Carbohydrate Polymers 82 (2010) 251–255

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

Compatibility studies of chitosan/PVA blend in 2% aqueous acetic acid solution at 30 °C

H.M.P. Naveen Kumar[a,*], M.N. Prabhakar[a], C. Venkata Prasad[a], K. Madhusudhan Rao[a], T.V. Ashok Kumar Reddy[a], K. Chowdoji Rao[a], M.C.S. Subha[b]

[a] *Dept. of Polymer Science & Tech., S.K.University, Anantapur, 515003, AP, India*
[b] *Dept. of Chemistry, S.K.University, Anantapur, 515003, AP, India*

ARTICLE INFO

Article history:
Received 13 January 2010
Accepted 13 April 2010
Available online 21 April 2010

Keywords:
Polymer blends
Compatibility
Miscibility
Chitosan
Poly(vinyl alcohol)

ABSTRACT

The miscibility of chitosan (CS) and poly(vinyl alcohol) (PVA) blends in aqueous acetic acid solution was studied using viscosity, ultrasonic velocity and refractive index techniques at 30 °C. From the viscosity data by using Sun and Chee et al., approaches, the interaction parameters ΔB, μ and α are also calculated to predict the blend compatibility of the blend solutions. The results of these blends data suggest that CS/PVA blends were completely miscible in all proportions. The results pertaining to variation of ultrasonic velocity (v) and their derived parameters such as adiabatic compressibility, acoustic impedance, relaxation strength and Rao number also supports the miscibility nature of these blends. This is further confirmed by refractive index results also. Differential scanning calorimetry (DSC), XRD and FT-IR were also used to confirm the compatibility of the CS/PVA blends in the solid state (thin films). Experimental results showed that the blends of CS and PVA are miscible at all the compositions due to the strong intermolecular hydrogen bonding interactions between CS and PVA.

1. Introduction

To satisfy the growing needs of new materials with specific properties such as engineering materials, new polymers have been synthesized (Lipscomb & Banerjee, 1993; Pinnau, 1993; Stadler et al., 1995) and chemical modifications in conventional polymers have also been proposed (Gagnon, Lenz, & Farris, 1994; Ikada, 1994; Ohya, Okawa, Murata, & Ouchi, 1996). But the mixture of two or more polymers, forming a polymer blend, continues to be an economical method to obtain new polymeric material (Utracki, 1989). The final properties of a polymeric blend will commonly depend on the properties of its polymeric components, its composition and, mainly, on the miscibility of the constituent polymers (Olabisi, Robeson, & Shaw, 1979). In some cases, by synergistic effects, the blend can present better properties than the pure components (Olabisi et al., 1979; Utracki, 1989).

Several works on polymer–polymer miscibility have been developed in the last 20 years (Cowie, 1985; Paul, Barlow, & Keskula, 1973). For such investigations, the techniques most commonly and widely used are electron microscopy (Inoue & Ougizawa, 1989), spectroscopy (Colemann & Printer, 1984), thermal analysis (Hourston, Zhang, Song, Pollock, & Hammiche, 1997) and inverse gas chromatography (Mandal, Bhattacharya, & Bhattacharya, 1989). Other techniques, using alternative properties (Muniz, Vasquez, Bruns, Nunes, & Wolf, 1992) or less expensive techniques, for instance viscometry, ultrasonic velocity and refractometry methods are also been proposed (Chandralekha Fadnis, Illiger, Rao, & Demappa, 2008; Sashidhara, Guruprasad, & Vararadarajulu, 2002). Chee (1990) and Sun et al. (1992) suggested the viscometric method for the study of polymer–polymer miscibility. Paladhi and Sing (1994a, 1994b) showed that the variation of ultrasonic velocity and viscosity with blend composition is linear for miscible blends and non-linear for immiscible blends. Basav Raju, Damappa, and Rai (2006) also used refractive index method for the miscibility of polymer blends.

Chitosan is a linear polysaccharide composed of randomly distributed β-(1-4)-linked D-glucosamine (deacetylated unit) and N-acetyl-D-glucosamine (acetylated unit). It has a number of commercial and possible biomedical uses.

PVA is a non-toxic, water soluble, bio-compatible and biodegradable synthetic polymer which is widely used in bio chemical and bio medical applications.

Literature reveals that there were no reports on the blend compatibility of chitosan/PVA. Hence in the present work viscosity, ultrasonic velocity, density and refractive index techniques were used to determine the miscibility of CS/PVA blends in 2% acetic acid solution at 30 °C. Further, the blends of natural/synthetic polymers

---

* Corresponding author.
E-mail address: naveen_hmp@yahoo.com (H.M.P. Naveen Kumar).

0144-8617/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2010.04.021

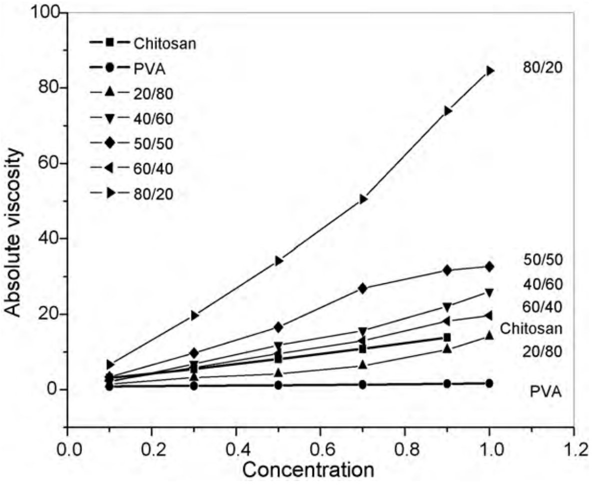

Fig. 1. Variation of absolute viscosity with concentration of different compositions of CS/PVA blend in 2% acetic acid solution at 30 °C.

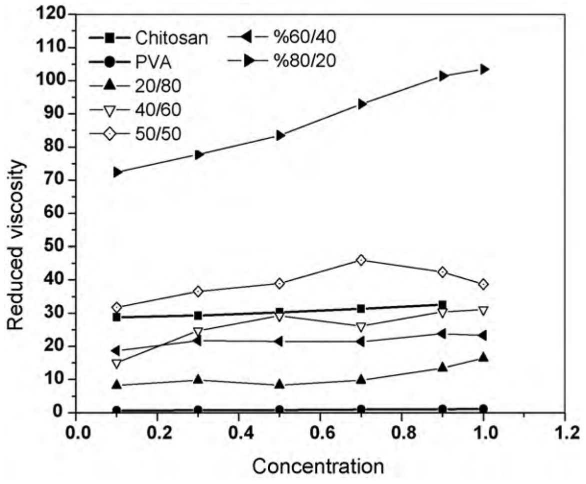

Fig. 2. Variation of reduced viscosity with concentration of different compositions of CS/PVA blend in 2% acetic acid solution at 30 °C.

useful for preparing polymers with bio-degradable nature which further useful to avoid polymer pollution.

2. Experimental

75–85% deacetylated chitosan of analytical grade with low molecular weight from Aldrich chemicals, USA. PVA (mol wt. 1,25,000) from s.d. fine chemicals, Mumbai and AR grade acetic acid from E-Merck India Ltd., were used in this work. A dilute polymer solution of 1% (w/v) was prepared for all studies. Stock solution of homo-polymers and the blends of CS/PVA of different compositions 20/80, 40/60, 50/50, 60/40, 80/20 were prepared in 2% acetic acid solution. The viscosity measurements at constant temperatures were made using an ubbelohde suspended level viscometer with the flow time of 96 s for distilled water. The total weight of the two components in the solution was always maintained at 1.0 g/dl. The ultrasonic velocity measurements were performed by using an ultrasonic interferometer manufactured by M/s. Mittal enterprises, New Delhi (Chowdoji Rao et al., 2006) at constant temperature maintained by circulating water from a thermostat through the double-walled jacket of the ultrasonic experimental cell. The experimental frequency was 2.0 MHz, and the velocity measurements were accurate to better than ±0.05%. The densities of the solutions were measured at constant temperature by the specific gravity bottle. The refractive indices of the solutions were measured using an Abbe's Refractometer with a thermostat water-circulation system (Vijay Kumar Naidu, Chowdoji Rao, & Subha, 2002). All the above measurements were carried out at a constant temperature at 30 ± 0.05 °C. The accuracy of the refractive index measurements is ±0.02%. The constant temperature was maintained in a thermostat bath, with a thermal stability of ±0.05 °C.

3. Results and discussions

3.1. Viscosity studies

The measured values of densities (ρ) and absolute viscosities (η_{ab}) were used to calculate the reduced viscosities (η_{red}) over the wide range of concentrations of the blend solutions for different compositions 0/100, 20/80, 40/60, 50/50, 60/40, 80/20 and 100/0 of 1% (w/v) of CS/PVA blends in 2% acetic acid solution at 30 °C.

The absolute viscosity vs. concentration curves for CS, PVA and their blends of different compositions are shown in Fig. 1. It is clearly evident from Fig. 1, that all these curves show linear nature. It was well established earlier by many workers (Kuleznev, Melnikova, & Klykova, 1978; Singh & Singh, 1984) that the variation of viscosity vs. concentration plots are linear for compatible blends and non-linear for incompatible blends. On this basis in the present study, it is noticed that the curves varied almost linearly for all the compositions of this blend and which in turn indicates miscibility nature.

From Fig. 1, it is also observed that as the concentration of CS increases in the blend, the absolute viscosity also increases. This may be attributed that the molecules of PVA can interact with several chains of chitosan and can form highly cross linked structure, which causes high solution viscosity. Further, with the increase in proportion of CS in the blend along with cross linking effect, the effect of hydrogen bonding between the hydroxyl groups of CS and PVA also increases.

The Huggins plots of reduced viscosity against concentration for different compositions of CS/PVA blends at 30 °C are shown in Fig. 2. On extrapolating to zero concentration, the intrinsic viscosities are determined and the values of CS, PVA and CS/PVA blends of different compositions (20/80, 40/60, 50/50, 60/40, 80/20) are 27.5, 0.57, 9, 13, 19.5, 23 and 26 dl/g respectively. These values indicate that the intrinsic viscosity values of CS/PVA blends for different compositions are in between the pure polymer values. The reasonable interpretation may be that the attractive interactions between CS and PVA existed in blend solution. These attractive interactions may lead to decrease the intermolecular excluded volume effect and decrease the hydrodynamic volume. As a consequence, the CS/PVA blend coils expand, which causes an increase in the intrinsic viscosity of CS/PVA blends (Fig. 3).

From these graphs, it is also clearly evident that all the Huggins plots are linear in nature which may be attributed to the mutual attraction of macromolecules in solution which further favors the polymer miscibility. A similar observation was reported by (Yang Haiyang, Zhupingping, & Yuanyun Jhangtio, 1999) from their viscometric investigations on intermolecular interactions between PMMA and PVAc in cyclohexane.

3.2. Chee and Sun Interaction Parameters

In order to quantify the miscibility nature of the present polymer blend system, interaction parameters ΔB and μ suggested by Chee (1990) and 'α' suggested by Sun, Wang, and Fung (1992) are calculated with the help of the equation 1 at 30 °C and are presented

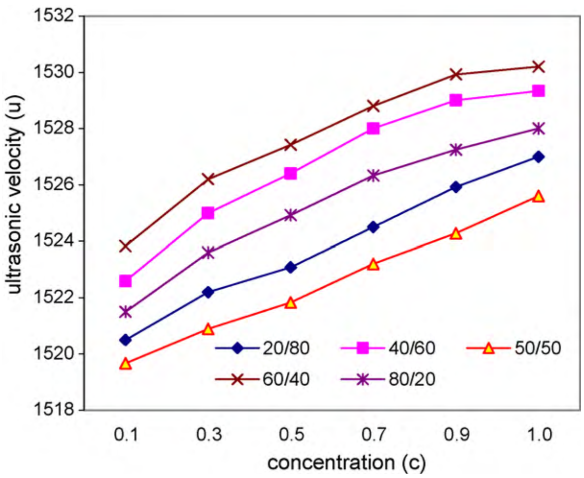

Fig. 3. Ultrasonic velocity vs. concentration of CS/PVA blends in 2% acetic acid solution at 30 °C

in Table 1.

$$\mu = \frac{\{(b - b_{22})/([\eta] - [\eta]_2)\} - \{(b_{33} - b_{22})/([\eta]_3 - [\eta]_2)\}}{2([\eta]_3 - [\eta])} \qquad (1)$$

It is observed from Table 1 that the values of ΔB, μ, and α are positive for all the compositions of CS/PVA blend in 2% acetic acid solution at 30 °C. In general if ΔB, μ and α are positive for any poly-blend system, it is considered as a miscible one whereas if these values are negative, the poly-blends are considered as immiscible one. Based on this, it is concluded that CS/PVA blend shows miscibility nature for all the blend compositions. A similar observation was made by (Sarswathi et al., 2008) in the case of sodium alginate/poly(acrylamide) blends from their viscosity studies.

3.3. *Ultrasonic velocity and refractive index studies*

To confirm the miscibility/immiscibility nature of this polymer blend the authors have measured the ultrasonic velocity and refractive index for CS, PVA and different compositions of CS/PVA blends in water at 30 °C. For further confirmation of the compatibility of this system, the derived acoustical parameters such as the adiabatic compressibility (β_{ad}), acoustic impedance (z), relaxation strength (γs) and Rao number (R) are calculated. These parameters vary linearly for different concentrations of all the blend compositions in 2% acetic acid solution. In general the variation of these parameters with blend composition is linear, if it is miscible blend and non-linear if it is immiscible.

From the results, we can conclude that the linear variation of the curves relating the different acoustical parameters indicate miscibility nature of (CS/PVA) blends in 2% acetic acid solutions. A similar observation was reported by (Basav Raju et al., 2006) from their ultrasonic investigation on compatibility of CS/Gelatin blends. The compatibility nature of this blend supports the conclusions drawn from the viscosity studies.

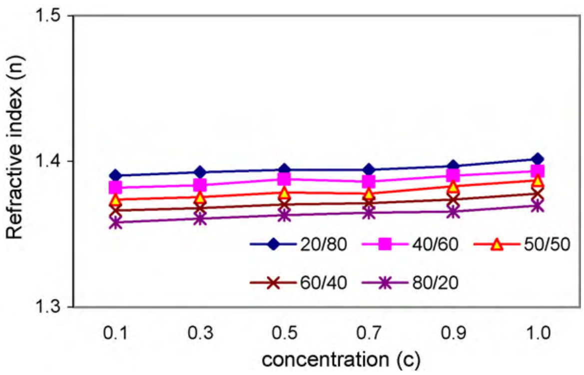

Fig. 4. Refractive index vs. concentration of CS/PVA blends in 2% acetic acid solution at 30 °C.

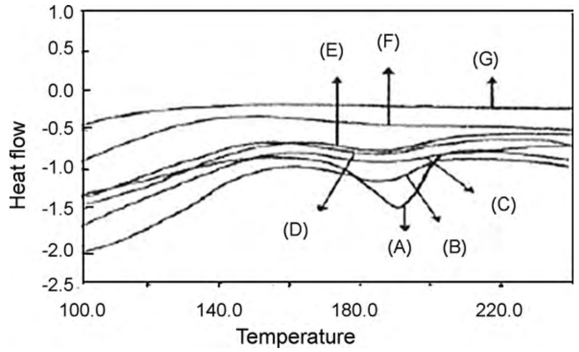

Fig. 5. DSC thermograms of CS/PVA blends: (A) pure PVA, (B) 20/80 (CS/PVA), (C) 40/60 (CS/PVA), (D) 50/50 (CS/PVA), (E) 60/40 (CS/PVA), (F) 80/20 (CS/PVA) and (G) pure CS.

It is also evident from Fig. 4 that the refractive index values varied linearly with the concentrations of different blend compositions as observed in case of ultrasonic and different acoustic parameters. This further confirms the miscibility of CS/PVA blend systems.

3.4. *DSC studies*

We can estimate the polymer–polymer miscibility by determining the glass transition temperature (T_g) of the blend and its comparison with the T_g of component polymers, if one of the components is crystalline, then depression in the melting temperature T_m can also be used to study the blend the compatibility (Nishil and Wang, 1975; Imken et al., 1976; Miura et al., 1999).

By estimating the depression in the melting temperature (T_m) of blend, we can estimate the blend miscibility of one of the components is crystalline in nature.

In the present study, DSC was used to estimate the T_m of the blends to investigate the compatibility of PVA and CS blends. Fig. 4 displays the DSC thermograms of PVA in CS/PVA blends together with individual polymers, since CS did not show any significant transition in the temperature range of the DSC scans. From Fig. 5,

Table 1
Chee and Sun's interaction parameters for CS, PVA and for different compositions of 1% (w/v) CS/PVA blend in acetic acid solution at 30 °C.

Blend composition (%)	Chee's differential interaction parameters		Sun's miscibility parameter
	ΔB	μ	$\alpha \times 10^3$
20/80	+1.14	+0.0015	+3.45
40/60	+22.60	+0.0310	+3.16
50/50	+21.40	+0.0290	+3.93
60/40	+4.90	+0.0062	+4.49
80/20	+51.40	+0.0084	+5.59

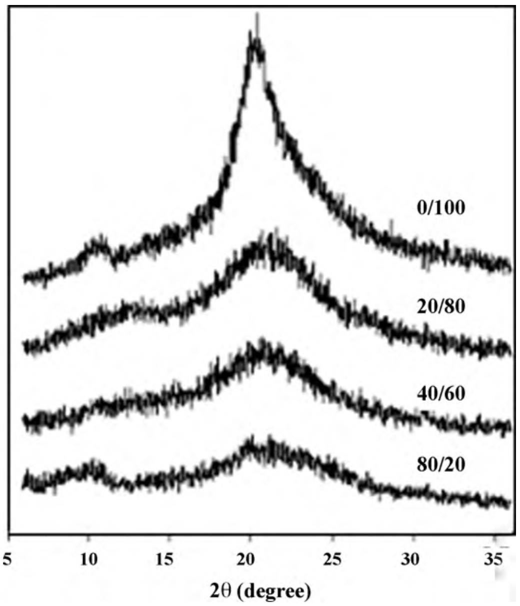

Fig. 6. XRD patterns of the membranes with different weight ratio of CS/PVA.

it was observed that the T_m of PVA was 190.55 °C. In the present study, variations in T_m of PVA in the blend were considered as a measure of blend compatibility. The melting temperature of the blends has decreased from 188 to 182 °C, as the composition of CS in the blend varied from 20 to 80 wt% respectively, which indicated the blend compatibility in the above mentioned range.

The pure PVA blend films showed a relatively large and sharp endothermic curve with a peak at 188 °C. However, for CS/PVA blend, endothermic curve became broad and obtuse, and the peak shifted toward the low temperature. This indicated that the crystalline nature of PVA was decreased by the addition of CS. It was observed that the peaks of the endothermic curves shifted toward the low temperature from 188 to 182 °C with increasing CS content in the blend. This demonstrated that the CS content in the blend leaded to decreasing tendency of crystallization of the blend.

3.5. XRD spectra

Fig. 6 presents the XRD patterns of CS/PVA blends under study. For the pure PVA, there were two peaks around $2\theta = 10.7^\circ$ and $2\theta = 20.4^\circ$ (Nakane, Yamashita, Iwakura, & Suzuki, 1990). The diffraction model of CS fiber showed three typical peaks at $2\theta = 0.5^\circ$, $2\theta = 15.4^\circ$, and $2\theta = 20.1^\circ$ (Samules, 1981). If there were no or weak interaction between CS and PVA molecules in the blend films, each component would has its own crystal region in the blend films, and XRD patterns would be expressed as simple mixed patterns of CS and PVA with the same ratio as those for mechanical blending. In fact, the peak of PVA at $2\theta = 10.7^\circ$ became weak until disappearing with increasing CS content in the blend. The diffraction peak of CS at 15.4° disappeared in the blends. Moreover, the peak of electrospun fibers of CS/PVA blends around $2\theta = 20.4^\circ$ slightly shifted towards high 2θ from 20.7° to 21.4° with increasing CS content in the blend. These evidences further concluded that strong interaction occurred between CS and PVA molecule in the blends.

3.6. FT-IR spectra

FT-IR measurements were taken to confirm the compatibility of CS/PVA and to understand the interactions between these blends. The PVA films exhibited a number of absorption peaks at 2940, 1448, 1333, 1248, 1095 and 847 cm^{-1}, which were attributed to the $V_\alpha(CH_2)$, δ(CH–OH), δ(CH–OH), ω(CH), ν(C–O) and ν(C–C) resonance, respectively (Zheng et al., 2001). CS membrane showed FT-IR absorption features around 898 and 1151 cm^{-1} peaks assigned saccharine structure and a weaker amino characteristic peak at 1255 cm^{-1} was the absorption of δ(O–H), and the peak at 1383 cm^{-1} was assigned to the CH_3 symmetrical deformation mode (Zheng et al., 2001). From Fig. 7, It was observed that the absorption peak at about 3441 cm^{-1} concerned with –OH and –NH stretching vibrations shifted to a lower wave number with the increase of PVA content in the blends. Moreover, compared with FT-IR spectra of pure CS membrane, the absorption peak of CS/PVA nano-fibers at 1255 cm^{-1} disappeared. These results suggested the formation of hydrogen bond between CS and PVA molecule.

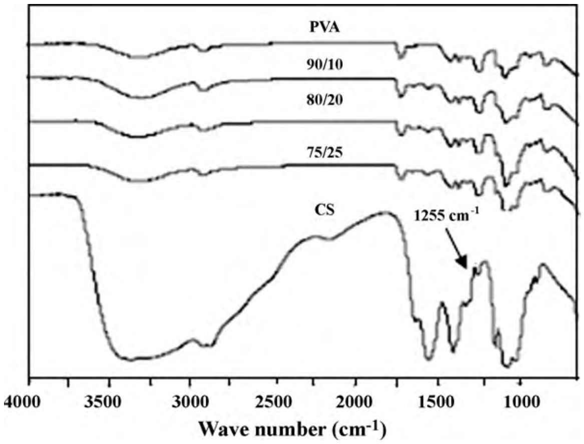

Fig. 7. FT-IR spectra of the membranes with different weight ratio of CS/PVA.

4. Conclusion

Based on viscosity, ultrasonic velocity and refractive index measurements, it is concluded that the CS/PVA blend has been found to be miscible in all compositions. The reason may be due to strong intermolecular interactions between CS/PVA. FT-IR, XRD and DSC analysis demonstrated that there were strong intermolecular hydrogen bonds between CS and PVA molecules.

References

Basav Raju, K. C., Damappa, T., & Rai, S. K. (2006). *Carbohydrate Polymers*, *74*, 779.

Chandralekha Fadnis, Illiger, S. R., Rao, K. P., & Demappa, T. (2008). *Carbohydrate Polymers*, *74*, 779.

Chee, K. K. (1990). *European Polymer Journal*, *26*, 423.

Chowdoji Rao, K., Krishna Rao, K. S. V., Lokesh, B. G., & Subha, M. C. S. (2006). Compatibility of Chitosan/Polyvinyl alcohol blend in aqueous acetic acid Solutions at various temperatures. *Asian chitin journal*, *2*, 21–28.

Colemann, M. M., & Printer, P. C. (1984). *Applied Spectroscopy Reviews*, *23*, 255.

Cowie, J. M. G. (1985). Miscibility. In H. F. Mark (Ed.), *Encyclopedia of polymer science and engineering. Supplement* (p. 455). New York: Wiley.

Gagnon, K. D., Lenz, R. W., & Farris, R. J. (1994). *Polymer*, *35*, 4368.

Hourston, D. J., Zhang, H. X., Song, M., Pollock, M., & Hammiche, A. (1997). *Thermochem Acta*, *294*, 23.

Imken, R. L., Paul, D. R., & Barlow, J. W. (1976). Transition behavior of poly(vinylidene fluoride)/poly(ethyl methacrylate) blends. *Polymer Science and Engineering*, *16*, 593–601.

Inoue, T., & Ougizawa, T. (1989). *Journal of Macromolecular Science-Chemistry*, *A26*, 147.

Kuleznev, V. N., Melnikova, O. L., & Klykova, V. D. (1978). *European Polymer Journal*, *44*, 455.

Lipscomb, G. G., & Banerjee, T. (1993). *Polymer Advanced Technology*, *5*, 708.

Mandal, B. M., Bhattacharya, C., & Bhattacharya, N. S. (1989). *Journal of Macromolecular Science-Chemistry A*, *26*, 175.

Miura, K., Kimura, N., Suzuki, K., Miyashitha, Y., & Nishio, K. (1999). Thermal and viscoelastic properties of alginate/poly (vinyl alcohol) blends cross-linked with calcium tetraborate. *Carbohydrate Polymers*, *39*, 139–144.

Muniz, E. C., Vasquez, P. A. M., Bruns, R. E., Nunes, S. P., & Wolf, B. A. (1992). *Makromolekulare Chemie-Rapid Communications*, *13*, 45.

Nakane, K., Ymashita, T., Iwakura, K., & Suzuki, F. (1990). Properties and structure of poly(vinyl alcohol)/Silica composites. *Journal of Applied Polymer Science*, *74*(1), 133–138.

Nishil, T., & Wang, T. T. (1975). Melting Point Depression and Kinetic Effects of Cooling on Crystallization in Poly(viny1idene fluoride)-Poly (methyl methacrylate) Mixtures. *Macromolecules*, *8*, 909–915.

Ohya, Y., Okawa, K., Murata, J., & Ouchi, T. (1996). *Angewandte Makromolekulare Chemie*, *240*, 263.

Olabisi, O., Robeson, L. M., & Shaw, M. T. (1979). *Polymer–polymer miscibility*. New York: Academic press.

Paul, D. R., Barlow, J. W., & Keskula, H. (1973). *Polymer blends*. New York: Academic press.

Paladhi, R., & Sing, R. P. (1994a). *Journal of Applied Polymer Science*, *28*, 1559.

Paladhi, R., & Sing, R. P. (1994b). *Journal of Applied Polymer Science*, *30*, 251.

Pinnau, I. (1993). *Polymers for Advanced Technologies*, *5*, 733.

Samules, R. J. (1981). Solid state characterization of the structure of chitosan films. *Journal of Polymer sciences Polymer physics Edition*, *19*(7), 1081–1105.

Sarswathi, M., Prasad, C. V., Prasad, M., Chandra Babu, B., Subha, M. C. S., & Chowdoji Rao, K. (2008). *Journal of Pure and Applied Ultrasonics*, *30*, 117.

Sashidhara, G. M., Guruprasad, K. H., & Vararadarajulu, A. (2002). *European Polymer Journal*, *38*, 611.

Singh, Y. P., & Singh, R. P. (1984). *European Polymer Journal*, *20*, 201.

Stadler, R., Auchra, C., Bekmann, J., Krape, U., Voigt-Martin, I., & Leibler, L. (1995). *Macromolecules*, *28*, 3080.

Sun, Z., Wang, W., & Fung, Z. (1992). *European Polymer Journal*, *28*, 1259.

Utracki, L. A. (1989). *Polymer alloys and blends*. Munich: Hanser Publishers.

Vijay Kumar Naidu, B., Chowdoji Rao, K., & Subha, M. C. S. (2002). *Journal of Chemical Engineering Data*, *48*, 625.

Yang Haiyang, Zhupingping, & Yuanyun Jhangtio. (1999). *European Polymer Journal*, *36*, 21.

Zheng, H., Du, Y. M., Yu, J. H., Huang, R. H., & Zhang, L. N. (2001). Preparation and Charecterization of Chitson/Polyvinyl alcohol blend fibres. *Journal of Applied Polymer Science*, *80*(13), 2558–2565.