thermal decomposition profiles, were it observed thermal stability of the polymer films increased with blending. The 60/40 Guar gum/PVP blend showed highest thermal stability.

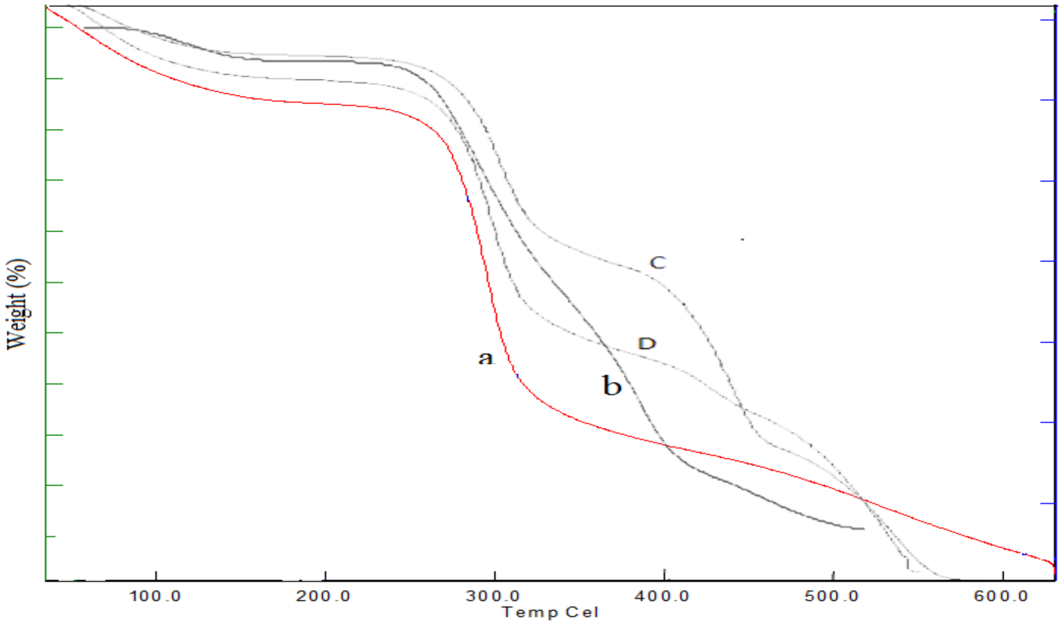

Fig 8: TGA curves of (a) Guar gum, (b) PVP, (c) 60/40 GG/PVP, and (d) 80/20 GG/PVP

Table 3: Parameters Evaluated from the Thermo Grams of GG/PVP Blend

Blend comp of GG/PVP	**Temperature at different weight loss (°C)**					
	T_0	**T_{20}**	**T_{40}**	**T_{60}**	**T_{80}**	**T_∞**
100/0	231	264	292.5	315	530	595
80/20	220	270	300	365.5	508.8	550
60/40	235	284	378	429	467	558
0/100	215	262	307	359	440	467

IV. CONCLUSION

Based on viscosity, ultrasonic velocity and density measurements the Guar gum/PVP polymer blend found to be miscible only when Guar gum content in the blend is more than 50% at room temperature. Below this critical guar gum concentration, the blends are found to be immiscible. At higher temperature blends are found immiscible in all concentration range. FTIR analysis confirmed hydrogen bonding type intermolecular interaction between the polymer components, where as morphology study also revealed homogeneity in dispersion when Guar gum content is more than 50% in the blend. The DSC analysis also confirmed semi-miscible nature of the polymer blends. Thermal studies indicated blending increased thermal stability of the polymers.

V. ACKNOWLEDGEMENTS

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