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Characterization and Viscometric Study of Poly (vinyl alcohol) / Poly (ethylene glycol) Blends

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Abstract
In this study, we measure the viscosity of polyvinyl alcohol (PVA)/polyethylene glycol (PEG) blends in dimethyl solfoxide (DMSO) as a prevalent solvent. We carried out at the different percentages of the blend compositions (70/30,60/40, 50/50, 40/60, and 30/70) at 30, 40 and 50 Cº respectively. The viscosity information, μ interaction parameters have been computed to determine miscibility. These values proved that the blend was miscible in the all-percentages of the two content. Further, the results revealed that the change in temperature has significant effect on the miscibility of PVA/PEG polymer blends. Scientifically, simple (PVA / PEG) blends and unblends have been defined by the use of (FTIR).

Keywords: poly vinyl alcohol (PVA), poly ethylene glycol (PEG), PVA/PEG blends viscosity, characterization

1. Introduction
During the last two decades, the phenomenon of inter-diffusion in miscible polymer blends has been the subject of many investigations and is of interest in several applications such as welding and blending of polymers [1]. Intermolecular hydrogen bonding interaction by hydroxyl, halogen, carbonyl, and amide groups leads to the improvement of miscibility based on favorable enthalpy interaction between polymer chains. It also increases compatibility of immiscible polymer blends which improves the miscibility and the physical properties [2, 5].
Viscosity probes the interaction of molecular structure with the solution of several theories in polymer physics literature [6]. The viscometric method was used successfully in compatibility characterization of polymer blends, It was found to be of low cost, and rapid technique to study the miscibility of polymer blend [8, 7]. This technique was studied thermodynamics and interaction to alt of mixed of polymer blends [9, 12] in order to make two mixed polymers have energy lesser than them separated. Similarly, the PVA has been the subject of intensive researches due to its common applications in industry and it is of relatively low cost [14, 19]. Poly ethylene glycol (PEG) is a hydrophilic, nontoxic, water-soluble polymer and has a wide range of applications, mostly in cosmetic industries. This can be attributed to the fact that it does not cause damage or harm when it comes in contact with the skin or lips [20]. The miscibility characteristics of Methylcellulose (MC) and Poly (vinyl alcohol) (PVA) have been investigated [13].
PVA and PEG blends as water- soluble polymers which have been widely explored for numerous industries, such as biomedical and pharmaceutical applications due to its advantages like nontoxic, non-carcinogenic and bio adhesive properties [21].
In this study, we measured the viscosity of poly vinyl alcohol (PVA)/poly ethylene glycol l (PEG) blends in dimethyl solfoxide (DMSO) as a common solvent, for different blend compositions at 30, 40 and 50°C. The viscosity data and interaction parameters μ were computed to determine miscibility also IR of (PVA/PEG) blends and unblends were deeply characterized.

2. Experimental section
Materials and solution preparation
Poly (ethylene glycol) (PEG) with an average molecular weight of 3500-4500was supplied by Scharlu. Poly (vinyl alcohol) (PVA) of molecular weight was 76000 by Aldrich. Di methyl Solfoxide (DMSO) was supplied by Aldrich with purity 99.9% HPLC grade was used as reagent grades and used without further purification. The polymer solutions were prepared by dissolving 0.5g of each polymer separately in 100 ml DMSO, from these solutions were prepared different concentrations for each polymer within the range from 0.2 to 0.5 (g/dl) of polymer. Stock solutions of polymers and the blends of PVA/PEG of different compositions, 30/70, 40/60, 50/50, 60/40, and 70/30, were prepared in dimethysolfoxide. Viscosity measurements 30, 40 and 50 Cº were made using Ubbelohde viscometer that was placed in a thermostatically controlled bath with a precision of 0.01 Cº. The total weight of the two components in the solution was always maintained at 1 g/dL. All the viscosity measurements were performed according to Literatures [6, 8, 12].

FTIR Analysis
Fourier Transform Infrared Spectroscopy (FTIR) method was applied to characterize vibrations in molecules by measuring the absorption of light of certain energies that correspond to the vibration of the molecules from low to high frequency. FTIR spectra of polymer blends carried out by (SHIMADZU, FT-IR Spectrometer, Scimitar) with KBr pellets.

3. Results ad Dissections
Solution Properties
From Viscometric measurements reduced viscosity of polymers data for PVA, PEG pure and their blend in DMSO at 30,40 and 50 Cº. are presented in Tables 1,2 3 respectively. The plots reduced viscosity versus concentration curves for the pur components PVA and PEG

and their blends at 30, 40 and 50 Cº are shown in Figures1 to 3 respectively. From these plots, it is also clear evidence that the Huggin's curves are linear in nature indicating that PVA/PEG blends are miscibility. This cast may be attributed to the attraction of macromolecules' in solution that favors the polymer miscibility which leads to increase of hydrodynamic volume [23].

Table 1: Reduced viscosity data for PVA/PEG and their blends in solution at 30 Cº

Conc.	0.5 wt% of PVA/PEG blend composite (g/dl) at 30 Cº						
g/dl	100/0	0/100	70/30	60/40	50/50	40/60	30/70
0.5	1.01	0.221	0.75	0.67	0.57	0.47	0.40
0.4	0.981	0.208	0.72	0.65	0.56	0.45	0.39
0.3	0.955	0.181	0.70	0.64	0.54	0.44	0.37
0.2	0.943	0.169	0.68	0.62	0.52	0.41	0.35

Table 2: Reduced viscosity data for PVA / PEG and their blends in solution at 40 Cº.

Conc.	0.5 wt% of PVA/PEG blend composite (g/dl) at 40 Cº						
g/dl	100/0	0/100	70/30	60/40	50/50	40/60	30/70
0.5	0.943	0.180	0.68	0.63	0.54	0.46	0.36
0.4	0.915	0.176	0.66	0.61	0.53	0.43	0.35
0.3	0.890	0.162	0.64	0.59	0.51	0.41	0.34
0.2	0.875	0.153	0.61	0.58	0.49	0.39	0.33

Table 3: Reduced viscosity data for PVA / PEG and their blends in solution at 50 Cº.

Conc.	0.5 wt% of PVA/PEG blend composite (g/dl) at 50 Cº						
g/dl	100/0	0/100	70/30	60/40	50/50	40/60	30/70
0.5	0.850	0.164	0.64	0.57	0.46	0.38	0.29
0.4	0.835	0.151	0.61	0.55	0.44	0.36	0.28
0.3	0.818	0.138	0.60	0.53	0.42	0.34	0.26
0.2	0.798	0.122	0.58	0.52	0.41	0.33	0.25

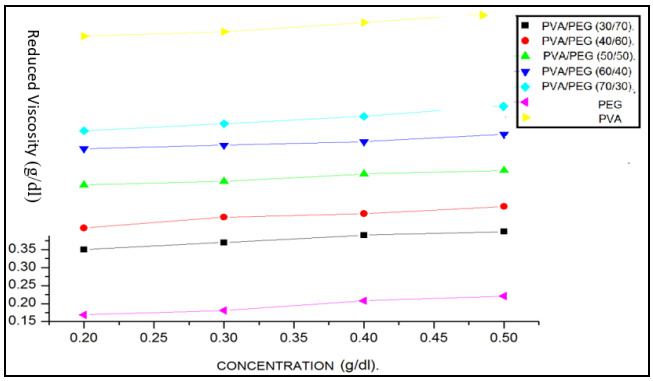

Fig 1: The variation of reduced viscosity 0.5 wt% of PVA/PEG blend composite at 30 Cº.

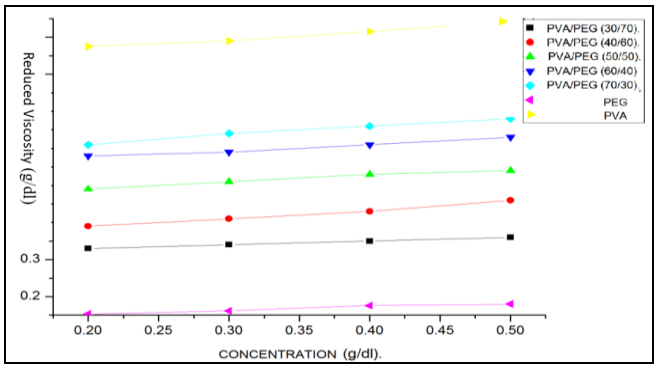

Fig 2: The variation of reduced viscosity 0.5 wt% of PVA/PEG blend composite at 40ºC.

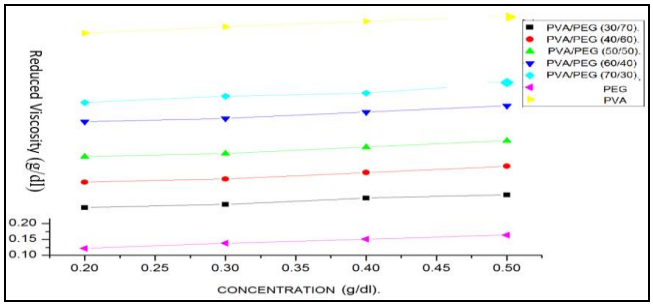

Fig 3: The variation of reduced viscosity 0.5 wt% of PVA/PEG blend composite at 50 Cº.

The intrinsic viscosity [η] and Huggins Coefficient K_H are determined from taking intercept and slop to liners of figures (1, 2, 3) these values show in Table 4.

Table 4: The Huggins constant K_H and Intrinsic viscosity [η] at different temperatures.

(PVA/PE	30 Cº		40 Cº		50 Cº	
	KH	[η]	KH	[η]	KH	[η]
100/0	0.227	0.8928	0.229	0.8256	0.173	0.7647
70/30	0.230	0.6320	0.230	0.5670	0.192	0.5410
60/40	0.190	0.5890	0.198	0.5430	0.196	0.4830
50/50	0.170	0.4880	0.171	0.4580	0.174	0.3730
40/60	0.190	0.3760	0.232	0.3410	0.178	0.2930
30/70	0.171	0.3180	0.10	0.3110	0.141	0.2210
0/100	0.083	0.1307	0.095	0.1345	0.139	0.0951

From the above data, it can be observed that the intrinsic viscosity for PVA and PEG, decreases for all the three systems with increases temperatures and that the intrinsic viscosity remains less than PVA and higher than PEG throughout the investigated temperature. Also K_H is referred to as the Huggins dimensionless constant and relates to the size and shape of polymer segments, as well as to hydrodynamic interactions between different segments of the same polymer chain. The K_H values of fall in the range 0.3 (for good polymer–solvent interactions) to 0.5 (for poor polymer–solvent interactions [24]. However, the K_H values in table4 are less than of 0.3. This value takes rang 0.083-0.232, so that they indicate that the solvent used (DMSO) was a good solvent for polymers due to its high polarity. In addition, the two polymers mixed are Polars, which increase interaction with each other and with the solvents as literature [25] and due to solvent quality improves the coiling sets in and reduction in viscosity is observed [26]. In addition to each PVA and PEG contains the -OH group, which increases the overlap between them by forming hydrogen bonds and thus increase the value of hydrodynamic and this corresponds with What has been reported in the literature [27, 28].

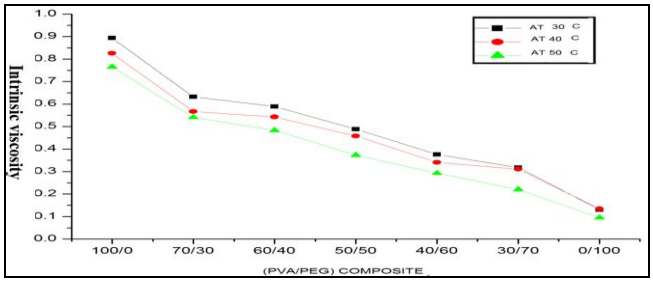

Fig 4: Intrinsic viscosity versus composition ratios at different temperatures.

According to figure5, Huggins constant K_H increases with temperature increasing. It is well- known fact that the K_H varies oppositely to the intrinsic viscosity when the quality of the solvent is changed. That's oppositely trend between [η] and K_H can be clearly observed in figure 6. That's increase can be attributed to the fact that Huggins constant depends upon the shape of molecule, its degree of association at high dilution in addition to quality of the solvent and some other hydrodynamic factors, so such trend is expected [29].

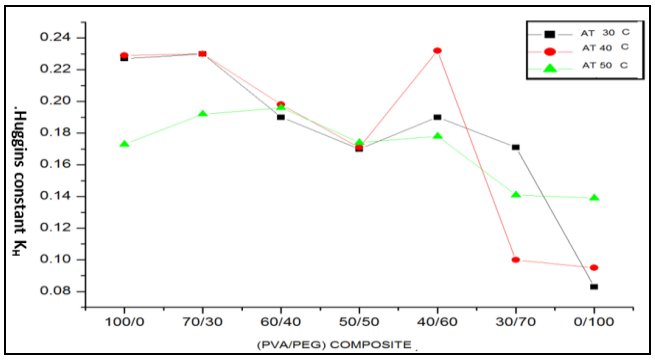

Fig 5: Huggins constant K_H versus composition ratios at different temperatures.

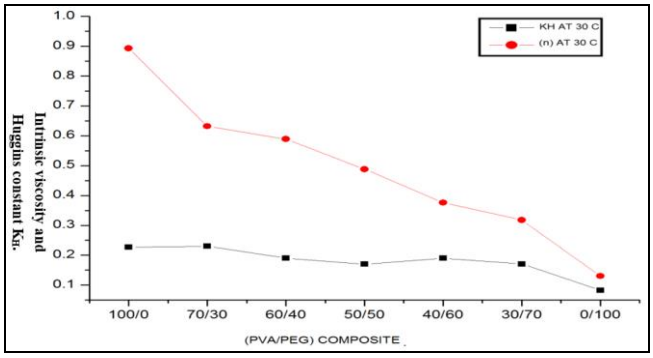

Fig 6: Intrinsic viscosity and Huggins constant K_H versus composition ratios at 30 Cº.

Using these values, Chee [7] suggested the general expression for interaction parameter when the polymers are mixed in weight fractions w1 and w2 as

$$\Delta B = \frac{(b - b')}{2w1.w2} \quad (1)$$

Where b = w1b11+w2b22 where b11 and b22 are the slopes of the viscosity curves for the components and b is related to Huggins coefficient K_H (30) as,

$$b = K_H[\eta]^2 \quad (2)$$

b defined a more effective interaction parameter, as follows: For ternary system, it is also given by

$$b = w_1^2 b11 + w_2^2 b22 + w_1 w_2 b12 \quad (3)$$

Where is slope for the blend solution? However, when intrinsic
viscosities of pure parts are far apart, Chee's theory does not account for the experimental information. He described a more effec tive parameter for predicting compatibility in such instances

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

Where [η] 1 and [η] 2 are the intrinsic viscosity for the pure component solutions.
The blend is miscible when (μ >= 0) and immiscible when (μ < 0) [22]. The values of μ calculated with the preceding expression at 30, 40 and 50 Cº are represented in Table5.

Table 5: Interaction parameters μ of PVA/PEG blends at 30, 40 and 50 Cº.

Compositions PVA/PEG	Interaction parameter (μ).		
	At 30 ℃º	At 40 Cº	At 50Cº
70/30	0.9543	0.7821	0.6654
60/40	1.2546	0.8445	0.8543
50/50	0.7132	0.3654	0.3754
40/60	0.8520	0.5321	0.4889
30/70	0.5429	0.2021	0.1652

The relation between the interaction parameters (μ) and intrinsic viscosity[η] are inverses according to equation (4), which can also be observed in Table 4 and 5.
In general, the results of interaction parameters (μ) in table5 enhancing and confirm that (PVA/PEG) blend in solutions may be miscible for all ratios which were investigated.

Fourier Transform Infrared Spectroscopy (FT-IR).
The representative FTIR spectra of Pure PVA and PEG are shown in Figure 6 the O-H stretching band in the FTIR range is the most distinctive feature of alcohols. In the PVA sample spectra, the wide range centered at 3385cm^{-1} was the stretching curve of the hydroxyl group with powerful hydrogen bonding as intra-and/or inter-type[31-32].The absorption band at 1436 cm^{-1} is allocated as the bending vibration of -CH_2 while the deformation vibration of C – CH_3 is linked with the absorption band at 1348 cm^{-1}. The signal at 1211 cm^{-1} is due to CH_2 wagging and is allocated at 1133 cm^{-1} to C – C and C – O – C stretching vibrations. In the PEG spectrum, the absorption at 3450 cm^{-1} due to stretching of terminal bonded (–OH) groups, and the broadened absorption bands for(-C-O-) from(1063 to1152)cm^{-1}are assigned to C–O group.
The bending absorption of (–OH) has two bands at1415 cm^{-1} and 1340cm^{-1}refer to the vibration coupling with wagging vibration of (C-H). The stretching of the methylene –CH_2- group in (-CH_2-O-) gives a broadened and strong bands at the region from (2845 to 2968)cm^{-1}and the bending has scissoring vibrations at (1468)cm^{-1}.

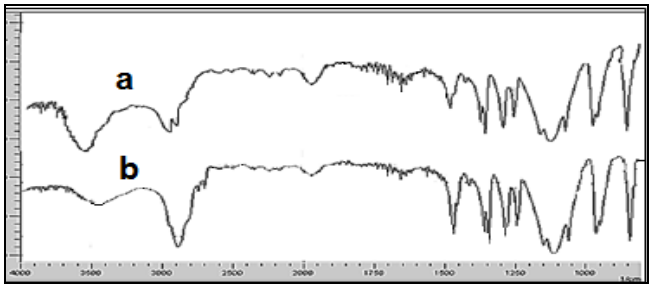

Fig 7: FTIR spectrum for both the pure PVA (a) and PEG (b).

The bands which appear in pure PEG at the (1968, 2166 and 2238) cm^{-1} are refer to the over tons and combination-tons for the low vibration bands [33]. This association results in a toothed shape of the wide band in the range (1062–1152) cm^{-1}, implying a large variety of the conformations states of C-O-C groups in self-associated PEG [34].

Fig 7 demonstrates the FT-IR spectra of PVA / PEG mixtures of a (1:1), b (2:1) and c (1:2) respectively. As the absorption peak at 2741 cm^{-1} for C-H stretching can be seen, the band intensity improved with the growing PEG component (1:2) as the PEG content rises, the absorption band frequency at 1646 cm^{-1} has risen, while the absorption peak intensity at 1557 cm^{-1} has decreased significantly. The intensity of the C-H stretching band at 1358 was discovered to decline with growing PEG content until the shoulder is soft or the peak at 1465 cm^{-1} is confused. The vibrations bands in the spectral region of 700-1300 cm^{-1} showed a declining tendency and moved to greater wave numbers.

The decline in absorption peak strength of 1133 cm^{-1} can be ascribed to a rise in PEG content and this represents the adverse position of PEG in the crystalline nature of PVA. Thus, in a combination (1:1), the spectra of PVA / PEG blends showed a decent resolution of 3380cm^{-1} band. This peak still low intensity with enhanced PEG content (1:2) at 3378cm^{-1} in Figure 7c and Strong intensity with enhanced PVA content (2:1) at 3385cm^{-1} in Figure 7b. In the spectrum of PVA / PEG mix (1:2) bands in the same region 1517cm^{-1} have low intensity relative to that (1:1 and 2:1). This may have been ascribed to enhanced intra-H bonding between PEG chains with enhanced PEG in blend. In the other hand the pure PVA hydroxyl group emerged mostly in the hydrogen bonded setup, corresponding to PVA containing a high density hydroxyl group and a more flexible chance to form intramolecular hydrogen bonding.

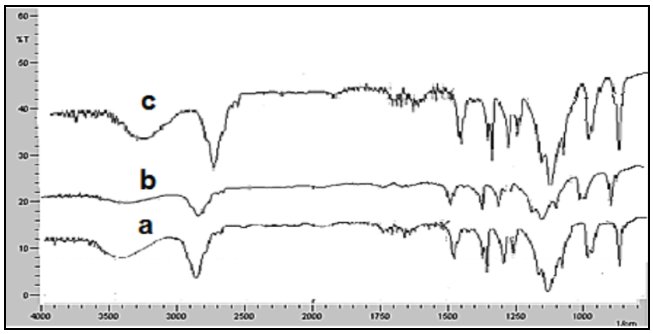

Fig 8: FTIR spectrum of (a, b, c) (1:1, 2:1 and 1:2) ratios of (PVA/PEG) blends.

Conclusion

From the previous analysis we conclude that the thermodynamic affinity (similarity - suitable)of the solvent for the polymer affect the flexibility of the polymer chains, degree of aggregation of chains and the structure of the solutions effect the viscosity of solutions. The shape of the reduced viscosity versus concentrations curves is similar to those for the homo polymers and it is possible to predict the intrinsic viscosity of blends from those of the constituent polymers. In the case of blending, it is concluded that all ratios and concentrations of polymer blend systems have been either miscible or compatibility. We are confirmed from the linear lines of the reduced viscosity versus concentrations plots and from the absence of crossover over the whole range of ratios and concentrations at temperatures which were used. Interaction parameters (μ) enhancing and confirm that (PVA/PEG) blend in solutions were miscible for all ratios which were investigated. It is also concluded that the viscometry is simple technique determine the miscibility or compatibility of polymer blend. The different sizes of spheres indicate the interaction effect with PVA, which is confirmed by the new peak that appeared and the wave numbers shifted to other peaks in the FT-IR spectrum.

References

1. Kausch HH, Tirell M. Polymer Inter diffusion Annual Rev Mater Sci. 1989; 19:341-377.
2. Sato M, Koshino T, Kajitani Y, Inamura I, Kubo Y. Miscibility study of polymer blends composed of semirigid thermotropic liquid crystalline polycarbonate, poly (vinyl alcohol), and chitosan J Appl Polym Sci. 2004; 93:1616.
3. Chen W, Wu J, Jiang M. Phase behavior and phase separation in blends of a liquid crystalline polymer and an amorphous polymer containing hydrogen- bonding interaction Macromol. Chem Phys. 1998; 1683.http://dx.doi.org/10.1002/ (SICI) 1521-3935(19980801)199:83.0.CO; 2-O, 1993, 6.
4. De Ilarduya MA, Euiburu JL, Espi E, Iruin JJ, Fernandez-Berridi MJ. Macromol. Blends of poly (hydroxy ether of bisphenol- A) with poly (2- vinylpyridine) and poly (4- vinylpyridine). Chem Phys. 194, 501. http://dx.doi.org/10.1002/macp,1993, 021940213.
5. Landry MR, Massa DJ, Landry CJT, Teegarden DM, Colby RH, Long TE, *et al*. Miscibility in binary blends of poly (vinyl phenol) and poly (n-alkylene 2,6-naphthalates). J Appl Polym Sci. 1994; 54:991. http://dx.doi.org/10.1002/app.1994.070540801
6. Yamakawa H. Modern Theory of Polymer Solutions, 1971.
7. Chee K. Determination of polymer-polymer miscibility by viscometry, Eur Polym. J. 1990; 26:423-426.
8. Sun Z, Wang W, Fung Z. Criterion of polymer-polymer miscibility determined by viscometry Eur Polym J. 1992; 28:1259-1261.
9. Cemile O, Gu¨ ner A. Solution thermodynamics of poly (ethylene glycol)/water systems J Applied Polymer Science. 2006; 101:203-216.
10. Jayaraju K, Rai K. J Mac. Science w Part B Physics. 2006; 45:741-47.
11. Aqeel S, Lath D, Bohdanecký M, Lathová E. The behavior of poly (n-dciyl methacrylate) in homologous series of n-alkanes: a methode for prediction of its application as viscosity index improver in motor oils and its miscibility with polymethylene. Kuwait J Sci Eng. 2003; 30:23.
12. Al-Hussam AM, Aqeel SM, Al-Gunaid MQ. Characterization and Solution Properties of Poly (Methyl Metha-Acrylate) – Poly (Ethylene Glycol) Blends, Thamar University Journal of Natural & Applied Sciences. 2011; A(4):67-75.
13. Guru GS, Prasad P, Shivakumarand HR, Rai SK. Miscibility, thermal and mechanical studies of methylcellulose/poly (vinyl alcohol) blends. IJRPC. 2012; 2(4).
14. Abd Alla SG, Nizam El-Din HM, El-Naggar AM. Electron beam synthesis and characterization of poly (vinyl alcohol)/montmorillonite nanocomposites J Appl

Polym Sci. 2006; 102:1129. http://dx.doi.org/10.1002/app.24370.
15. Abd El- Kader KM, El- Lawindy AYM, Mansour AF, Abdel Hamied SF. Cut- out filter for ultraviolet radiation from poly (vinyl alcohol), J Appl Polym. Sci. 2002; 84:1295. http://dx.doi.org/10.1002/app.10486
16. Abd El-Kader KM, Orabi AS. Spectroscopic behavior of poly (vinyl alcohol) films with different molecular weights. Polym Testing. 2002; 21:591. http://dx.doi.org/10.1016/S0142-9418(01)00129-5
17. Abd El-Kader KM, Abdel Hamied SF. Preparation of poly (vinyl alcohol) films with promising physical properties in comparison with commercial polyethylene film, J. Appl. Polym. Sci. 2002; 86:1219. http://dx.doi.org/10.1002/app.11068
18. Abd El-Kader KM, Abd Hamied SF, Mansour AB, El-Lawindy AM, El-Tantaway F. Effect of the molecular weights on the optical and mechanical properties of poly (vinyl alcohol) films. Polym. Testing. 2002; 21:849.
19. Sato M, Koshino T, Kajitani Y, Inamura I, Kubo Y. Miscibility study of polymer blends composed of semirigid thermotropic liquid crystalline polycarbonate, poly (vinyl alcohol), and chitosan. J Appl Polym. Sci. 2004; 93:1616. http://dx.doi.org/10.1002/app.20610
20. Dog Y, Niholy V, Jean MJ. Macromolecules. 1999; 32(16):518.
21. Teresa M, Adilson RG, Pessoa A. Ultraviolet- induced crosslinking of poly (vinyl alcohol) evaluated by principal component analysis of FTIR spectr, Polym. Int. 2001; 50:1068
22. Singh Y, Singh R. Compatibility studies on solutions of polymer blends by viscometric and ultrasonic techniques. Eur. Polym. J. 1983; 19:535-541
23. Ravi prakash SD, Rama HV, Rai SK. Miscibility studies of sodium alginate/poly (vinyl alcohol) blend in water by viscosity, ultrasonic, and refractive index methods, Journal of Applied Polymer Science. 2003; 90:33-39.
24. Rubinstein M, Colby R. Polymer Physics, 2003.
25. Cowie J. Lactone polymers. II. Hydrodynamic properties and unperturbed dimensions of poly- ε- caprolactone. Polymer. 1966; 7:487.
26. Bartram E, Goldsmith H. Rheological and extrusion characteristics of glass fiber- reinforced polycarbonate, Mason S. ACTA. 1975; 14:776.
27. Moore J, Kaur S. Blends of Poly (amide-enaminonitrile) with Poly (ethylene oxide), Poly (4-vinylpyridine), and Poly (N-vinylpyrrolidone), Macromolecules. 1998; 31:328-35.
28. Coleman M, Graf J, Painter P. Lancaster, Polymer Synthesis Polymer-Polymer Complexation PA: Technomic, 1991.
29. Muthukumar M, Freed K. Characteristic ratios of atactic poly (vinylethylene) and poly (ethylethylene). Macrumolecules. 1977; 10:899.
30. Huggins M. The Viscosity of Dilute Solutions of Long-Chain Molecules. IV. Dependence on Concentration. J Am Chem Soc. 1942; 64:2716.
31. Morrison RT, Boyd RN. Organic chemistry, 6th ed. (Prentice-Hall, New Jersey. 1992; 363089.
32. Ali ZI, Essa WH. Characterization of Electron Beam Irradiated Poly Vinyl Alcohol / Poly Ethylene Glycol Blends. J Sci. Res. 2014; 6(1):29-42.
33. Jayasekara R, Harding I, Bowater I, Christie GBY, Lonergan GT. Preparation, surface modification and characterisation of solution cast starch PVA blended films. Polym. Test. 2004; 23:17.
34. Bellamy LJ. Advances in Infrared Group Frequencies, Methuen & Co: Bungay, Suffolk, Chapter. 1968; 8:44.