

Studies on Novel Chitosan / Polyvinyl Alcohol Polymer Blends

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ABSTRACT: Polymer blends using chitosan and polyvinyl alcohol were prepared in the presence of peroxide as hardening agent. Peroxide improves the properties of polymer film. The prepared blends were characterised by X-ray diffraction, scanning electron microscopy, thermal studies, tensile and water absorption measurement. The XRD results show that the film containing higher content of polyvinyl alcohol has more crystalline character compared to the other. In thermal analysis it was found that when the amount of polyvinyl alcohol increases the thermal stability of film increases. SEM micrographs taken from the surface of sample illustrate a uniform dispersion of chitosan inside the matrix. When the amount of chitosan increases agglomeration of particles takes place which decreases the properties. In tensile studies when the amount of polyvinyl alcohol increases the tensile strength increases with decreases in elongation percentage. Moreover, addition of hydrogen peroxide to the blends increases the mechanical properties.

KEYWORDS: Polyvinyl alcohol, Chitosan, Hardening agent

I. INTRODUCTION

More recently due to large quantities of plastic waste being generated and increasing price of oil, attention has been given to development of environmentally friendly composites from renewable resources [1, 2]. Polymer modification by mixing two or more distinct polymers to obtain compounds with improved or special properties arise an increasing interest. Blends of natural and synthetic polymers are investigated as biodegradable material due to their various biomedical and pharmaceutical applications in food industries especially for packaging [3 - 5].

Polyvinyl alcohol (PVA) has good film forming properties because of its hydrophilicity with water and chemical stability. Due to this character it was blended with other synthetic and natural polymers and used in many applications such as control delivery system, membrane preparation, recycling and packaging [6, 7]. Chitosan (CH) is a natural and biodegradable polymer used in many areas like cosmetics, pharmaceuticals, food additives, agriculture etc. Chitosan is commercially produced by the deacetylation of chitin obtained from shell fish, shrimp waste and crab [8 - 10]. Chitosan blended with synthetic polymers like PVA is a convenient method for the preparation of synthetic biodegradable polymer. On adding hydrogen peroxide to this blend it enhances the properties. In the present work PVA/CH blends have been prepared and the films were studied using XRD, SEM, tensile and thermal studies.

II. EXPERIMENTAL

The materials used in this study are chitosan which was purchased from Indian sea foods Cochin and PVA by SD fine chemicals. Acetic acid and hydrogen peroxide was purchased from Merck. Distilled water was used throughout the study.

PVA/CH blends were prepared by dissolving appropriate proportions of polymer to obtain a series of blends. 120 ml of blend was prepared in three different ratios (75:25, 50:50, 25:75). To prepare blends chitosan was dissolved

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 6, June 2016

in 8% CH₃COOH and PVA in hot water. The two solutions were mixed and the mixture was stirred for 3 hrs and finally cured by adding 3 drops of 1% H₂O₂. The solution was again ultrasonicated for 10 min to eliminate air bubbles present in the solution. The prepared solution was poured into a Petri dish and was physically cross linked by drying at 4^o C to 6^o C for 1week. The film obtained was peeled off from the plate and stored for further analysis.

III. CHARACTERISATION

The characterisation techniques used in this study are 1. X-ray diffraction patterns were obtained using a Bruker AXS D8 advance diffractometer with Cu.K α radiation. 2. The surface morphology of prepared composites was studied using scanning electron microscopy (JEOL model JSM-6390LV). 3. Thermal studies of the films have been performed at a rate of 15^o C in nitrogen using Perkin Elmer diamond instrument (model STA6000). 4. Degradation studies were done according to the ASTM D-570-81 method.

IV. EXPERIMENTAL RESULTS

The XRD pattern of PVA/CH blends shows changes in their crystallinity shown in figure 1, 2 and 3. By combining PVA with chitosan intensity of PVA peak reduced and the peak intensity increased with increase in chitosan. The broadening of peak is due to strong interaction exist between PVA and Chitosan. In the case of PVA/CH blend (75:25) the peak intensity increases when PVA content increases. The film shows the characteristic pattern of a semi crystalline phase with the typical peak at 2 θ of 19.40^o and another of low intensity at a 2 θ of 11.27^o and 26.39^o. When the amount of chitosan increases the intensity of peak decreases and the same happens to 2 θ values. For PVA/CH (50:50) blends the 2 θ values decreases from 19.4^o to 19.2^o and the intensity of peak also decreases due to increase in amount of chitosan. In the case of 25:75 combinations the intensity of peak decreases due to decrease in amount of PVA. The main peak has 2 θ value 18.04^o which is comparatively lesser than the other two combinations. This decrease in value is due to the decrease in crystallinity may be due to increase in amount of chitosan.

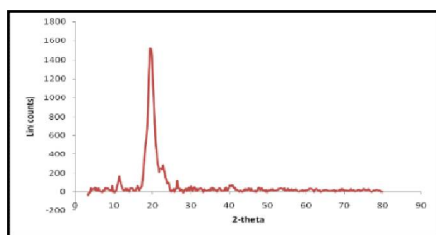


FIGURE 1: XRD PATTERN OF PVA/CH (75:25) BLEND

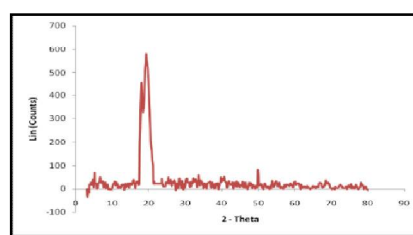


FIGURE 2: XRD PATTERN OF PVA/CH (50:50) BLEND

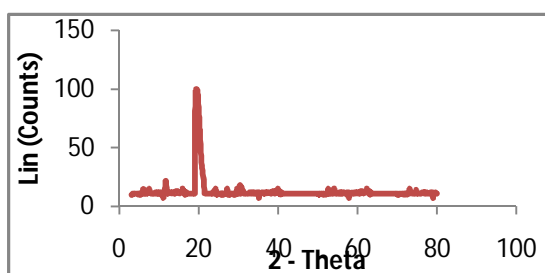


FIGURE 3: XRD PATTERN OF PVA/CH (25:75) BLEND

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(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

From the morphology, the SEM images of surface of PVA/CH (75:25) shows surface with minute pores which indicates on adding chitosan to PVA the polymer matrix gets disturbed and affects the uniform distribution. From figure 4 the morphology shows distorted geometry contain crystalline and amorphous region which may due to the disorientation of the crystals in the backbone. In the case of PVA/CH 50:50 the morphology shows a uniform dispersion of chitosan in the polymer matrix hence the perfect blending gives homogeneous surface which represent high immiscibility due to hydrogen bonding and intermolecular interaction of these polymers (from figure 5). The uniform dispersion improves the degree of reinforcement and hence the property of this composition is higher than other blends. In 25:75 composition shows an agglomeration and the properties also vary compared to the other two (figure 6).

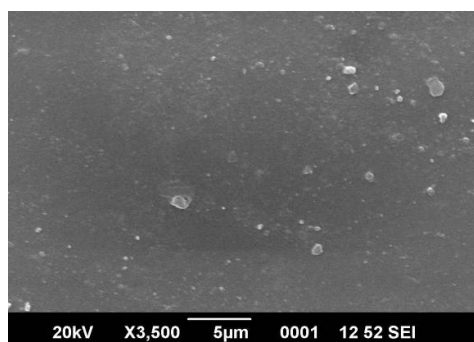


FIGURE 4: MORPHOLOGY OF PVA/CH (75:25)

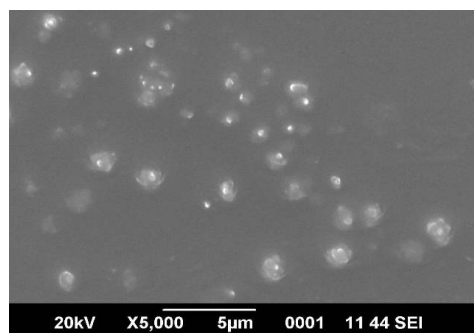


FIGURE 5: MORPHOLOGY OF PVA/CH (50:50)

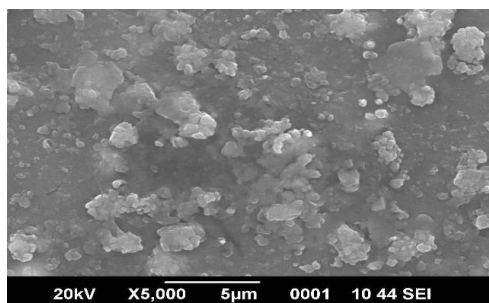


FIGURE 6: MORPHOLOGY OF PVA/CH (25:75)

In the TGA run with the increase in temperature, the thermal degradation of the blends and composites occurs in stages. Low boiling material in the films decomposes first, followed by the decomposition of plasticizers, polymers and fillers respectively. The weight loss and the rate of degradation of chitosan and PVA with peroxide have lower thermal stability compared to blends. The reason is related to new bonding between chitosan and PVA. The T_{max} value of chitosan occurred at 309°C and PVA at 295°C . The blend films undergo degradation in higher temperatures which has T_{max} 332°C with percentage degradation 71% at 400°C . For the blend with 75: 25 compositions the degradation temperature was higher than that with comparison 25:75. The T_{max} value is 343°C for 50:50 combinations with weight loss of 77% at 500°C and 322°C for 25: 75 compositions with weight loss of about 68% at 500°C (fig.7, 8 & 9).

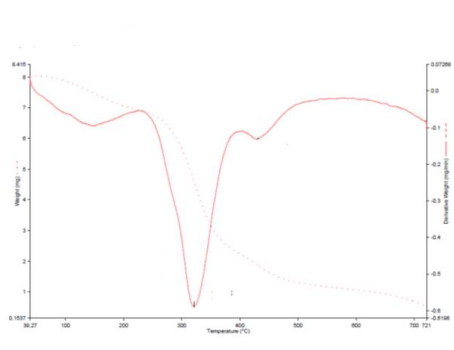


FIGURE 7: TGA/DTA CURVE OF PVA/CH (75:25) BLEND

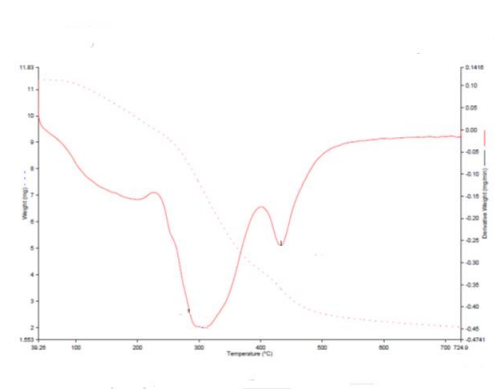


FIGURE 8: TGA/DTA CURVE OF PVA/CH (50:50) BLEND

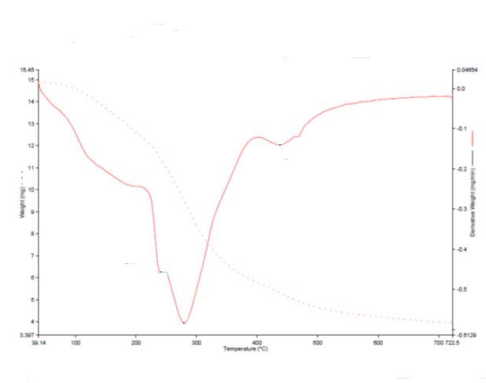


FIGURE 9: TGA/DTA CURVE OF PVA/CH (25:75) BLEND

Water absorption measurement is the most important factor for the biodegradable materials. Table. 1 shows the water absorption % of different combinations of PVA/CH blends. The blend film 75:25 shows higher water absorption percentage (117%) due to the hydrophilic nature of PVA. When the amount of chitosan increases the water absorption decreases due to the non hydrophilic nature of chitosan.

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 6, June 2016

TABLE 1: WATER ABSORPTION MEASUREMENT OF BLENDS

Samples	Initial weight	Final weight	% of water absorption
PVA/CH (75:25)	0.138	0.30	117%
PVA/CH (50:50)	0.138	0.28	102%
PVA/CH (25:75)	0.175	0.345	97%

From table.2 PVA/CH of all the three different combinations (75:25, 50:50, and 25:75) shows good tensile properties. Increase in PVA content increases the tensile strength until 50 % addition and then decreases [12]. The sample 50:50 ratio exhibits maximum tensile strength (21.6 MPa) among the three. The increase of tensile strength may be attributed to the compatibility of chitosan on PVA. Further increase of chitosan decreases the tensile strength. There is a small change in tensile strength for sample 75:25 composition (21.2 MPa). Hence both combinations are choosing for further studies. When the amount of chitosan increases there is a decrease in tensile strength which may be due to their less incompatibility between the polymer. The elongation % of samples 75:25 and 50:50 are less and the maximum value is obtained for sample 25:75 with 225.7 %. The increase in PVA percentage increases the tensile modulus to some extent and then decreases when chitosan percentage increases. The maximum value for young's modulus is recorded in 50:50 samples having 50 % of chitosan.

TABLE 2: TENSILE PROPERTIES OF PVA/CH BLENDS

Sample	Tensile strength	Elongation %	modulus
PVA/CH (75:25)	21.16	201	807
PVA/CH (50:50)	21.2	190	816
PVA/CH (25:75)	19	225.7	780

V. CONCLUSION

The present study shows the behavior of PVA/CH blends with different percentage. Results indicate that the modified blends have good mechanical, thermal properties. When chitosan is added to PVA they participate in intermolecular bond interaction. The PVA films are not suitable for making blends because of its high hydrophilicity and improvement in water resistance is a necessity. Therefore chitosan is added to improve the properties. The water absorption studies show that when the amount of chitosan increases the percentage of water absorption decreases. In tensile studies when the amount of PVA increases the tensile strength and modulus increases with decrease in elongation %. The morphology of films shows the even distribution of polymer. When the amount of chitosan increases there may agglomeration inside the polymer blends, this may decrease the properties.

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ISSN(Online): 2319-8753
ISSN (Print): 2347-6710

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 5, Issue 6, June 2016

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