EFFECT OF DEGREE OF DEACETYLATION OF CHITOSAN ON THERMAL STABILITY AND COMPATIBILITY OF CHITOSAN-POLYAMIDE BLEND

Zainoha Zakaria,[a]* Zatil Izzah,[a] Mohammad Jawaid,[b] and Azman Hassan [b]

The effect of the degree of deacetylation of chitosan on the chemical structure, thermal properties, and compatibility of chitosan/polyamide66 (CS/PA66) blends were investigated. Blends of CS with PA66 were prepared via the solution casting technique by using 85% formic acid. Structural interaction between PA66, CS, and CS/PA66 blends were analyzed by infrared spectroscopy. FT-IR spectra showed displacement of the carbonyl band of the amide group of chitosan toward smaller wave numbers, indicating possible existence of hydrogen bonding between the two macromolecules. Thermal and morphological behavior of films containing chitosan with degree of deacetylation (DD) ranging from 52.9% to 85% in the polymer blends were investigated by thermogravimetric analysis and scanning electron microscopy. Thermal analysis showed that the CS/PA66 blends became more thermally stable than pure chitosan. The morphological behavior observed by scanning electron microscopy indicated phase segregation in all types of blending. Acetyl content in chitosan was found to influence the degree of compatibility. Decreasing the acetyl group or increasing the DD of chitosan increases the compatibility of the CS/PA66 blends.

Keywords: Chitosan; Polyamide66; Deacetylation; Polymer blends; Thermal properties; Morphological properties

Contact information: a: Chemistry Department, Faculty of Science, Universiti Teknologi Malaysia, 81310 Skudai UTM, Johor, Malaysia; b: Department of Polymer Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia;
**Corresponding author: zainoha@kimia.fs.utm.my*

INTRODUCTION

Seafood industries around the world are producing a voluminous amount of waste materials rich in chitin and are finding ways to reuse chitin to benefit industry and society. Conventionally, chitin can be extracted from the waste through chemical treatments. Chitin can be converted to chitosan (CS) by the removal of the acetyl group using concentrated sodium hydroxide solution. The extent of such reaction can be characterized by the degree of deacetylation (DD). It has been reported that when chitin is at least 50% deacetylated, it becomes soluble in dilute or aqueous acidic media and is known as chitosan (Rinaudo 2006; Sionkowska 2011).

Chitosan differs from chitin by the presence of a higher proportion of amino groups, and it is widely used in different applications due to properties such as non-toxicity, good biocompatibility, biodegradability, and antibacterial properties (Rinaudo 2006; Kumar 2000). Chitosan is the only pseudo-natural cationic polymer, and due to its unique character, it finds applications as flocculants for protein recovery and can therefore be used to reduce pollution of the environment (Rinaudo 2006). Polyamide66 (PA66) is a semicrystalline synthetic polymer that contains four methylene groups, one amide group, and another six methylene groups. It is characterized by its high mechanical strength, stiffness, and superior processability. However, it exhibits high moisture absorption and a low heat deflection temperature. PA66 is blended with different polymers and is commonly used in fiber applications such as carpeting, clothing, and tire cord.

Chitosan can be used as a biopolymer for the production of biocomposites which show improved adsorption and resistance properties (Rangel-Mendez *et al.* 2010). Recent reports describe the development of chitosan-coated cellulosic/soya protein membrane (Wang *et al*. 2011), cellulose/chitosan composite materials (Duan *et al*. 2011), and starch/chitosan biocomposites (Tome *et al*. 2012). Biocomposite films prepared from ionic liquid solutions of chitosan and cellulose exhibit morphology of the polymeric blends that is quite different from that of pure chitosan and depends on the chitosan–cellulose weight percent ratio (Stefanescu *et al*. 2012). The application of chitosan in kenaf paper (Ashori *et al*. 2005), antibacterial filter paper from chitosan, and nanosilver capped with polyacrylic acid has also been reported (Imani *et al*. 2011).

The field of synthetic polymer blends has experienced an enormous growth in recent years in terms of scientific research. Synthetic polymer blends' unique structural and mechanical properties make them suitable for different industrial applications (Sionkowska 2011). Polymer blending is widely recognized as the most common method for developing new polymeric materials. One of its main advantages is found in the properties of the final product, which can be changed by changing the blend composition. Previous studies reported that blends of chitosan with other polymers showed significant mechanical properties and prolonged the biodegradation (Pillai *et al*. 2009).

According to the Flory-Huggins theory, the miscibility and compatibility of two polymers are dependent on the ability of the mixing polymer to form a hydrogen bonding interaction (Flory 1953; Boyd and Philips 1993). It is expected that the intensity of the hydrogen bonding and the steric effect of acetyl group would be the determinants for compatibility and miscibility between chitosan and polyamides. Chitin can form different types of hydrogen bonds with other chitin molecules (Gonzalez *et al*. 2000). Firstly, interaction can occur between two hydroxyl groups (OH···OH); secondly, some interactions may happen between hydrogen in the amide group with oxygen in the hydroxyl group (NH···OH); and lastly, a strong interaction between the hydrogen of heteroatoms and the carbonyl of the amide (C=O···HO and C=O···HN) can be formed. The ability of two chitosan polymers to interact between carbonyl groups within chitosan molecules themselves is quite low. This may be due to the deacetylation process, which removes the carbonyl group (C=O). Blending of chitosan with other polymers results in negligible probability of formation of hydrogen bonds of chitosan with other chitosan molecules. It has also been emphasized that chitosan could be more effective than chitin in the formation of hydrogen bonds. Previous studies reported that the interaction between chitosan and poly-(vinyl alcohol) is mainly due to hydrogen bonding (Sionkowska *et al*. 2005).

Gonzalez *et al.* (2000) reported the effect of different structures of chitin and chitosan (72% DD) on the chemical interaction of chitin and chitosan with similar structures to those of protein such as polyamide6 (PA6) and PA66 (Fig. 1). They reported effectiveness of compatibility with them in the following sequence: PA6/CS ≈ PA66/CS > PA6/chitin > PA66/chitin. The compatibility sequence could be related to the ability of the chitosan to form hydrogen bonds and capacity of the packing of PA66 (Gonzalez *et* *al*. 2000; Zhang *et al*. 2009; Yeh *et al*. 2006). Zhang *et al*. (2009) had successfully electrospun CS and PA6 with different weight ratios of PA6 and CS. They also reported possible hydrogen bond formation between the carbonyl group (C=O) in nylon-6 with hydroxide (–OH) and amine group (–NH_2) in chitosan as shown in Fig. 2 (Zhang *et al*. 2009).

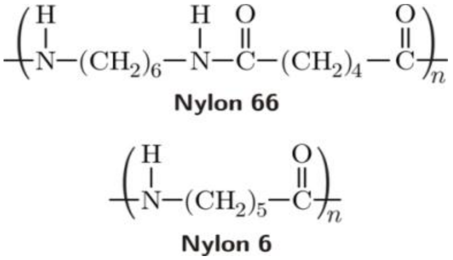


Fig. 1. Structure of polyamide 66 and polyamide 6

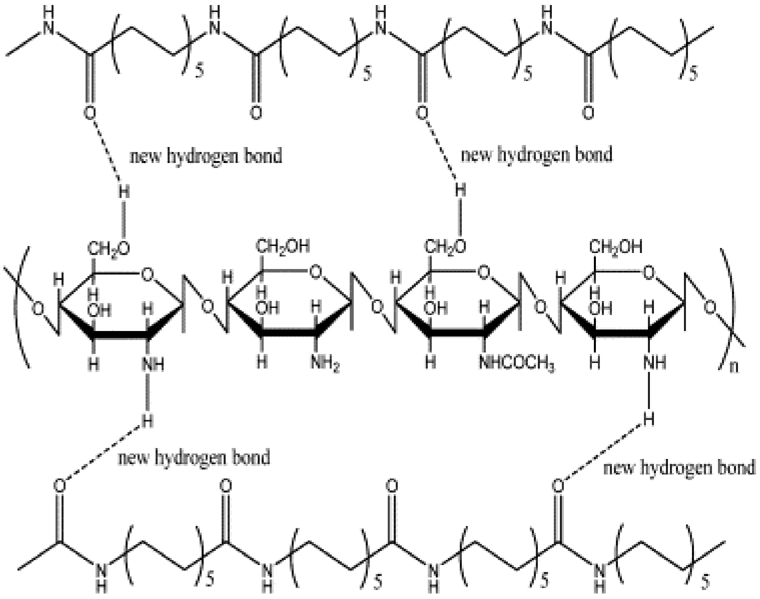


Fig. 2. Hydrogen bond between polyamide chains (nylon-6) and chitosan (Zhang *et al*. 2009) (With Permission from Elsevier)

In the present study, CS was blended with PA66 to produce man-made polymer blends that confer unique structural, thermal, and morphological properties. Structural, thermal, and morphological behaviors of CS/PA66 blends were compared with respect to the effect of DD of the chitosan. Commercial chitosan of 75% and 85% DD were used to compare with other chitosan products, which were produced from chitin in the laboratory. It is difficult to achieve production of chitosan with 100% DD (Islam *et al*. 2011). Previous work makes it clear that production of high DD chitosan is expensive, so if this compatibility is acceptable, then it is possible to produce CS/PA66 blends by using a lower DD chitosan. Production of CS/PA66 blends with low DD chitosan could reduce production cost, as well as increase its potential for biodegradability. Previous studies have reported properties of polyamide-chitin and chitosan blends, but until now, no researchers have carried out a systematic study on the effect of DD of chitosan.

EXPERIMENTAL

Materials

Sigma Aldrich supplied chitin, NaOH pellets, and acetic acid were used in this study. Polyamide66 (molecular weight, 226.32 g/mol) was procured from Zarm Scientific & Supplies Sdn., Malaysia. The degree of deacetylation of chitosan was measured by using the baseline method of Domszy and Robert (1984).

Deacetylation of Chitin to Chitosan (Autoclave Method)

Chitin (3 g) was mixed with various concentrations of NaOH (40%, 50%, and 60%, w/v) at a ratio of 1:10 (w/v) and was left to steep in NaOH solution for two days. After that, the samples were treated under a pressure of 101.3 kPa at 121°C for 30 minutes in an autoclave (Hirayama, HVE-50) (Hong *et al*. 2000). After autoclaving, the solid products were washed to neutrality under running tap water, rinsed with distilled water, and filtered to remove excess NaOH. The obtained product was dried for 24 h at 60 ^{o}C, after which it was further treated with 2% acetic acid solution (1:15 ratio, w/v) under stirring for 10 minutes which dissolved the chitosan, leaving the remaining chitin as an insoluble solid. The mixture was filtered using a sieve and chitosan collected in a beaker.

Chitosan-Polyamide66 Blends

Chitosan/PA66 blends (CS/PA66) 1:1 were prepared by mixing with 85% formic acid in a ratio of 1:10 (w/v), and the prepared mixture was stirred until the solid dissolved (Zhang *et al*. 2009). The blend ratio (1:1) was based on a previous study by Gonzalez *et al*. (2000). At this ratio, a co-continuous morphology occurred, and therefore a good contribution of mechanical properties from PA66 and biodegradable properties from chitosan is expected. The viscous solution was poured into a petri dish with a thickness of 2 to 4 mm to form a thin film. The obtained films were washed several times with distilled water and then dried. The solution was left to dry overnight at room temperature to avoid breakage of the blend film. Several CS (85%DD)/PA66, CS (75%DD)/PA66, CS (60.3%DD)/PA66, and CS (52.9%DD)/PA66 formulation of samples were prepared (Table 1).

Table 1. Polymer Blend Composition

Samples	Composition	Wt%		
		CS	PA66	DD
CS	Chitosan	100	0	75
PA66	Polyamide	0	100	0
CS(85%DD)/PA66	CS/PA66	50	50	85
CS(75%DD)/PA66	CS/PA66	50	50	75
CS(60.3%DD)/PA66	CS/PA66	50	50	60.3
CS(52.9%DD)/PA66	CS/PA66	50	50	52.9

Characterization of Chitosan and CS/PA66 Blends

FT-IR spectra of the CS, PA66, and polymer blend films were recorded with a Shimadzu FT-IR 8300 Spectrometer. Chitosan solution was prepared by dissolving chitosan in 2% acetic acid (1:25, w/v); it was then poured into a petri dish (2 to 4 mm thick) and dried at room temperature for 1 to 4 days. Prior to FT-IR analysis, CS and CS/PA66 blend films were heated in an oven at 60 °C for 3 hours, and they were kept dry in desiccators. FT-IR spectra were obtained with at least 65 scans per sample and a 2 cm^{-1} resolution. Thermal analysis was characterized using a Perkin Elmer Thermogravimetric analyzer (Model TGA7) with a scanning rate of 10 °C/min at temperatures ranging from 30 °C to 950 °C. Samples were gold-sputtered, and the morphologies of the CS/PA66 blends were observed using a Philips XL-40 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Infrared Spectroscopy of DD of Chitosan

Typical absorption bands for chitosan and significant peaks are tabulated in Table 2. A characteristic broad band at 3438 cm^{-1} is typically attributed to the stretching vibrations of $–NH_2$ groups, –OH groups, and intermolecular hydrogen bonds which overlap with each other. The FT-IR spectrum shows only one $N\text{-}H_2$ spike formed around 3438 cm^{-1}, which suggests that there is a secondary amide group. Peaks at 1639 cm^{-1} indicate the presence of a carbonyl group. This carbonyl peak of amide is attributable to incomplete deacetylation of chitin to chitosan. A significant peak is also observed at 1561 cm^{-1}, which indicates the amide II adsorption band. The other significant peak at 1152 cm^{-1} is due to –C-H vibration and visible–CONH- group adsorption spectra present at 1090 and 1024 cm^{-1}. In the spectrum of chitosan (Fig. 3), distinctive absorption bands are found at 3449 cm^{-1} and 1655 cm^{-1}. FT-IR spectrum shows slight differences in the intensity of the carbonyl group at the 1655 cm^{-1} peak and the amide group peak at 3449 cm^{-1} as deacetylation progresses. The lower the intensity of C=O, the higher the DD of chitosan. The peak in the range 3400 to 3100 cm^{-1} became wider with increasing DD. This may be due to the hygroscopic nature of chitosan, as well as the calculated DD tabulated in Table 3.

Table 2. Absorptions Bands for Chitosan Samples

Frequency (cm^{-1})	**Functional Group**
898 and 1150 cm^{-1}	Saccharine structure in the macromolecule
1090 and 1024 cm^{-1}	C-O stretching
1152 cm^{-1}	–CH vibration
1255 cm^{-1}	(O–H) or C–O–C bands
1348 cm^{-1}	$–CH_3$ symmetrical deformation
1639 and 1561 cm^{-1}	C=O and amide band –CONH-
3438 cm^{-1}	$N–H_2$ stretching and ---OH stretching

Table 3 shows that DD increased as the concentration of NaOH solution increased. Similar results were also reported by Abdou *et al*. (2008), and Rusmin and Zakaria

(2007). Kurita *et al*. (2001) indicated that deacetylation of chitin can be highly facilitated by steeping in strong sodium hydroxide solution at room temperature before heating. The use of an autoclave also led to a dramatic reduction in the time of deacetylation to just 30 minutes as compared to several hours when using the boiling method. Based on this result, only samples having a DD of more than 50% were used for blending experiments.

Table 3. Effect of Concentrations of NaOH Solutions on DD of Chitosan

Sample*	Adsorbance at 1655 cm^{-1}	Adsorbance at 3450 cm^{-1}	Degree of deacetylation (DD) %
A	0.37	0.45	38.2
B	0.87	1.39	52.9
C	1.04	1.97	60.3
D	-	-	75.0
E	-	-	85.0

*A = deacetylated using 40% NaOH (w/v); B = deacetylated using 50% NaOH (w/v); C = deacetylated using 60% NaOH (w/v); D, E = commercial chitosan (75 and 85 DD)

Characterization of CS/Polyamide66 using FT-IR Analysis

The interaction between chitosan and polyamide66 can be detected from FT-IR spectra of CS, PA66, and CS/PA66 blends. FT-IR is a well-defined method to detect the intermolecular interaction between two polymers (Yeh *et al*. 2006). Figure 4 shows the FT-IR results for CS (A), CS/PA66 (B) blend, and PA66 (C). The three spectra, A, B, and C, showed distinct C=O groups at 1629.23 cm^{-1}, 1631.08 cm^{-1}, and 1635.23 cm^{-1}. The gradual shift of C=O peaks of PA66 toward lower frequency is due to CS blends with PA66 and also may be due to the formation of new secondary bonds in the CS/PA66 blends; similar findings have also been reported by Zhang *et al* (2009) and Yeh *et al*. (2006). Differences in absorption spectra were also clearly observed from A, B, and C samples in the range of 3369 cm^{-1} to 3200 cm^{-1}, which corresponds to the O-H and N-H groups. The chitosan O-H and N-H group absorption spectra at about 3300 cm^{-1} was found to drift toward a lower frequency zone (around 3297.99 cm^{-1}) with the addition of PA66 to form CS/PA66 blend polymers (Yeh *et al*. 2006). This shifting of the absorption band of chitosan towards the lower frequency zone suggests the formation of new hydrogen bonding between the molecules in the blended polymer. Researchers have observed that interaction of chitosan with poly (vinyl pyrrolidone) (PVP) is mainly due to hydrogen bonding (Sionkowska *et al*. 2005).

The small shift of the FT-IR spectra of CS/PA66 blend indicates that CS and PA66 are only physically blended, and this mixing does not affect individual CS and PA66. In another interesting study of chitosan blends with cellulose acetate, a shift of the broad peak for OH and NH groups from 3528 to 3483 and to 3479 cm^{-1} with the increase of chitosan content in the hollow fibres was observed (Liu and Bai 2005). Researchers reported that –OH band in CS/PVP blends shifts towards lower frequency and changes its shape (Lewandowska 2011). Figure 5 shows FTIR spectra of the effect of degree of deacetylation (DD) of chitosan on CS/PA66 blends. A similar shift pattern, as displayed in spectra A, B, and C (Fig. 4) are also observed in Fig. 5. However, overlapping of significant peak at 1655 cm^{-1} due to C=O from chitosan with C=O from PA66 makes the FT-IR method difficult to observe small differences in the effect of DD on the blending of PA66 with chitosan.

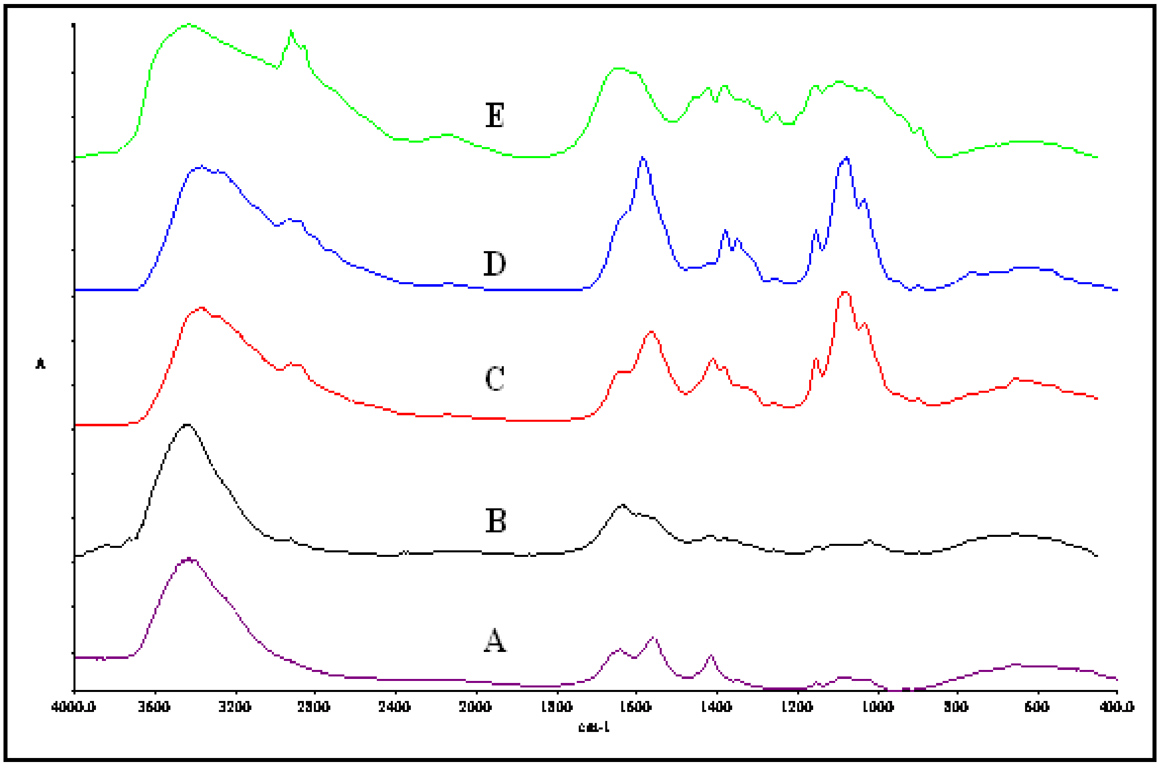


Fig. 3. FTIR spectrum of (A) deacetylated using 40% NaOH (w/v); (B) deacetylated using 50% NaOH (w/v); (C) deacetylated using 60% NaOH (w/v); (D) commercial chitosan (75% DD); and (E) commercial chitosan (85% DD)

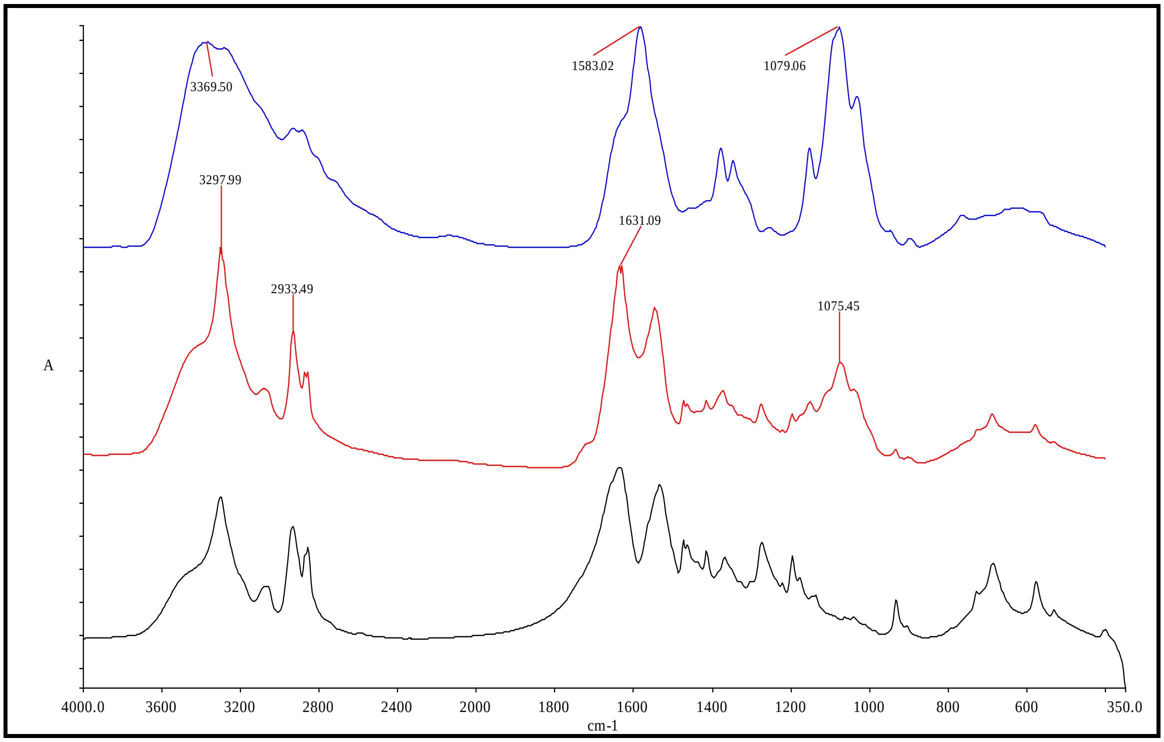


Fig. 4. FT-IR spectrum of A) pure CS, B) CS/PA66 blend, and C) pure PA66

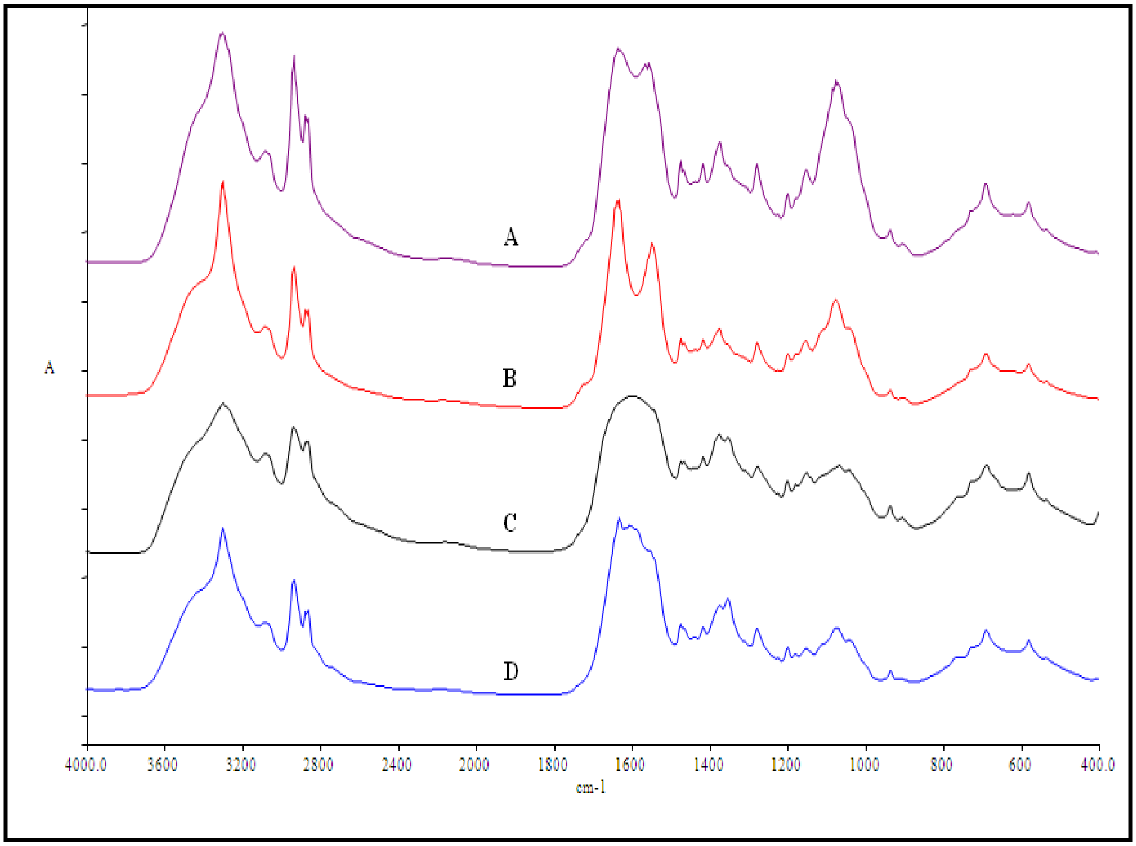


Fig. 5. The FT-IR spectrum of polymer blends. (A) 85% DD CS/PA66; (B) 75% DD CS/PA66; (C) 60.3% DD CS/PA66; (D) 52.9% DD CS/PA66

Thermal Analysis

From thermogravimetric analysis (TGA) curves (Fig. 6), it was observed that chitosan showed two steps of degradation (Fig. 6E). The initial degradation occurred at around 30 to 100 °C and displayed 22.33% weight loss. This degradation may correspond to a loss of adsorbed and bound water (Gonzalez *et al*. 2000; Yeh *et al*. 2006). The chitosan has a greater capability to form hydrogen bonding as compared to chitin, and chitosan will be more hygroscopic when blended with other materials (Gonzalez *et al*. 2000). This means that the initial decomposition around 100 °C can be attributed to the strong water-adsorptive nature of chitosan. Table 4 displays the degradation temperature and char residue of CS, PA66, and CS/PA66 blends. The second stage of degradation occurred at 210.8 °C and continued up to 370.8 °C. There was 32.06% weight loss occurring in the second stage due to degradation of chitosan polymer, and the temperature at which maximum degradation occurred (T_{max}) was 280.8 °C. Similar results were observed by Liu *et al*. (2003) and Gonzalez *et al*. (2000). Mishra *et al*. (2009) reported that a sharp endothermic peak in the thermogram curve of chitosan at 310 °C is due to decomposition of chitosan polymer. Both chitin and chitosan samples showed a similar trend in TGA curve, and chitin has a higher thermal stability as compared to chitosan (Abdou *et al*. 2008). Therefore, by increasing DD of chitosan sample, chitosan-blended products (B, C, D, and F) will become less thermally stable (Table 4).

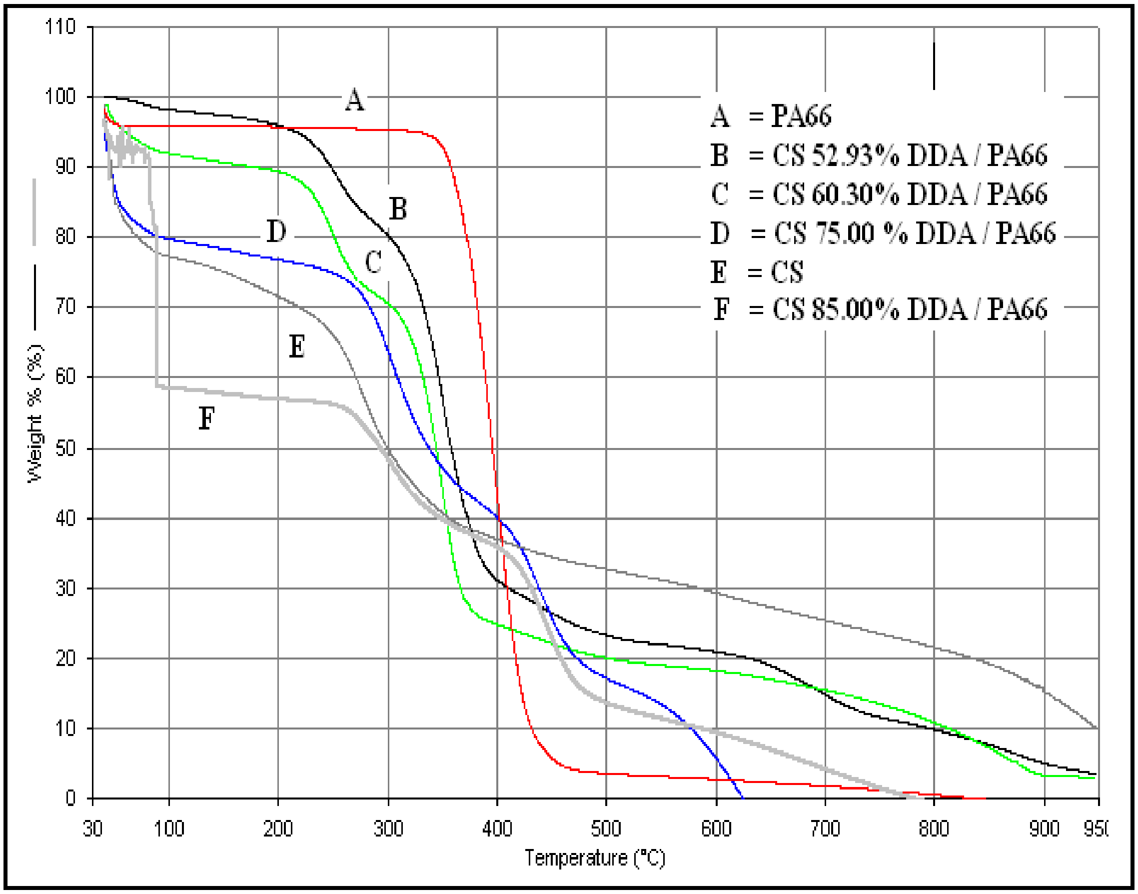


Fig. 6. TGA curve for chitosan, polyamide66, and CS/PA66 blends

Table 4. Thermal Stability of CS, PA66, and CS/PA66 Blends

Samples	**Weight loss At (T_{max})(%)**	**Maximum degradation temperature (T_{max}) °C**	**Decomposition rate**		**Residue (%)**
			At 250°C (%/°C)	**At 500°C (%/°C)**	
A	89.70	390. 84	0.3821	-	3.6
B	47.64	351.27	0.3548	0.0464	22.2
C	19.21	353.20	0.3260	0.0400	20.1
D	33.65	310.44	0.2996	0.0342	17.1
E	32.06	280.82	0.2636	-	32.7
F	17.18	301.13	0.2244	0.0270	13.7

A) PA66, B) CS 52.93%DD/ PA66, C) CS 60.3%DD/PA66, D) CS 75% DD/ PA66,
E) CS 75% DD, F) CS 85%DD/PA66

The TGA curve for PA66 is shown in Fig. 6A. PA66 also exhibited two steps of degradation. First stage decomposition occurred between 10 °C until 60.8 °C, which showed about 4.84% loss in weight due to water absorption of the polyamide (Gonzalez *et al*. 2000). The second stage of decomposition showed a weight loss of 89.70%. A maximum degradation temperature (T_{max}) of 390.8 °C was observed, which is due to degradation of polyamide66 (Table 4). The residue content of polyamide66 at 500 °C was only about 3.6% of the initial weight. TGA curves for the 52.93% DD chitosan when blended with PA66 are displayed in Fig. 6B. The curve shows two stages degradation.

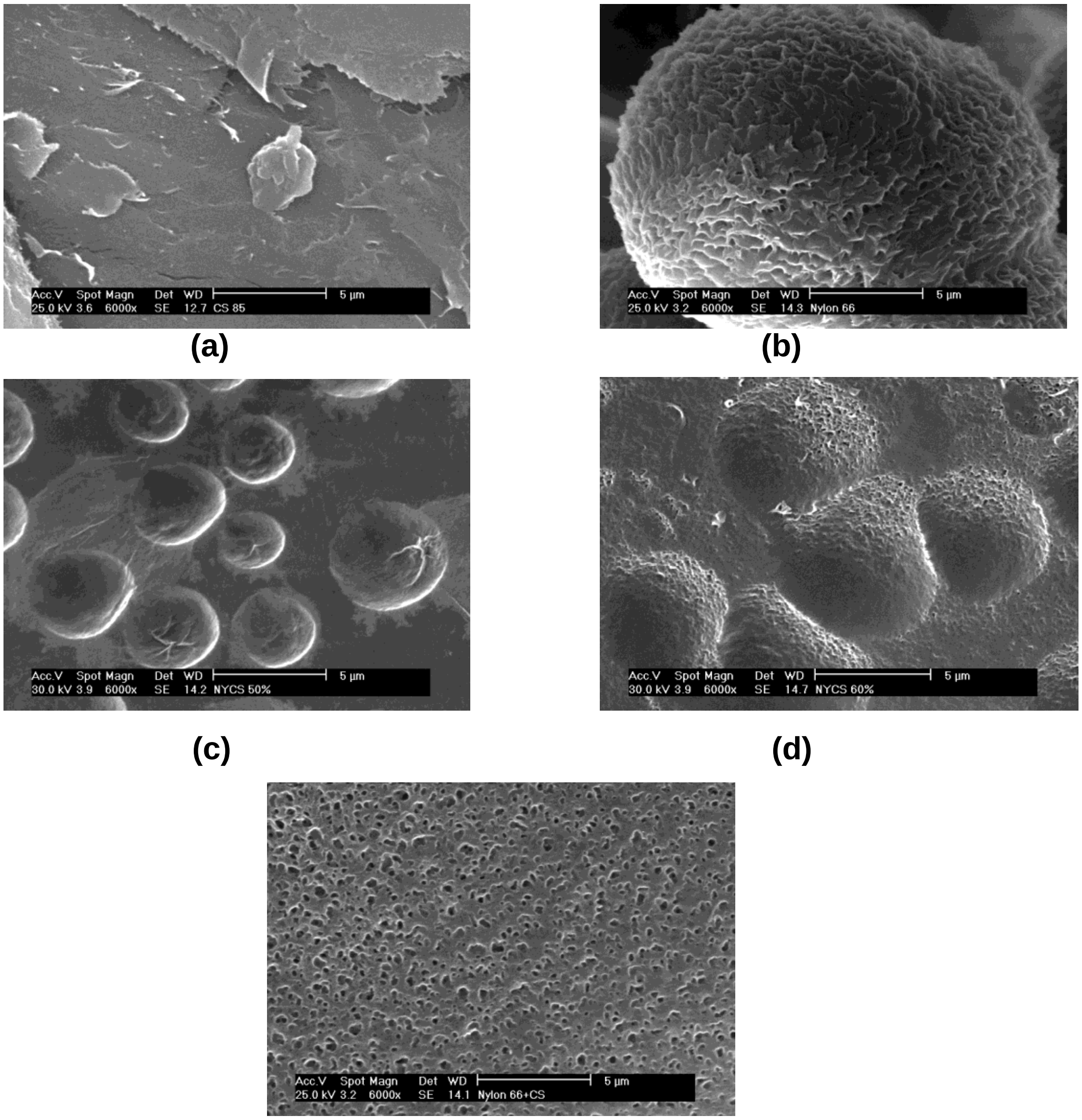
The first stage corresponds to decomposition of chitosan at about 250 °C, and the second stage shows the decomposition of PA66 polymers at a T_{max} of 351.3 °C (Gonzalez *et al*. 2000). The weight loss of sample B (52.93% DD chitosan/PA66 blend) was about 47 % for the second stage due to polyamide degradation (Table 4). There was a relatively smaller weight loss (33.65%) on sample D. No prominent maximum degradation temperature was observed for sample C and the weight loss of 19.21 %. Sample F with the highest DD of 85.00 % showed the smallest weight loss of 17.18%.

With respect to the PA66 component, polymer blends became less thermally stable, whereas with respect to the chitosan component the polymer blends become more thermally stable. The decomposition temperature of the PA66 component in the blended polymer increased as the DD decreased. Similarly, the decomposition temperature of the chitosan component in the blended polymer also increased as the DD decreased. It is reported that when polyamide content increases in CS/PA66 blends, the intensity of the dehydration endotherm decreases (Gonzalez *et al*. 2000). The obtained results differed from those of Yeh *et al*. (2006), who used different chitosan weight ratios on PVP. The decomposition rate of PVP part in the blended polymer increased as the amount of PVP increased, and the decomposition rate of chitosan component in the blended polymer increased as the amount of chitosan increased (Yeh *et al*. 2006). At 500 °C, the residue of blended polymers decreased as the degree of deacetylation increased. The residue for PA66, as illustrated in Table 4, was 3.6% due to faster decomposition of PA66, and similar behaviors have been reported by Yeh *et al*. (2006) in the case of CS/PVP blends.

Scanning Electron Microscopy (SEM)

Figure 7 displays SEM images for the CS, PA66, and CS/PA66 blends at 6000x magnification. Blending of chitosan with PA66 changed the morphology and spherulitic morphology observed in polymer blends (Fig. 7C). Previous work on chitosan/PVA indicated that cellular compatibility of PVA improved due to incorporation of chitosan (Don *et al*. 2006). Spherulitic morphology is detected in all images (Fig. 7C-7E) (Gonzalez *et al*. 2000). This indicates that semicrystalline polyamide became encapsulated in amorphous chitosan and inserted in the continuous phase of chitosan and amorphous polyamide. By using the SEM technique, the morphology exhibited phase segregation at high acetyl group contents. Figure 7(C-E) shows the smooth evolution of morphology with increasing DD.

Chitosan was blended with PA66 in a weight ratio of 50/50. If the quantity of chitosan exceeds 75% in the blending, incompatibility will occur (Yeh *et al*. 2006). SEM micrographs gave evidence that, by increasing the DD of the chitosan-polyamide blends, higher compatibility of the compound was achieved. This may be due to strong hydrogen bonding between molecules and acetyl contents in the chitosan polymers. According to Gonzalez *et al*. (2000), acetyl content influences the degree of compatibility and miscibility due to steric impediment presented by the acetyl groups, affecting the formation of hydrogen bonding. They also reported that increasing DD causes less hindrance to acetyl group by interacting polyamide with chitosan via hydrogen bonding. The morphological observations are compatible with the FT-IR and TGA measurements in the light of obtained results that CS/PA66 blends with high DD are more compatible because of hydrogen bonds as compared with low DD of chitosan in blends.



(a) **(b)**

(c) **(d)**

(e)

Fig. 7. The SEM images of (a) Chitosan 85% (6000x), (b) PA 66 (6000x), (c) CS(52.94% DD)/PA66 (6000x), (d) CS (60.3% DD)/ PA66(6000x), (e) CS (85% DD)/PA66(6000x)

CONCLUSIONS

The chitosan-polyamide blend product gave significant results, which were confirmed by structural, thermal, and morphological analysis. FT-IR analysis confirmed structural changes in chitosan by varying DD of chitosan in CS/PA66 blends, and the two polymers were well mixable. Blending of chitosan with PA66 enhanced thermal stability of CS/PA66 blends, and the DD of chitosan in blends also affects thermal properties of polymer blends. SEM micrographs showed that spherulitic morphologies are produced when blending chitosan with PA66. By increasing DD of chitosan, the images become smoother and show that the intermolecular hydrogen bonding promoted better compatibility on polymer blends. For the four different blends, the following compatibilization sequence can be established: CS(85%DD)/PA66>CS(75%DD)/PA66> CS(60.3%DD)/PA66 > CS(52.9%DD)/PA66.

Results of this study indicate that CS/PA66 blends are superior in thermal and morphological properties as compared to chitosan alone. Blending the chitosan with the less expensive PA66 is one approach to reduce the cost of materials. It was judged that CS/PA66 blends can be used in biomedical applications, formulation in drug delivery systems, and mammalian cell culture designed to adequately mimic human tissue. Blends of natural and synthetic polymers have the potential to create immense interest in the production of new products. It can be anticipated that research on the blends of chitosan with synthetic polymers will be developed in the near future for different applications.

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