MISCIBILITY STUDIES OF GG/PVA BLENDS IN AQUEOUS SOLUTION

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ABSTRACT

Miscibility of blends of Guar Gum (GG) and Poly(vinyl alcohol) (PVA) in common solvent water were studied by viscometry, ultrasonic, density, and refractometric methods at 30°C and 40°C. Based on ultrasonic velocity, density and refractive index measurements, it is found that the polymer blend of GG/PVA is miscible only when the GG content is more than 60%. Below this critical GG concentration the blends were found to be immiscible. Using the viscosity data, interaction parameters were computed and it suggests that the blend is miscible when the GG content is more than 60% of the blend. Variation of temperature did not have any significant effect on the miscibility. Hence GG/PVA blend in aqueous solution at 30ºC and 40ºC is semi-miscible in nature.

Keywords: blends, PVA, Guar Gum, miscibility, viscosity interaction parameters.

I. INTRODUCTION

The blend materials from either synthetic or natural polymers alone are not always able to meet all the complex demands of the biomaterials [1 – 4].The success of synthetic polymers as biomaterials relies on their wide range of mechanical properties, transformation processes that allow a variety of different shapes to be easily obtained and at low production cost. Biological polymers present good biocompatibility, but their mechanical properties are often poor [5 – 9]. The necessity of preserving biological properties complicates their processability and their production or recovery costs are very high. Therefore, biologically important polymeric materials based on the blends of synthetic and natural polymers have been prepared, such as GG/CMC [10, 11], PVP/Lignin [53], poly (ethylene oxide)/sodium alginate [58], poly (ethylene oxide)/keratin [12], PVA/starch [13], poly (ethylene oxide)/starch [14], Xanthan gum/PEO [15].

Guar gum is water soluble, hydrophilic polymer obtained from guar bean (Cyamopsistetragonoloba), a commercially important crop of India. It’s a natural biocompatible polysaccharide and has important applications in cosmetic and pharmaceutical industries [10]. Poly (vinyl alcohol) is recognized as a biodegradable polymer, and its biodegradation in various microbial environments has been reported by several researchers [16 – 22]. PVA has been widely used in biomedical industries [23 – 25].

In this research work, miscibility of natural polymer guar gum and a synthetic polymer poly (vinyl alcohol) at different compositions were studied by refractive index, density, ultrasonic velocity and viscosity measurement techniques in their dilute solution at 30ºC and 40ºC

II. EXPERIMENTAL PROCEDURE

The polymers employed in the present study are guar gum (Merck, India) and PVA (Rolex, India).

Blends of GG/PVA of different compositions were prepared by mixing aqueous polymer solutions. Ultrasonic velocity of the blend solutions of 0.1 % (w/v) were measured at 30ºC and 40ºC by an interferometric technique employing an ultrasonic interferometer (Mittal Enterprises, New Delhi) at frequency 2MHz. The densities and refractive index of the GG/PVA blend solutions (0.1%, w/v) were measured at 30ºC and 40ºC using specific gravity bottle and Abbe's refractometer, respectively.

Stock solutions of GG, PVA, and their blends (20/80, 40/60, 50/50, 60/40, and 80/20) were prepared (0.1% w/v) by stirring the mixtures at room temperature for about 45 minutes. Using the above pure and blend stock solutions, different blend solutions (0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, and 0.1 w/v concentrations) were prepared and viscosity measurements were done at 30ºC and 40ºC using an Ubbelohde suspended level viscometer. Different temperatures were maintained using a thermostat bath with a thermal stability of ± 0.05ºC.

III. RESULTS AND DISCUSSIONS

3.1 Refractive index, ultrasonic velocity, density and adiabatic compressibility measurements

The plots of variation of refractive index (n), ultrasonic velocity (υ), density (ρ) and adiabatic compressibility (βad) over an extended range of concentrations of GG/PVA blend solutions at 30ºC and 40°C were given in Figs.1, 2, 3, and 4, respectively.

These graphs show both linear and non-linear regions indicating the semi-miscible nature of the GG/PVA blend. It was already established that the variation is linear for miscible and non-linear for immiscible blends [1 - 4]. In the present investigation the variation is found to be linear only when the GG content is more than 60 wt% at 30°C and 40°C. The linearity in the graph may be due to the specific interaction like hydrogen bonding between the polymer segments, which is more when the GG content is more than 60 wt%, leading to miscibility of these blends [8, 9]. Below this composition there may not be much interaction between the polymer segments which leads to immiscibility of the blend. Hence the present study indicates the existence of the miscibility window only when the GG content is more than 60 wt% at 30°C and 40°C. Hence GG/PVA blend is semi-miscible in aqueous solution.

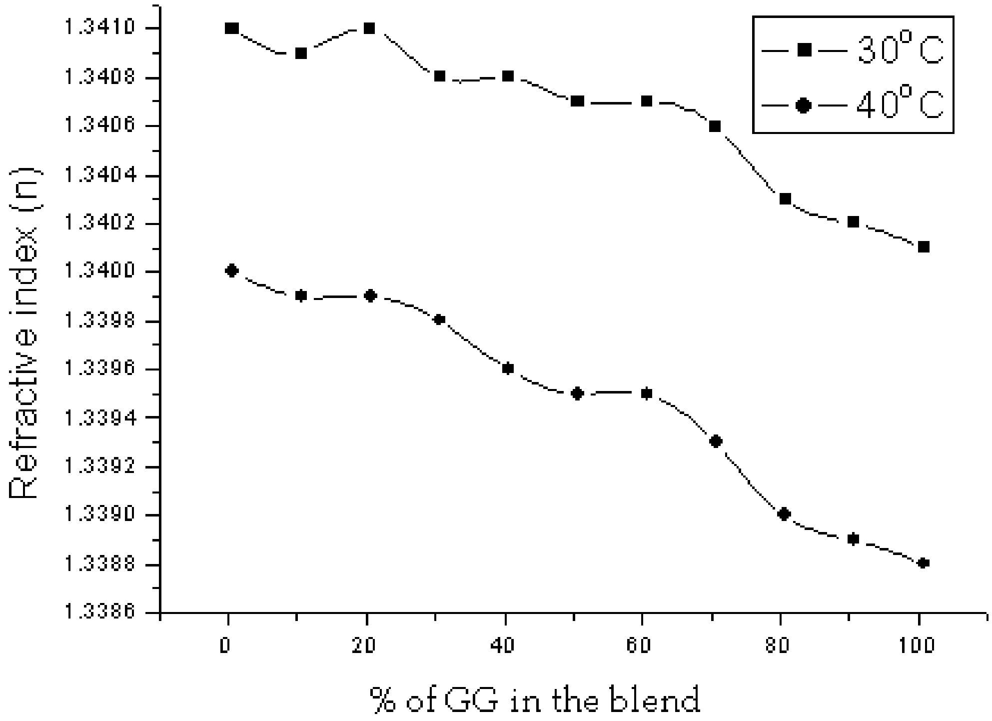

Figure 1: Variation of refractive index with composition of GG/PVA blend in aqueous solution at 30°C and 40°C

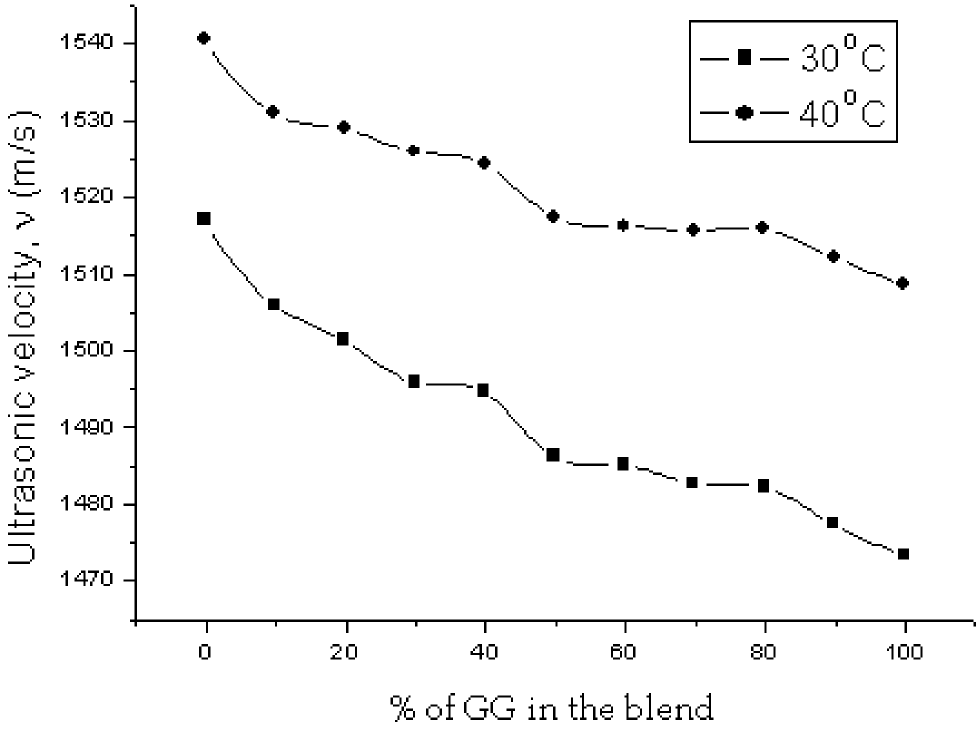

Figure 2: Variation of ultrasonic velocity with composition of GG/PVA blend in aqueous solution at 30°C and 40°C

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ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346

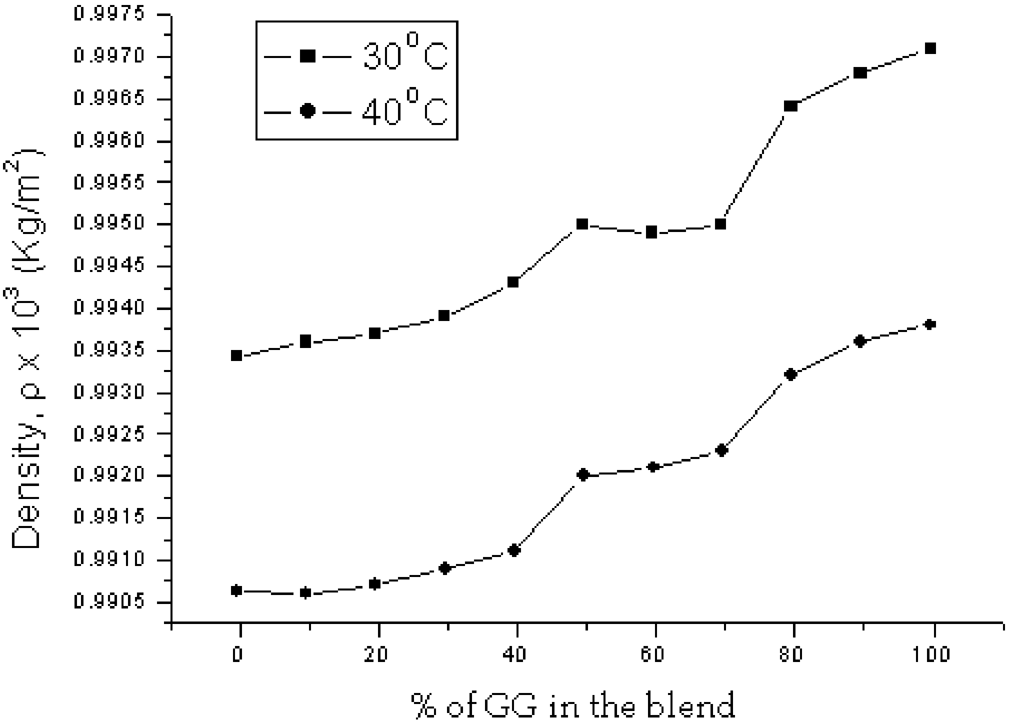

Figure 3: Variation of density with composition of GG/PVA blend in aqueous solution at 30°C and 40°C

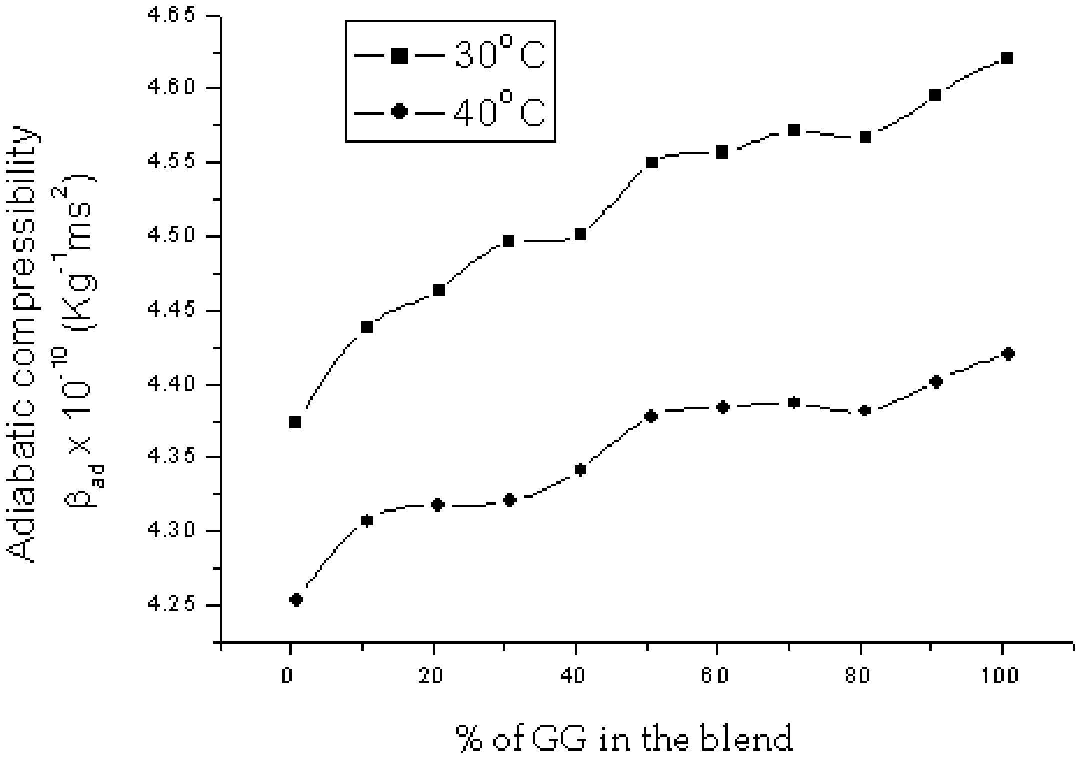

Figure 4: Variation of adiabatic compressibility with composition of GG/PVA blend in aqueous solution at 30°C and 40°C

3.2 Reduced viscosity measurements

Reduced viscosities of homo-polymers GG, PVA, and their blend compositions (20/80, 40/60, 50/50, 60/40, and 80/20) were measured at 30ºC and 40ºC. Huggin's plots of reduced viscosities of the pure polymers and their blend compositions against concentrations are shown in Figs.5, and 6, respectively.

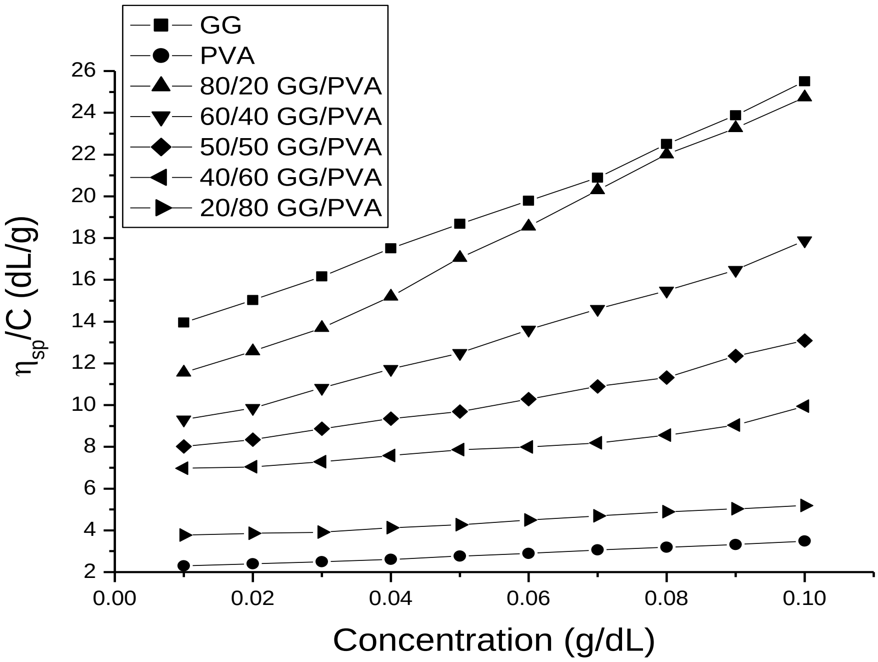

Figure 5: Huggins's plot for 0.1% (w/v) GG/PVA blend at 30°C

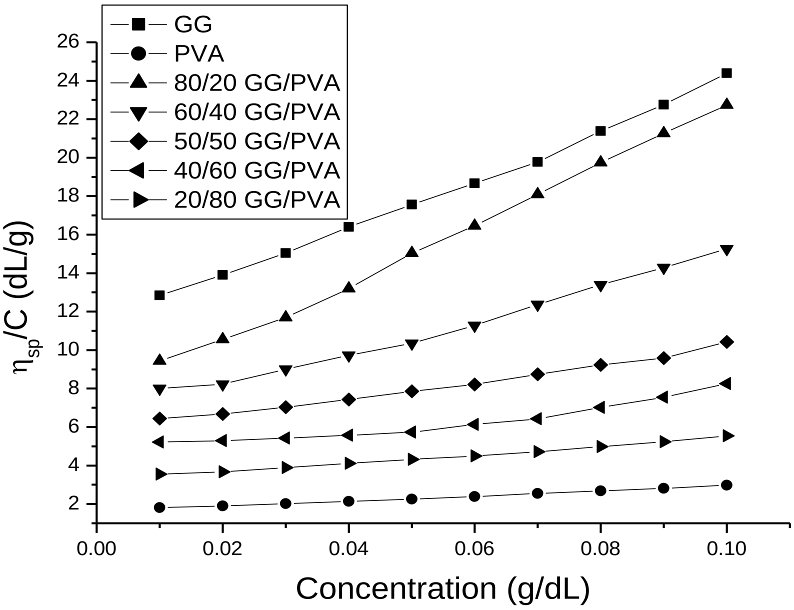

Figure 6: Huggins's plot for 0.1% (w/v) GG/PVA blend at 40°C

The plots were linear. A higher slope variation for 80/20 GG/PVA blend compositions may be attributed to the mutual attraction of macromolecules in solution which leads to the increase of hydrodynamic volume [5, 6, 10]. The intercept of reduced viscosity versus concentration plots gives the intrinsic viscosity of the corresponding polymer and their blend, and the computed values of Chee's [26]interaction parameters μ,and Sun et al.'s [27]interaction parameters α of GG/PVA blend compositions at 30°C and 40°C are which are presented in Tables 1, and 2, respectively.

It is observed from the table that the μ values are negative when the GG content is up to 50% in the blend and then positive beyond this value at 30°C and 40°C. However, a values are found to be positive for the 80/20 blend compositions of GG/PVA at both temperatures and negative for the remaining compositions. The secondary interactions are taken into account in computing α values [10]. Hence, it confirms that the GG/PVA blend is miscible only when the GG content in the blend is more than 60 wt% at 30°C and 40°C. The temperature did not have any significant effect on the miscibility of GG/PVA blends.

Table 1: Intrinsic viscosity and interaction parameter of GG/PVA blends at 30°C

Blend Composition (GG/PVA)	$[\eta]_{exp}$ (dL/g)	μ	α
0/100	2.114	-	-
20/80	3.048	- 0.4999	- 0.0904
40/60	6.409	- 0.3785	- 0.2735
50/50	7.182	- 0.1389	- 0.1238
60/40	7.778	0.2342	- 0.0162
80/20	10.33	0.7772	0.0095
100/0	12.422	-	-

Table 2: Intrinsic viscosity and interaction parameter of GG/PVA blends at 40°C

Blend Comp. GG/PVA	$[\eta]_{exp}$ (dL/g)	μ	α
0/100	1.631	-	-
20/80	3.241	- 0.5097	- 0.0491
40/60	4.465	- 0.3961	- 0.1655
50/50	5.784	- 0.2833	- 0.2229
60/40	6.579	0.1501	- 0.0335
80/20	7.456	0.9206	0.0357
100/0	11.313	-	-

VI. CONCLUSION

Based on viscosity, ultrasonic velocity, density and refractive index measurements, it is found that the polymer blend of GG/PVA is miscible when the GG content is more than 60%. Below this critical GG concentration the blends were found to be immiscible. Hence GG/PVA blend in aqueous solution is semi-miscible in nature at 30ºC and 40ºC. Variation of temperature did not have any significant effect on the miscibility.

REFERENCE

[1] P. Prasad, G. S. Guru, H. R.Shivakumar, K. S.Rai, Miscibility, thermal, and mechanical studies of hydroxypropyl methylcellulose/pullulan blends, *Journal of applied polymer science 110 (1)*, (2008), 444-452.

[2] G. S. Guru, P. Prasad, H. R.Shivakumar, S. K.Rai, Miscibility studies of polysaccharide xanthan gum/PVP blend, *Journal of Polymers and the Environment 18 (2)*, (2010), 135-140.

[3] G. S. Guru, P. Prasad, H. R.Shivakumar, S. K.Rai, Miscibility, thermal and mechanical studies of methylcellulose/poly (vinyl alcohol) blends, *Int. J. Res. Pharm. Chem 2 (4)*, (2012), 957-968.

[4] G. S. Guru, P. Prasad, H. R.Shivakumar, S. K.Rai, Studies on the Compatibility of Pullulan–Carboxymethyl Cellulose Blend Using Simple Techniques, *Malaysian Polymer Journal 3 (2),* (2008), 13-23.

[5] P. Prasad, G. S. Guru, H. R.Shivakumar, K. S.Rai, Investigation on miscibility of sodium alginate/pullulan blends, *Journal of Polymers and the Environment 20 (3)*, (2012), 887-893.

[6] B.Vishwanath, H. R.Shivakumar, R. K.Sheshappa, S. Ganesh, P. Prasad, G. S. Guru, B. B.Bhavya, In-vitro release study of metoprolol succinate from the bioadhesive films of pullulan-polyacrylamide blends, *International Journal of Polymeric Materials 61 (4),* (2012), 300-307.

[7] V.Bhat, H. R.Shivakumar, R. K.Sheshappa, S. Ganesh, P. Prasad, G. S. Guru, B. B.Bhavya, Miscibility and thermal behavior of pullulan/polyacrylamide blends, *Journal of Macromolecular Science, Part A 48 (11)*, (2011), 920-926.

[8] G. S. Guru, P. Prasad, H. R.Shivakumar, S. K.Rai, Miscibility and thermal studies of PVP/Pullulan blends, *International Journal of Plastics Technology 14 (2)*, (2010), 234-245.

[9] G. S. Guru, B. B.Bhavya, H. R.Shivakumar, V.Bhat, P. Prasad, Investigation on miscibility of biocompatible Guar Gum/Pullulan blend, *Malasian Polymer Journal 8 (1)*, 2013, 33-37.

[10] Bhavya M. S., Savitha M. B., Prasad P., Miscibility studies of GG/CMC blends in aqueous solution, *International Journal of Advanced Research in Science and Engineering, 6 (1)*, (2017), 514-523.

[11] Prasad P., Bhavya M. S., Abhijith P. P., Sreelakshmi S. K., Savitha M. B., Physico-chemical and thermal property studies of GG/CMC blend thin films, *International Journal of Advanced Research in Science and Engineering, 6 (6)*, (2017), 572-578.

[12] Changhua Liu, Chaobo Xiao, Hui Liang, Properties and structure of PVP-Lignin blend films, *J. Appli. Polym. Sci., 95*, (2005), 1405-1411.

[13] TuncerCaykara, SerkanDemirci, S. Mehmet Eroglu, OlgunGuven, PEO and its blends with sodium alginate, *Polymer*, *46*, (2005), 10750-10757.

[14] C. Tonin, A. Aluigi, C. Vineis, A. Montarsolo, F. Ferrero, Thermal and structural characterization of PEO/keratin blend films, *Journal of Thermal Analysis and Calorimetry, 89*, (2007), 601-608.

[15] B. Ramaraj, Crosslinked PVA and starch composite films: study of their physicomechanical, thermal and swelling properties, *J. Appli. Polym. Sci., 103*, (2007), 1127-1132.

[16] G. B. Antonio Pereira, F. RubiaGouveia, M. Gizilene de Carvalho, F. AdleyRubira, C. Edvani Muniz, Polymer blends based on PEO and starch: Miscibility and spherulite growth rate evaluated through DSC and optical microscopy, *Material Science and Engineering: C, 29*, (2009), 499-504.

[17] K. C. Basavaraju, T. Demappa, S. K. Rai, Miscibility studies of polysaccharide xanthan gum and PEO in dilute solution, *Carbohydrate Polymers, 69*, (2007), 462-466.

[18] RanjithJayasekara, Ian Harding, Ian Bowater, B. Y. Gregor Christie, T. Greg Lonargan, Biodegradation by composting of surface modified starch and PVA blended films, *Journal of Polymers and the Environment, 11*, (2003), 49-56.

[19] Lijun Mao, Syed Imam, Sherald Gordon, PatriziaCinelli, Emo Chiellini, Extrued corn starch –glycerol-PVA blends: Mechanical properties, morphology and biodegradability, *Journal of Polymers and the Environment, 8*, (2000), 205-211.

[20] G. G. D. Silva, P. J. A. Sobral, R. A. Carvalho, P. V. A. Bergo, O. Mendieta-Taboada, A. M. Q. B. Habitante, Biodegradable films based on blends of gelatin and PVA: Effect of PVA type or concentration on some physical properties of films, *J. Polym. Environ., 16*, (2008), 276-285.

[21] Dipa Ray, Papri Roy, SuparnaSen Gupta, Siba Prasad Sen Gupta, K. Amar Mohanty, ManjusriMisra, A study of dynamic mechanical and thermal behaviour of starch/PVA based films, *J. Polym. Environ., 17*, (2009), 49-55.

[22] J. Jayaraju, J. Keshavayya, S. K. Rai, K. C. Basavaraju, Miscibility studies on chitosan/poly (vinyl alcohol) blends, *J. Macro. Mol. Sci. Part A: Pure and Applied Chemistry, 45*, (2008), 271-275.

[23] WU Kai, XU Zhen-Liang, WEI Yong-Ming, Sodium alginate-PVA/polysulphone (SA-PVA/PSF) hollow fiber composite pervaporation membrane for dehydration of ethanol-water solution, *J. Shanghai Univ. (Engl Ed), 12*, (2008), 163-170.

[24] A. M. Bochek, I. L. Shevchuk, L. M. Kalyuzhnaya, Properties of aqueous solution of methyl cellulose/PVA blends, *Russian Journal of Applied Chemistry, 79*, (2006), 2007-2012.

[25] Kunal Pal, K. AjithBanthiya, K. DipakMajumdar, Preparation and characterization of PVA-gelatin hydrogel membranes for biomedical application, *AAPS Pharm. Sci. Tech., 8*, (2007), 1-5.

[26] Chee K. K., Determination of polymer-polymer miscibility by viscometry, *Eur. Polym. J., 26*, (1990), 423-426.

[27] Sun Z., Wang W., Feng Z., Criterion of polymer-polymer miscibility determined by viscometry, *Eur. Polym. J., 28*, (1992), 1259-1261.