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Research Article

ENHANCEMENT IN THE THERMAL STABILITY OF CHITOSAN/NYLON6 POLYMER BLENDS BY CROSS LINKING

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ABSTRACT

Mixing of two or more polymers together to produce blends is a well established strategy for achieving specific combination of physical properties. Polymer blend films of chitosan and nylon6 were prepared from homogeneous solutions in formic acid at various weight ratios of chitosan and nylon6. The cross linking agents formaldehyde and glutaraldehyde were incorporated into the polymer blends to improve the properties such as stiffness, surface hardness, resistance to temperature and resistance to solvent attack. FTIR study revealed that there is intermolecular hydrogen bonding interactions between the two polymer components. The glass transition temperature and the crystallization of the polymer blends were investigated on the basis of studies by differential scanning calorimetry. By TGA and DTG experiments, enhancement in the thermal stability of polymer blends in the presence of cross linking agents was found out.

Keywords: Chitosan**,** Nylon6, Cross linking, Thermal properties.

INTRODUCTION

Blending of two or more polymers to obtain materials with new and unique properties has become one of the most important researched topics in the field of polymers. Blending of polyamides with various polymers has been an extensively researched topic in the last couple of decades[1]. The main purpose of blending the polymers is to obtain materials of additional properties with minimum sacrifice of their original properties[2]. The use of interfacial agents to compatibles polymer blends containing polyamides has gained considerable importance because of the presence of amide groups on the polymer backbone[3].

These groups readily react with acids. Bases and carbonyl groups(C=O).Reactive interfacial agents with such functional groups have been successfully used to compatibles the blends of polyamides with various polymers[4]. Mixing of two or more polymers to produce blends or alloys is a well established route to achieve certain amount of physical properties without the need to synthesize specialized polymer systems[5, 6]. Well known examples of blends are the impact modified (rubber), toughened polymers, where polymers with different glass transition temperature are blended. Improving the mechanical properties of a blend is often done by compatibilisation which means modification of normally not miscible blends a block copolymer into the blend to improve the miscibility[7, 8, 9].

Blends of synthetic and natural polymers represent a new class of materials which have attracted much attention especially in bioapplication as biomaterial. The success of synthetic polymers as biomaterials relies mainly on their wide range of mechanical properties[5]. Polymer blending provides a convenient combination of individual homopolymer characteristics which is often non linear in composition and therefore yields a wide range of enhanced properties[10]. Blends are able to improve many properties such as mechanical and thermal properties[11, 12]. It has been reported that melt spinning of immiscible polymer blends into fibers with improved properties is of great interest in synthetic fiber industry[13]. In the present work, effort has been made to prepare blends of nylon6 with chitosan without and with compatibilisers such as formaldehyde and glutaraldehyde and alternation in the thermal properties have been investigated.

EXPERIMENTAL

Materials

Nylon6 in pellet form was obtained from DuPont and had a molecular weight of 19,000.Chitosan was obtained from India sea foods, Cochin which is 92% deacetylated. All the other materials such as formaldehyde and glutaraldehyde are of analytical grade.

Blend preparation

A known weight of the chitosan and nylon6 (1:1) were dissolved in formic acid separately. The chitosan and nylon6 solutions were mixed at various weight ratios at room temperature with moderate agitation for 40 minutes. Similar experiments were performed in the presence of formaldehyde and glutaraldehyde. These solutions were stored at 5˚C overnight and then they were poured into a large amount of acetone to form precipitates respectively. After drying in vacuum for more than 10 hrs' the series of precipitates were stored in desiccators. The precipitates were dissolved again in formic acid. Then these solutions were cast on plastic weighing boats and dried in vacuum for 10 hrs to remove the formic acid.

Characterization

FTIR measurements were performed using KBr pelleted samples with a Perkin Elmer 200 FTIR spectrophotometer with a resolution of 4 cm^{-1}, in the range of 400-4000cm^{-1}. DSC analysis of the polymeric blend samples were carried out with the NETZSCH DSC 200 PC in a pan Al, pierced lid in the nitrogen atmosphere at a heating rate of 10˚ K/min. The thermo gravimetric analysis of the nylon6/chitosan blends with and without the cross linking agents' formaldehyde and glutaraldehyde was carried out on a SDT Q600 V8.0 Build 95 instrument. In this technique the mass of the substance is measured as a function of temperature.

RESULTS AND DISCUSSION

Yield of polymer blends

The results showed that among the two cross linking agents' glutaraldehyde gives higher yield of the blend when compared to the formaldehyde. This may be because, as glutaraldehyde has two aldehydic groups which binds the blends effectively when compared to the formaldehyde[7].

Polymer blends	Yield
nylon6 / chitosan blend(1:1)	56%
nylon6 / chitosan blend(1:1) - formaldehyde	65%
nylon6 / chitosan blend(1:1) - glutaraldehyde	72%

FT-IR analysis

Figure-1 shows the FTIR spectra of nylon6-chitosan (1:1) blend. The prominent peak at 3448.28 cm^{-1} corresponds to the intermolecular hydrogen bonding. A peak at 2714.42cm^{-1} indicates the chelate ring

formation between the two components. Peaks observed at 1720.48cm^{-1}, 1397.37cm^{-1}and1637.00cm^{-1} respectively confirm the presence of C=O stretching, O-H bending and primary amino group. A strong peak observed at 1201.79cm^{-1} represents the C-N stretching which confirms the strong blending of chitosan and nylon6.

Figures (2) and (3) show the FT-IR spectra of Nylon6-chitosan (1:1) blend with cross linking agent's formaldehyde and glutaraldehyde respectively. On comparison with Figure-1 an additional peak was observed in Figures (2) and (3) at 1692 cm^{-1} which indicate the presence of C=N stretching, confirms strong blending of nylon6 and chitosan with the cross linking agents formaldehyde and glutaraldehyde respectively.

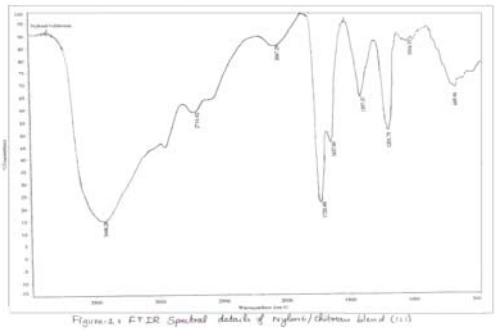

Figure-1: FT-IR Spectral details of nylon6/chitosan blend (1:1)

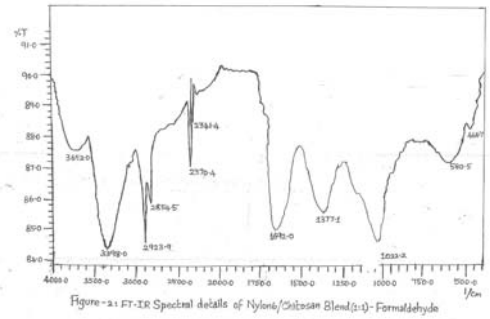

Figure-2: FT-IR Spectral details of Nylon6/Chitosan Blend(1:1)-Formaldehyde

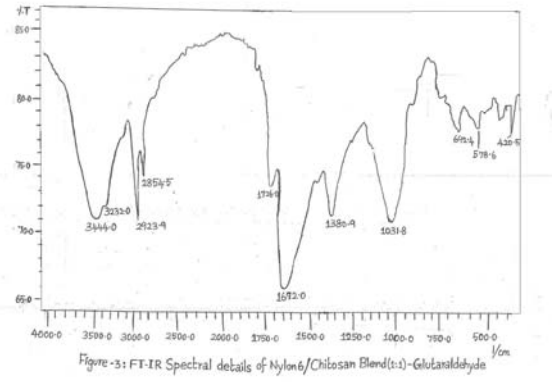

Figure-3: FT-IR Spectral details of Nylon6/Chitosan Blend(1:1)-Glutaraldehyde

Thermal analysis

Differential scanning calorimetry

Figures - 4, 5 and 6 show the DSC curves of nylon6 and chitosan (1:1) blend, nylon6 and chitosan (1:1) in the presence of formaldehyde and glutaraldehyde respectively. Broad endothermic peaks are observed at various temperatures indicating the crystallization of the blend polymers. Figure-4 shows that the glass transition temperature of the blend is observed at 48˚C.Figure -5 and 6 show the glass transition temperature of the blend in the presence of cross linking agents at 69.82˚C and 76.05˚C respectively. On comparing the DSC curves of nylon6 and chitosan (1:1) with and without the cross linking agents, it was found that the endothermic peaks and the glass transition temperatures are shifted to higher values. It confirms that the nylon6-chitosan polymer blend in the presence of the cross linking agent has higher thermal stability with the formation of different crystalline forms. For improving the strength and stability of the interface in the immiscible polymer blends, interface modifiers are added[15].

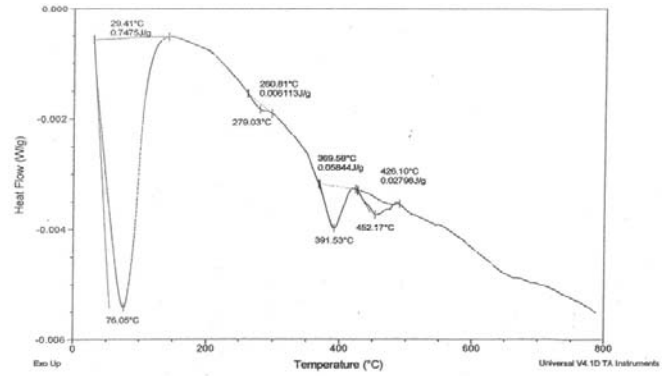

Figure – 6: DSC curve of Nylon6 / Chitosan Blend (1:1) - Glutaraldehyde

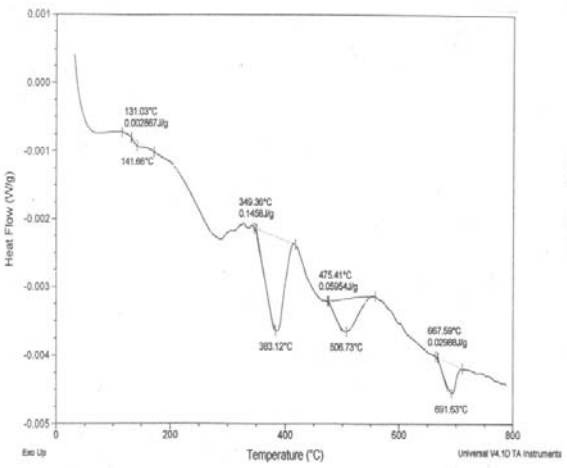

Figure – 4 : DSC curve of Nylon6 / Chitosan blend (1:1)

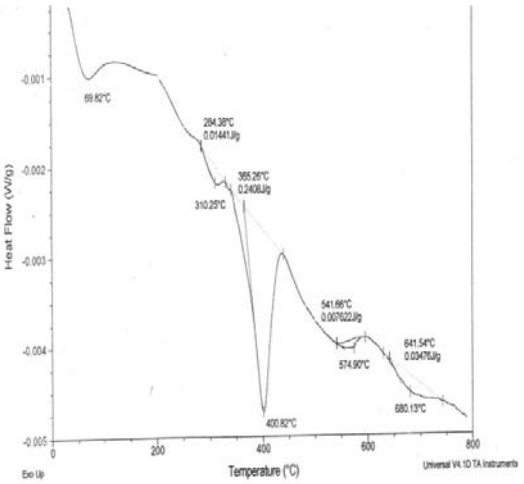

Figure – 5 : DSC curve of Nylon6 / Chitosan (1:1) - Formaldehyde

Thermo gravimetric analysis

The TGA thermogram of nylon6/chitosan blend (1:1) (Figure-7) shows that 80% of the blend is disintegrated within 400˚C. At the end of the experiment i.e., at 800˚C only 9% of the blend remained as a residue. Residual weight is found to be 0.365mg which is 8.97% of the sample taken. Figure-8 represents the thermogram of nylon6/chitosan blend in the presence of the cross linking agent formaldehyde. Around 88.85% of the sample is disintegrated within780˚C. Maximum weight loss occurs at the temperature range of 258˚C-375˚C. Only 11.14% of the blend remains as a residue. Figure-9 represents the thermo gram of nylon6/chitosan blend in the presence of the cross linking agent glutaraldhyde .Around 84% of the sample had disintegrated at the end of the experiment leaving behind 16% of the blend as residue. On comparing Figures -7, 8 and 9 it is found that the nylon6/chitosan blend with cross linking agent is found to be more thermally stable. This was confirmed from the amount of blend remained as residue at the end of the experiment, and the various decomposition temperatures.

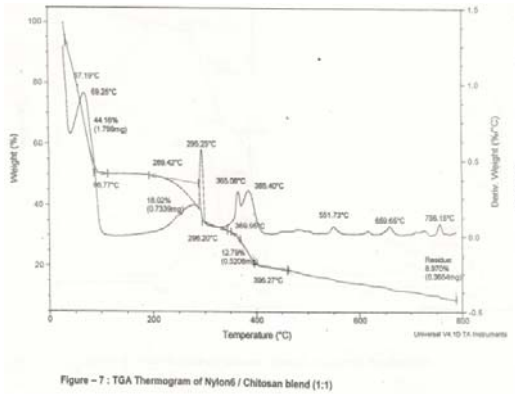

Figure – 7 : TGA Thermogram of Nylon6 / Chitosan blend (1:1)

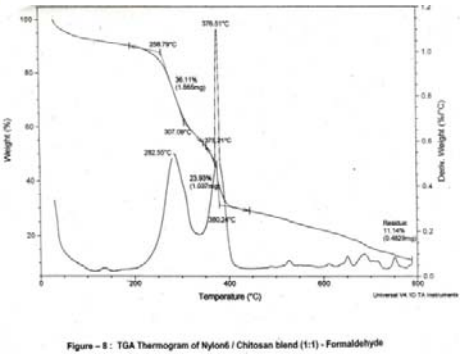

Figure – 8 : TGA Thermogram of Nylon6 / Chitosan blend (1:1) - Formaldehyde

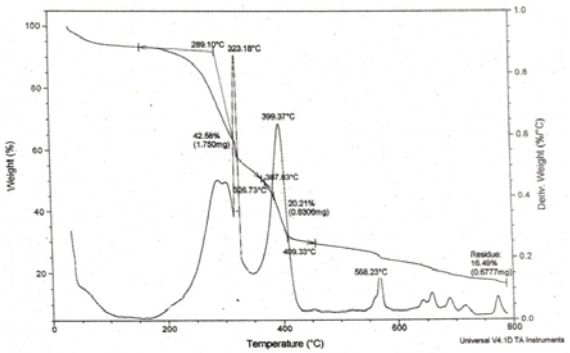

Figure – 9: TGA Thermogram of Nylon6 / Chitosan blend (1:1) - Glutaraldehyde

On comparing the DSC and TGA curves, it is observed that thermal stability of the polymer blend in the presence of cross linking agent is found to be increased. This is confirmed from the increased glass transition temperature and the amount of blend which remained as residue at the end of the experiment.

Differential thermogravimetry (DTG)

A differential themogravimetric curve is obtained by plotting the rate of change of weight with time against the temperature. The peak on the derivative curve corresponds to the maximum slope on the TG curve which indicates the maximum weight loss. However in the thermogram obtained in DTG, the shoulder has been clearly resolved into a peak. The differential thermo gravimetric curve of nylon6/chitosan blend (1:1) (Figure-7) shows two peaks at 295.25˚C and 385.40˚C with the derivative percentage of 0.5 and 0.1. Figure-8 represents the differential thermo gravimetric curve of nylon6/chitosan blend in the presence of formaldehyde which shows two peaks at 282.55˚C and 376.51˚C with the derivative percentage of 0.45 and 1.1.Figure-9 represents the differential thermo gravimetric curve of nylon6/chitosan blend in the presence of glutaraldehyde which shows two peaks at 323.18˚C and 399.37˚C with the derivative percentage of 0.95 and 0.7. From the results it was observed that the rate of change of weight with time was found to be higher in the case of nylon6/chitosan blend in the presence of cross linking agents (Figure-8 and Figure-9) when compared to the nylon6/chitosan blend(1:!) (Figure-7) .On comparing the DTG curves of figure-7, 8 and 9 it is found that a sharp peak is observed in the polymer blend in the presence of cross linking agents which indicates the higher thermal stability.

CONCLUSION

The results suggest that there is strong interaction between the molecular chains of chitosan and nylon6, which may lead to the miscibility at specific ratios of the two components blended. From the FTIR results, it was found that the C=N type of linkage were observed in the cross linked polymer showing the cross linking between the polymer and the cross linking agents. From the results of DSC and TGA it was observed that the cross linking agents enhanced the thermal stability of the polymer blend when cross linking agents are used. Among the two cross linking agents the blend prepared with glutaraldehyde showed better linking and higher thermal stability than that with formaldehyde because of two functional groups which binds the blends effectively when compared to formaldehyde.

REFERENCES

1. Huimin Lu, Xiangmin Xu, Xiaohong Li and Zhijun Zhang Morphology, crystallization and dynamic mechanical properties of PA66/nano-SiO2 composites.Bull .Mater.Sci.2006;29 (5): 485-490.
2. Hanfi Ismail, Zurina Mohamad and Azhar Abu Bakar. The effect of dynamic vulcanization on properties of rice husk powder filled polystyrene /styrene butadiene rubber blends.Iranian Polymer Journal.2004; 13(1):11-19.
3. Zaobin Chen, Tengsheng Li, Yuliang Yang, Xujun Liu, Renguo L. Mechanical and tribological properties of PA/PPS blend .Wear, 2004; 257:696-707.
4. Guo.H.F.Packirisamy. S, Mani. R.S, Aronson. C.L, Gvozdic. N. V, Meier. D.J, Polymer (Eds.), Multiphase polymers: Blends and ionomers, ACS, Washington, DC, 1997; 1989.
5. Cascone M.G. (Dynamic –Mechanical properties of Bioartificial Polymeric materials, Polym.Int1997; 43: 55-69.
6. Fukae R., YamamotoT., Sangen O., Saso T., Kako T.and Kamachi M.Dynamic behavior of poly(vinyl) alcohol film with high syndiotacticity,Polym.J.1990;22:636-637.
7. Xu J., M.cCarthy S.P and Gross R.A. Chitosan film acetylation and effect on biodegradability, Macromolecules 1996; 29:3436-3440.
8. Dunn, E.J.Zhang X., Sun D.and Goosen M.F.A .Synthesis of N-(amino alkyl) chitosan for microcapsules, J. Appl. Polym. Sci.1993; 50:353-365.
9. Lu, J.X., Prudhommeaux F., Meunie A., Sedel L., and Guillemin G. Effects of chitosan on rat knee cartilages, Biomaterials, 1999; 20:1437-1444.
10. Dagani, c&en washington. Speed and efficiency. ... Phase behavior of polymer blends, methods to assay the biocompatibility of polymer surfaces, and properties, 2002; 80(45): 58-60.
11. Utracki Stein HL, Ultra high molecular. The processing, thermal, and mechanical properties. J Macromol Sci— Phys 1987; 88: 37-58.
12. Lambla, M. and seadan M., poly Eng. Sci., 1992; 32: 1687.
13. Tsebrenko M.V., Yudin A.V., Mechanism of fibrillation in the flow of molten polymer mixtures, Polymer, 1976; 17: 831-834.
14. Heikens D., Barentsen W., Particle dimensions in poly-styrene/polyethylene blends as a function of their melt viscosity and of the concentration of added graft copolymer, Polymer, 1977;18: 69-72.