February 2006 Volume 2 Issue 1

Trade Science Inc.

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 2(1), 2006 [1-6]

Preparation, Properties Of Chitosan/Nylon 6 Blending Membranes

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Received: 27th December, 2005
Accepted: 22nd February, 2006

Web Publication Date : 13th March, 2006

ABSTRACT

This article deals with several blendings of chitosan and nylon 6 by various ratios and the effects of the ratio on the properties of the resulting blending membranes. Through the help of a scanning electron microscope (SEM), a fourier spectrophotometer (FT-IR), a differential scanning calorimeter (DSC), an X-ray diffraction instrument, a weight loss analyzer (TGA), a tensile test machine, a polarizing microscope, and a degradation test, we found that mixes of the two polymers are not compatible in the non-crystalline region, but there is a certain extent of reaction going on between them in the crystalline region causing an even distribution. The addition of a small amount of nylon 6 appears quite helpful to the strength and heat stability of chitosan, but the blending membranes are not that different from the membrane of pure chitosan when their degradation properties are compared. Furthermore, when nylon 6 is added, it seems to cause the molecular chain inside chitosan to become more rigid, thus enhancing its heat stability. However, when the ratio reaches beyond 60%, serious phase separation take place.

KEYWORDS

Chitosan;
Nylon 6;
Degradation;
Blending.

INTRODUCTION

Although polymer materials are commonplace and very useful nowadays, it is getting harder all the time for researchers trying to modify them or make them more versatile and more convenient to use. To mix polymers together is probably the simplest and also the most successful way so far of modifying properties of polymers. By mixing polymers of different characters, it is possible to greatly improve certain properties of the polymers. Reinforcing polymers with various fillers is a good example for this rather successful kind of character modifying practices. Mixing complementary polymers appropriately can also result in new materials of superior properties[1].

Recently, there are quite a few research groups engaging in studies of mixing high molecular weight polymers[2-6]. For instance, Nishio et al studied a series of blendings including cellulose polymers and reported their flow variation, reactivity, and mechanical properties. At the same time, Kubota et al. also have carried out a series of studies on the electrolytic properties and other characteristics of some thin membranes made of macromolecular materials such as chitosan and its derivatives[7-10]. Chitosan belongs to the second most abundant kind of biopolysaccha rides in nature, next only to cellulose. It can be made from the major raw material, chitin, through a process called deacetylation. Chitosan is chemically stable, nontoxic, renewable, and it is soluble in mild acidic aqueous solutions. It is an ideal biodegradable material, which, after being discarded into soil, has no problem in integrating into natural ecological cycle and thus will not cause any damages to the environment[11]. However, it has also quite a few shortcomings, i.e. its heat endurance is often less than desired, it's too easy to disintegrate when exposed to UV light, difficult to dissolve in plain water making it hard to process, and its weak wet-strength making spinning into threads almost impossible. On the other hand, we know that polycaprolactam or nylon 6 is a popular crystalline polymer material synthesized from ε-caprolactam. It's very tough, hard, and resistant to wear, low in water absorbance, rather good in heat resistance and strength, and soluble in organic acids. So the experimental work of this study was divided into two major parts. The first one was the preparation of chitosan-nylon 6 blending membranes with various mixing ratios, while the second part was to use various instrumental analyses to examine the nature of those blending membranes, and to investigate the effects of mixing ratio on the membranes.

EXPERIMENTAL

Materials

Chitosan was purchased from OHKA Enterprises, Company, Ltd., Kaoshiung, Taiwan, its degree of deacetylation was 85%, and MW = 400kDa. nylon 6 chip was supplied by Gan Song Company Ltd. formic acid used in the study was reagent grade and the humas agricultural grade.

Methods

Preparation of chitosan-nylon 6 blending membranes

Dissolved enough chitosan into an 88% solution of formic acid to make a 2% chitosan solution; filtered it after 4 hours of agitation. Nylon 6 chip was dissolved with formic acid into 2% solution. Took the above two solutions and mixed them thoroughly in various ratios, applied vacuum to rid of bubble, dumped them into individual glass membrane forming troughs, and dried them in a vacuum oven. After the membranes were formed and dried, took them off the troughs and rinsed them with plain water to pH neutral, and washed them with distilled water before drying them in air. The ratios of chitosan to nylon 6 in those membranes made were 100/0, 95/5, 90/10, 85/15, 80/20, 60/40, 40/60, 20/80, and 0/100.

Properties analyses of blending membranes

We carried out the specific functional group analysis of those blending membranes with the help of a Fourier spectrophotometer by Bio-Rad Digilab, Type FTS-40, and the measurement of crystalline varying 2θ angles through an X-ray diffraction spectrograph manufactured by Rigaku D/Max, Type 3C OD-2988N. The measurement of tensile strength (s_b) was taken with an Alphaten 400 tensile test machine in accordance with the method of ASTM D 412-75. As to the investigation of the surface and cross section situations, we employed a Nikon Optiphot-2 polarizing microscope and a Joel 5610 electron microscope. Later, we made use of a Perkin Elmer, Type p4-1.6G DSC and a Du Pont 2200 TGA to examine their thermal properties.

As to the degradation test for the blending membranes, we followed a method reported in reference[12]: Namely, we cut those blending membranes into pieces of 2cm×3cm each and buried them in algae soil about 10cm deep for degradation. After 4 weeks we dug them out, rinsed them clean with water, dried them out in an oven, and examined their surface under an SEM.

RESULTS AND DISCUSSION

FT-IR

The FT-IR absorption spectra of chitosan, nylon 6, and their various blending membranes are shown in figure 1. We find that our chitosan has a distinct -CONH- group absorption peak at 1655cm^{1}. This is due to the fact our chitosan has a deacetyla tion rate of 85%, which means that there is still quite a bit chitin left behind. Besides, we do see apparent absorption peaks corresponding to chitosan's-CONH- groups at 1599cm^{-1}, 1076cm^{-1}, and 1030cm^{-1}. On the other hand, since nylon 6 is a kind of polyacidamide, the adsorption peaks at 1644cm^{-1}, 1546cm^{-1}, and 1265cm^{-1} are all due to -CONH- functional groups in the molecule. When we compared these two spectra and those of the blending membranes of the two ingredients, we discovered that along with the increase in nylon 6 in the blending membrane, it seemed the peak height of C-O-C group absorption of the chitosan dropped gradually, and on the same token, the absorption peaks corresponding to C=O and -CONH groups in the blending membrane spectra were getting higher and higher.

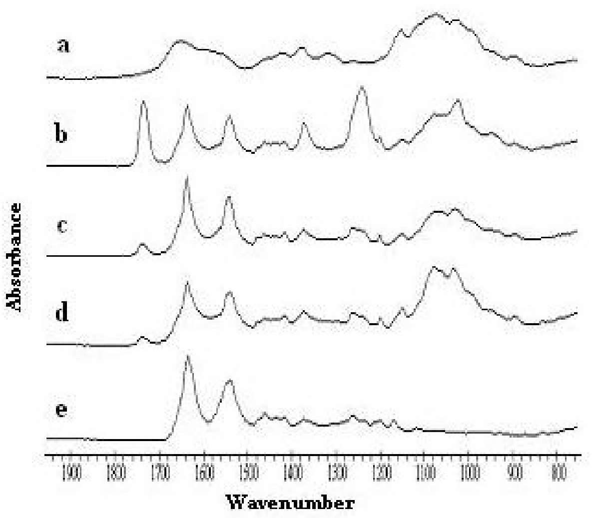


Figure 1: FTIR spectra of chitosan (a), nylon(e) and their blend films. C/N: 80/20(b), 60/40(c), 40/60(d).

X-ray

Figure 2 shows the X-ray diffraction spectra of chitosan, nylon 6, and their blending membranes. We find diffraction peaks of chitosan appearing at 2θ equivalent to 10.25°, 14.5°, and 20° [13], as it really is a blending of two crystals of chitin and chitosan. Comparatively, the molecular structure of nylon 6 turns out to be more regular and gives distinct diffraction peaks at 2θ equivalent to 19.7 ° and 23.85°. Then from those spectra of the blending membranes, we find that along with the increase in nylon 6 of the blending, the diffraction peak of the blending membrane at 2θ equivalent to10.25° is gradually disappearing. On the contrary, the diffraction peak of the blending membrane at 2θ equivalent to 23.85° is getting bigger and bigger. This phenomenon indicates that chitosan and nylon 6 react to each other in the crystalline region. Therefore, the addition of chitosan causes damages to the internal hydrogen bonds of nylon 6 and this destructive behavior becomes

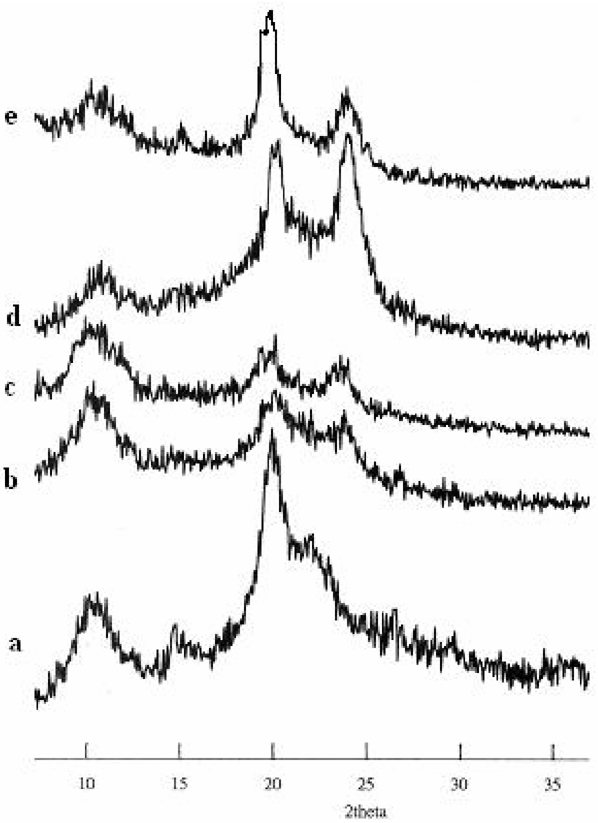


Figure 2: X-ray diffraction patterns of chitosan (a) nylon (e) and their blend films (C/N: b,c,d) C/N: 80/20(b), 60/40(c), 40/60(d).

greater as the amount of chitosan added to the blending increases.

SEM

Pictures of chitosan, nylon 6, and their various blending membranes taken through an SEM are shown in figure 3. We find that the membrane made of pure chitosan has a very smooth, fine, and neat surface (3a1) in contrast to those blending membranes (in 3-b1, c1, and d1). Most of the latter show prominent "islands" structure except blending membranes with low nylon 6 content (such as 20%), in which the nylon 6 appears having spread out quite evenly. To the other end of the content spectrum, more nylon 6 content causes an increase in the "island" size (3-d). This may suggest that the two ingredients are in general not compatible to each other, but small amounts of nylon 6 can evenly distribute throughout chitosan. This is further proven by what we see in the cross section pictures of the blending membranes ($b1_c$ and $d1_c$), in which the blending membrane with lower nylon 6 content (20%) displays a much more even distribution, whereas the one with higher content (60%) looks awful instead.

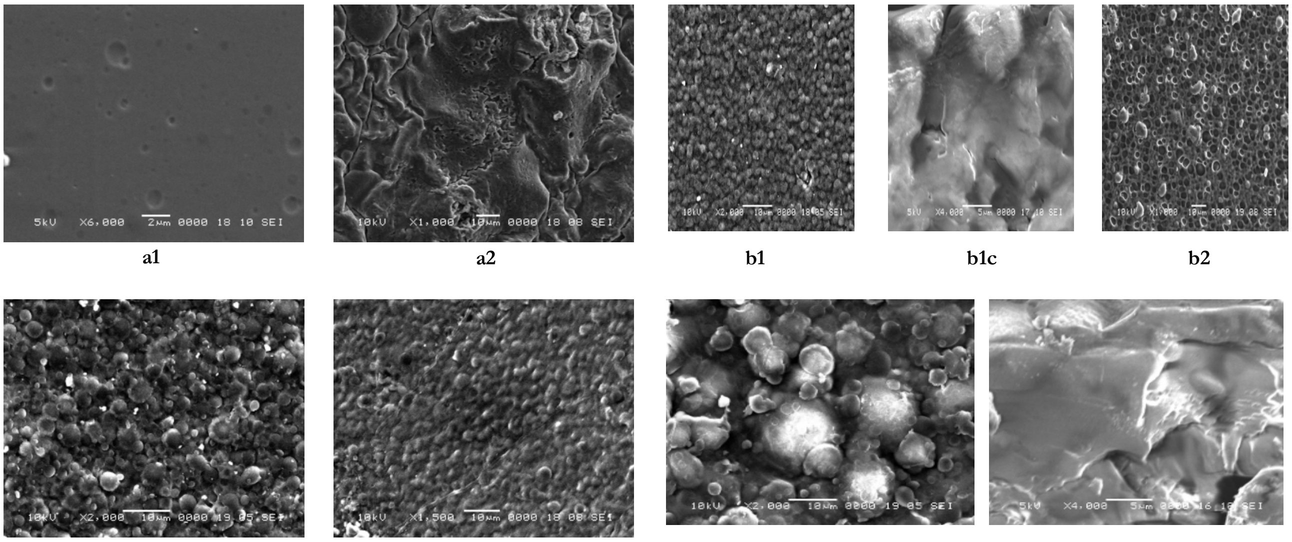
Thermal property

TABLE 1 shows the data of melting points (T_m) and decomposing temperatures (T_{dec}) of the blending membranes of different chitosan-nylon 6 ratios. From the figure and the table, we find that when chitosan is mixed with nylon 6, the initial or onset melting point (T_m^{Onset}) will gradually become higher along with the increase of nylon 6 content. So will be the peak melting point (T_m^{Peak}). We also find that the addition of a small amount of nylon 6 (5%) can raise the melting point about 5°C. This change also suggests that nylon 6 does react with chitosan in the crystalline region, which explains why the X-ray dif-

TABLE 1: The strength property and thermal properties of chitosan, nylon and their blend films (C/N).

C/N	T_m^{onset}	T_m^{peak}	T_d^{onset}	Strength (Kgf)
100/0	203.43	214.42	255.61	6.730
95/5	208.06	218.57	263.15	8.157
90/10	209.21	219.03	265.97	8.361
85/15	209.53	219.42	271.98	7.749
80/20	209.81	220.13	274.16	7.647
60/40	210.62	220.43	278.73	6.095
40/60	211.56	220.89	282.55	4.135
20/80	213.43	221.04	284.12	2.673
0/100	214.31	221.76	359.72	------[1]

[1] It can't film-forming.



a1 a2 b1 b1c b2

c1 c2 d1 d1c

Figure 3: The SEM photograph of chitosan and their blend films

a1, a2: 100% chitosan
b1, b2: C/N (4/1)
c1, c2: C/N (3/2)
d1: C/N (2/3)
a1, b1, c1, d1: before degrading
a2, b2, c2: after degrading
d1c, b1c: cross-section

fraction peak of chitosan at 2θ equivalent to 10.25° tends to gradually disappear. Furthermore, the decomposing temperature of the blending membranes also rises significantly (about 8 °C) with the addition of small amount of nylon 6 (5%). This may indicate that molecular chain in chitosan becomes more rigid when nylon 6 is added to it, thus it turns into more heat stable in the process[14]. Or from the opposite direction, we see the addition of chitosan significantly lowering the melting and decomposing temperatures of nylon 6, which explains that the mixed in chitosan does cause damages to the crystalline structure of nylon 6.

Polarizing microscope analyses of the blending membranes

Figure 4 is a collection of photos of our chitosan, nylon 6, and their blending membranes of different ratios taken with a polarizing microscope. It is evident that when nylon 6 content in the mix is higher, there are "islets" showing up and their size becomes bigger. At lower level, nylon 6 can spread out very evenly in chitosan and light can pass through in spite of some dark cloudiness. So the two ingredients must be partially compatible to each other or some limited reaction takes place between them.

Mechanical property analyses of the blending membranes

From TABLE 1 we find the addition of nylon 6 somehow strengthens chitosan but only to a certain extent since too much nylon 6 eventually weakens it. That is because when a small amount of nylon 6 is added, the hydrogen bond formed between the two makes the strength of the blending stronger. This theory is also supported by our data of X ray and DSC measurements. However, too much nylon 6 (say, over 60%) may cause severe phase separation inside the blending material, which leads to uneven formation of the membrane, thus a loss in strength. It means when the nylon 6 content reaches a certain level, the internal binding or aggregation force exceeds the

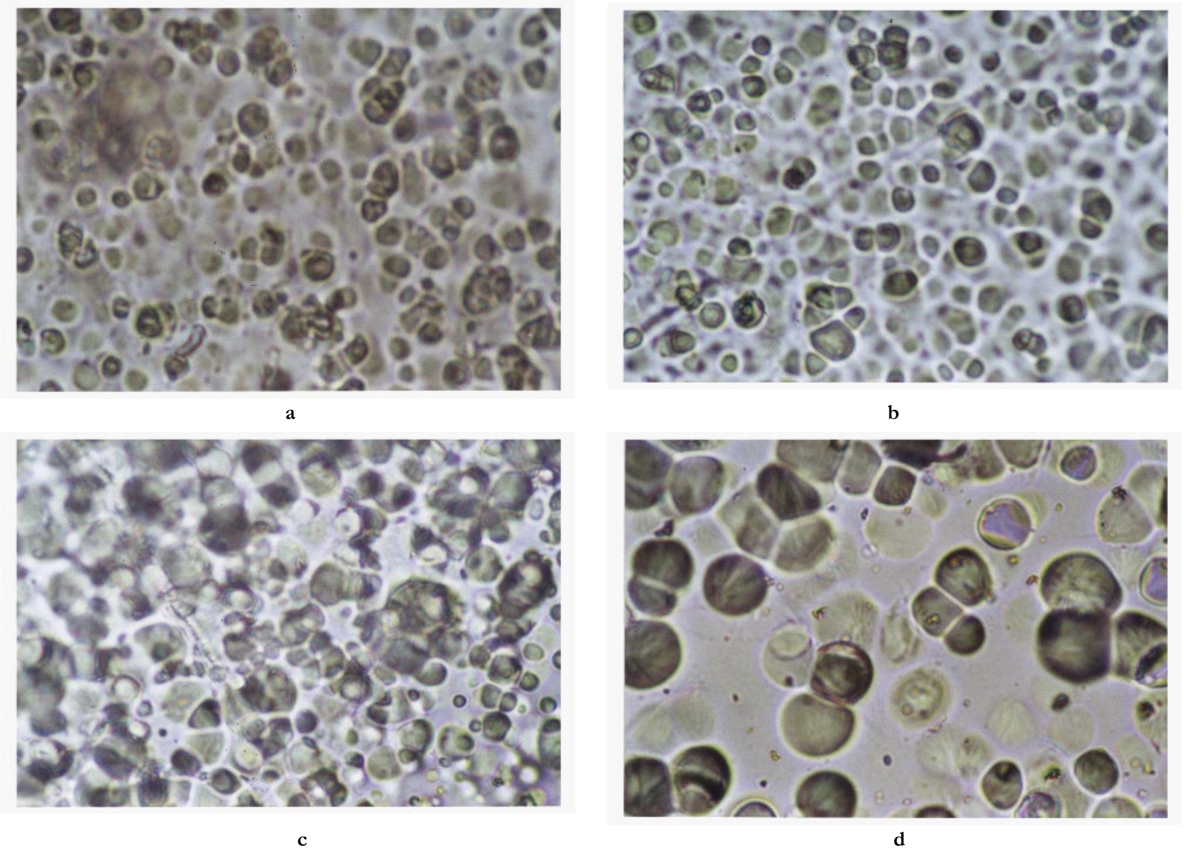


Figure 4: Polarizing microscopic of chitosan and nylon blend films C/N: 95/5(a), 90/10(b), 85/15(c), 80/20(d)

binding between chitosan and nylon 6, which is mainly a combination of van der waal's force and hydrogen bonding. Once that happens, the two become obviously incompatible.

Degradation test analyses of the blending membranes

Figure 3 is another picture collection of our chitosan, nylon 6, and their blending membranes. These pictures were taken through SEM before and after the degradation test. We find in the picture that the original chitosan membrane has a smooth, fine, and neat finish (Figure 3-a1). After 30 days of degradation in soil, its surface becomes very rough with lots of irregular holes (Figure 3-a2). In the cases of the blending membranes, as shown in figures 3-b1, c1, and d1, there are evident "island" structures of various sizes depending on the nylon 6 content before the degradation test. Whereas after the 4 weeks degradation test, as shown in figures 3-b2, and c2, the surfaces of sample also appear very rough and uneven with a lot of small and random holes. This indicates that nylon 6, after being blended with chitosan, would also disintegrate.

CONCLUSION

In this study we prepared several chitosan-nylon 6 blending membranes of various ratios and examined the effects of such mixing on the properties of the resulting products through relevant instrumental analyses. Based on our empirical data, the following conclusions are thus drawn:

1. The two ingredients of the blendings are incompatible in the non-crystalline region but react with each other to a certain extent in the crystalline region.
2. Addition of a small amount of nylon 6 to chitosan can improve its strength and heat stability.
3. Nylon 6 added to chitosan does not affect the degradability of the latter.
4. When nylon 6 content in the blending exceeds 60%, severe phase separation would occur.

ACKNOWLEDGEMENT

We want to especially thank Professor Yu Chian-Ping of Mechanical Engineering Department of this University for his generous help in solving many SEM problems we encountered during this study.

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