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EFFECT OF DEGREE OF DEACETYLATION OF CHITOSAN ON CHEMICAL STRUCTURE AND COMPATIBILITY OF CHITOSAN/POLYAMIDE 6 BLENDS

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ABSTRACT

Solution blending technique was used to prepare chitosan/polyamide 6 (PA6) blends, where both compounds contain suitable functional groups that can be expected to promote compatibility between the polymers. Four types of chitosan with various degrees of deacetylation (DD) values were used to form chitosan/PA6 and the effect of DD of chitosan on the structure and compatibility of the blends were evaluated. Films of PA6, chitosan and chitosan/PA6 blends were employed to investigate the interaction between the polymers. Fourier Transform Infrared (FTIR) results of the blend showed the displacement of carbonyl band of amide group of chitosan to a smaller wavenumber implying the existence of strong hydrogen bonding between them. DSC analysis of the blend showed a reduction of melting point (T_m) and heat of enthalpy (ΔH_m) due to the formation of new hydrogen bonds between the polymeric molecules. While, SEM analysis showed the disappearance of the smoothness surfaces of pure chitosan and gradually becoming undulating in the blends. The surface structure of blends are finer with increasing DD of chitosan indicating that there is effect of DD on the blends. Overall results showed that increasing the DD of chitosan increases the compatibility between chitosan and PA6 blend.

Keywords: Chitosan; Polyamide 6; Blend; Degree of deacetylation; Compatibility

1.0 INTRODUCTION

In recent years, polymer modification by blending of two or more different polymers to obtain the desired properties is becoming a common practice. The advantage of having blended polymer is that they sometimes exhibit superior and rare properties, unexpected from the individual homopolymers. The current interest is on blends of synthetic polymer with naturally occurring polymer which promises high potential especially in the field of making biodegradable, renewable biomass structure which is low in cost but superior in properties. Chitosan is a natural amino polymer which is abundantly available throughout the world. Chitosan possesses good film-forming, is highly hydrophilic and has excellent chemical-resistant properties. It is a copolymer of glucosamine and *N*-acetylglucosamine and is obtained from deacetylation of chitin [1]. During the deacetylation process, chitosan with different DD can be produced by modifying the reaction conditions used. The reaction of chitosan is more versatile than chitin due to the presence of more amino ($-NH_2$) groups. Chitosan is also biodegradable, biocompatible, and non-toxic. In general, chitosan properties is highly dependent on the DD of chitosan.

Polyamide 6 (PA6) on the other hand is a synthetic polymer made up of repeating units linked by peptide bonds. It is capable of forming specific interactions when blended with other polymers, due to its amide group. PA6 also possesses high elongation, durability, excellent abrasion resistance and high resistance to many chemicals. Being a synthetic polymer, it is typically non-biodegradable and can create environmental problem. Blending PA6 with chitosan may enhance the biodegradation properties of PA6. In addition if reasonable compatibility can be formed by using chitosan of lower DD, this will reduce production cost of the blends.

2.0 METHODOLOGY

2.1 Materials

Commercial chitin and chitosan (75% and 85% DD) were obtained from Sigma Aldrich (Germany). PA6 was procured from Zarm Scientific & Supplies Sdn., Malaysia. Chitosan with various DD were also prepared in the laboratory according to the method of No *et al.* [2] and Kurita [3] using autoclave method.

2.2 Preparation of Chitosan from Chitin via Autoclave Method

Chitosan was prepared by deacetylation of chitin using NaOH solutions of 40% and 50% (w/v) concentrations. Chitin was placed in an autoclavable bottle and NaOH solution was added at a 1:10 (w/v) ratio. Chitin was first kept soaking or steeping in the NaOH solution for 24 hours after which the samples were autoclaved under the pressure of 101.3 kPa, 121°C for 30 minutes [2]. It has been suggested that steeping prior to autoclaving can improve the deacetylation process [3]. The resulting chitosans were washed to neutrality under running tap water. Further treatment with 2% (v/v) acetic acid solution (1:15 ratio, w/v) dissolved the chitosan and was filtered off from the solid chitin. The DD of chitosan was measured by using baseline method by Domszy and Robert [4].

2.3 Preparation of Chitosan/PA6 blends

Four types of chitosan with various DD (85%, 75%, 56%, and 46%) were used to form chitosan/PA6 blends. Chitosan/PA6 blends (1:1) were prepared by mixing with 85% formic acid solution in a ratio of 1:10 (w/v), and the mixture was stirred for 10 minutes until both polymers dissolved. The blend ratio of 1:1 was used based on a previous study by Gonzalez *et al.* [4] whereby at this ratio, a co-continuous morphology occurred and therefore a good contribution of mechanical properties from PA6 and biodegradable properties from chitosan is expected [5]. Blend films were prepared by spreading a small amount of blended mixture in a petri dish to form a thin film. The film was allowed to dry for 24 h at room temperature. Several chitosan/PA6 blends were prepared and samples were designated as in Table 1.

Table 1 Samples of Chitosan/PA6 Blend

Samples (Chitosan/PA6, 1:1)	**Symbol**
chitosan (85% DD) /PA6	CN85/PA6
chitosan (75% DD) / PA6	CN75/ PA6
chitosan (56% DD) / PA6	CN56/ PA6
chitosan (46% DD) / PA6	CN46/ PA6

2.4 Characterization of Chitosan and Chitosan/PA6 Blend

Films were used for all FTIR analyses using Shimadzu FTIR 8300 Spectrometer. Chitosan solution was prepared by dissolving chitosan in 2% acetic acid (1:25, w/v) and poured into a petri dish (2~4 mm thick) and dried at room temperature for 1 to 4 days. Prior to FTIR analysis, chitosan and chitosan/PA6 blend films were heated in an oven at 60 °C for 3 hours and kept dried in a dessicator. The DD of chitosan was calculated using baseline method by Domszy and Robert [4]. The morphology of the chitosan/PA6 blends were observed using Philips XL-40 scanning electron microscope (SEM) and samples were gold sputtered prior to scanning. Thermal properties of the chitosan/PA6 blends were characterized using differential scanning calorimetry (DSC, Pyris 6 from Perkin Elmer) over a temperature range of 30-450 ^{o}C at a heating rate of 10 °C/min in nitrogen atmosphere.

3.0 RESULTS AND DISCUSSION

3.1 Production of Chitosan via Autoclave Method and Determination of DD of Chitosan

Sodium hydroxide solutions having concentrations lower than 40% were not successful in producing chitosan. Hence only two types of chitosan were successfully prepared. Figure 1 showed characteristic absorption bands for chitosan. A broad band at 3301-3348 cm^{-1} is attributed to N-H and O-H stretching vibration and intermolecular hydrogen bonding of the polysaccharides molecules. While peak at 1631 cm^{-1} is due to the C=O stretching and peak at 1543 cm^{-1} is due to the NH bending. Similar FTIR result was also obtained by Yamaguchi *et al*. [6] which prepared and characterized chitosan from crab tendon by deacetylation of chitin using 50% (x/v) NaOH solution at 100 ^{o}C [6].

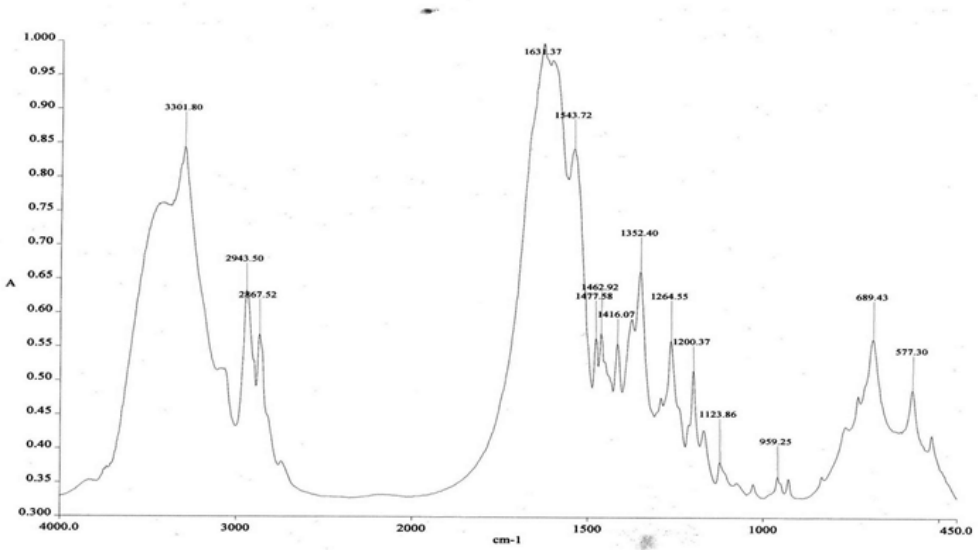


Figure 1 FTIR spectrum of chitosan film

Similar absorption bands existed in all types of chitosan films except for the difference in the height of the carbonyl stretching absorption bands at 1631 cm^{-1}. As more acetyl groups are being removed or deacetylated from chitin to form chitosan, intensity of C=O bands becomes less, hence the DD of chitosan can be calculated based on this

differences. Chitin with a degree of deacetylation of 50% or above is generally accepted as being chitosan**.** From the FTIR spectrum obtained using different samples of chitosan, DD is calculated and shown in Table 2.

Table 2 Degree of Deacetylation (DD) of Chitosan

Type of chitosan	Degree of deacetylation (%)
A	85
B	75
C	56
D	46

*A and B are commercial chitosan (Sigma); C- chitin deacetylated in 50% NaOH; D- chitin deacetylated in 40% NaOH

Table 2 shows that chitosan D which was deacetylated by a lower concentration of NaOH has a lower degree of decetylation of 46%. In this study, autoclave method has been used which employ high pressure and temperature leading to reduction in the time of deacetylation process which is consistent with other reported results [7,8]. Kurita [3] reported that deacetylation process is affected by heating a suspension of chitin powders in strong aqueous bases such as sodium and potassium hydroxides at 100-160^{o}C to give chitosan with DD between 70-95%. In the present study only two variations of NaOH concentrations were done as the higher DD Chitosan were already available.

3.2 Characterization of Chitosan/PA6 Blend

All that were prepared using commercial chitosan (CN85 and CN75), produced film which is opaque as compared to the pure transparent chitosan film. Meanwhile chitosan/PA6 blends prepared from the lower DD chitosan (CN56 and CN46) formed yellowish coloured films with slightly coarser appearance.

3.2.1 FTIR Analysis

FTIR is a well-defined method to detect the intermolecular interactions between two polymers [9]. It is able to show intermolecular interactions through hydrogen bonding. Figure 2 shows the spectrum of PA6, spectrum of chitosan (CN85)/PA6 blend and spectrum of chitosan.

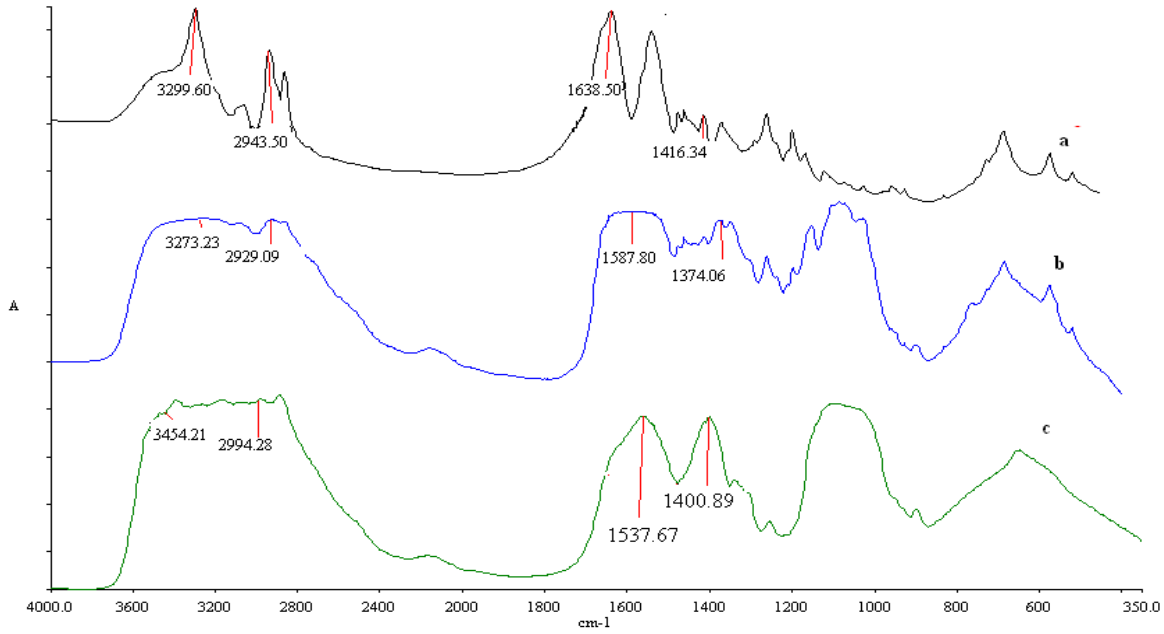


Figure 2 FTIR spectrum of a) PA6 film, b) chitosan (CN85)/PA6 blend film and c) pure chitosan film

Figure 2(a) shows the characteristic bands of PA6. A strong peak at 3299 cm^{-1} is due to H-bonded NH stretching, 2943 cm^{-1} for NH in bending plane. Another strong peak can also be observed at peak 1638 cm^{-1} due to the C=O stretching. As for other peaks was at 1416 cm^{-1} due to the C-N stretch and CO-N-H bend. Hendra *et al.* [10] also reported the same results when they were doing FTIR identification and characterization of various polyamides [11].

Figure 2(b) shows the FTIR spectrum of chitosan/PA6 blend. As reported in previous study, when two or more substances are mixed, physical blends versus chemical interactions are reflected by changes in the characteristic spectral peaks. Comparing with chitosan film, amide I bands shift to lower frequency which is from 3454 to 3272 cm^{-1}. Mixing chitosan with PA6 will break the hydrogen bond in the C=O···H-N amide plane of bending films and successively the dipoles will switch to a new direction to reduce energy and re-create a new amide plane with the inserted chitosan molecules [12]. The -C=O groups in PA6 are capable of forming hydrogen bonds with -OH and $-NH_2$ groups as shown in Figure 3 [12].

Meanwhile Figure 2(c) shows several important peaks for chitosan such as the broad band at 3454-2994 cm^{-1} is attributed to the O-H stretching which is an overlap with N-H stretching in the same region and also due to the intermolecular hydrogen bonding of the polysaccharide molecules. While peak at 1537 cm^{-1} indicates the presence of C=O stretching (amide I). A peak at 1400 cm^{-1} can be ascribed to C-O group.

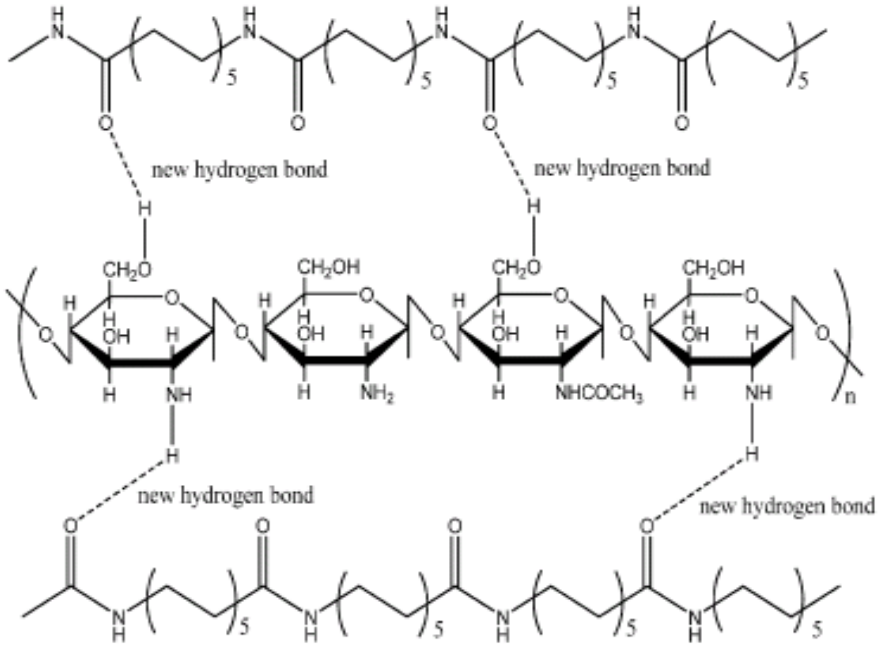


Figure 3 Formation of hydrogen bonds between polyamide chains in PA6 and chitosan [12]

Figure 4 shows FTIR spectra for different chitosan/PA6 blends. The entire blends show the displacement of both carbonyl and amino bands. Similar trend was also reported by Gonzalez *et al.* [5]. They stated that the hydrogen bonds formed between macromolecules of different polymers are stronger than those existing originally between chitosan molecules [13]. Although FTIR results is inconclusive to show the effect of DD towards compatibility of blend but it can show the existence of interaction between chitosan and PA6 blends.

3.2.2 Differential Scanning Calorimetry (DSC) Analysis

Both polymers and its blend were examined by DSC analyses. In this study, the melting (T_m) and crystallization (T_c) transition are reported as the maximum and minimum peak heights respectively. Glass transition temperature (T_g) is reported as the midpoint of the base – line of discontinuity.

Figure 5 shows the thermogram of pure chitosan film which displays sharp exothermic peak at 100 °C, attributed by water loss. Another broad endothermic peak at 270.7 °C is indicating decomposition of chitosan film [14]. As reported in the previous study, thermal decomposition temperature of chitosan was higher than 250 °C and it was considered that chitosan did not show a glass transition before the decomposition temperature [15-17].

While Figure 6 is the thermogram of PA6 which shows a single, well resolved endothermic peak at 220.3 °C. Glass transition temperatures (Tg) not observed for the PA6.

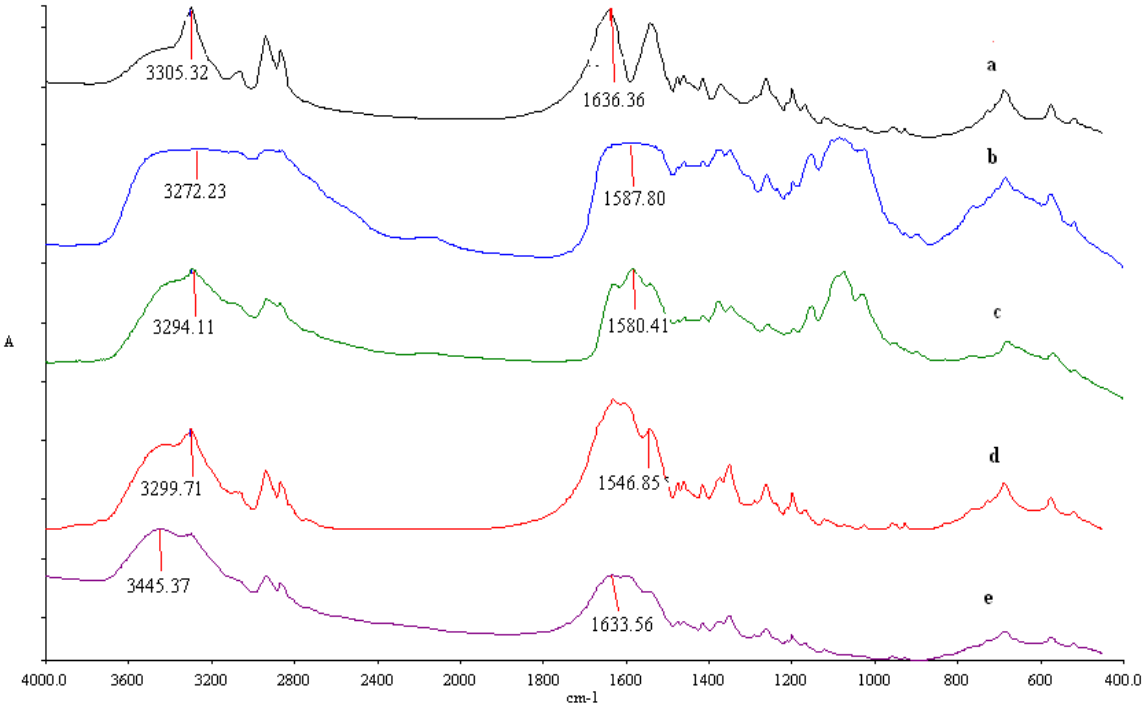


Figure 4 FTIR spectra for blends showing the displacement of the carbonyl band of amide group of: a) PA6; b) CN85/PA6; c) CN75/PA6; d) CN50/PA6; e) CN40/PA6

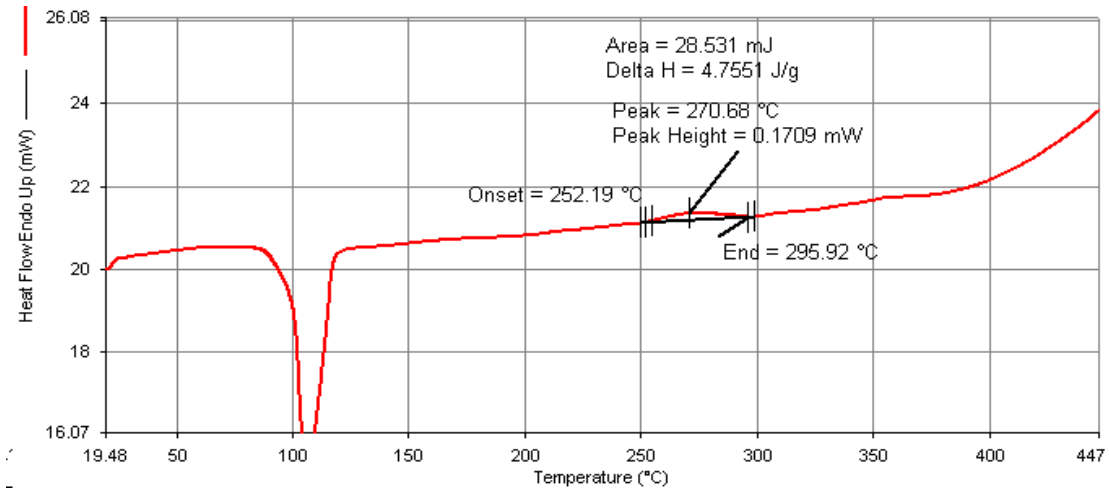


Figure 5 DSC thermogram of pure chitosan

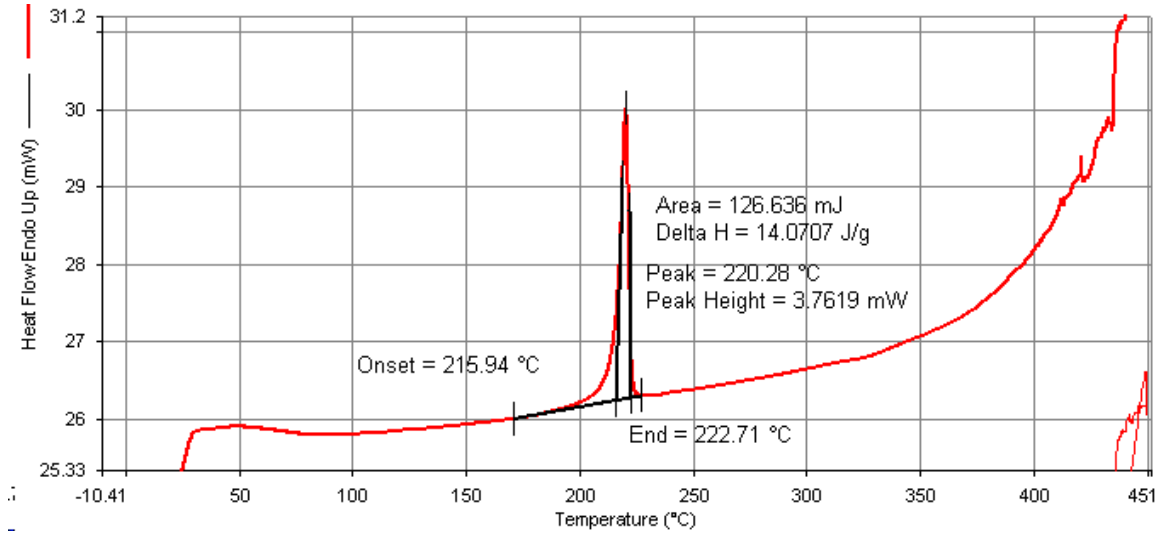


Figure 6 DSC thermogram of PA6

The thermograms of all CN/PA6 blends (Figures 7-10) show that the degradation pattern of all the film are different and they have either more numbers of degradation peak or have different energy values for degradation. For thermogram of CN85/PA6 blend (Figure 7), an exothermic peak can be observed at range of 100 °C, corresponding to the dehydration due to loss of water molecules which is strongly absorbed in the samples. The samples also show peaks at 216.5 °C, which resulted from the greatest thermal degradation of the samples.

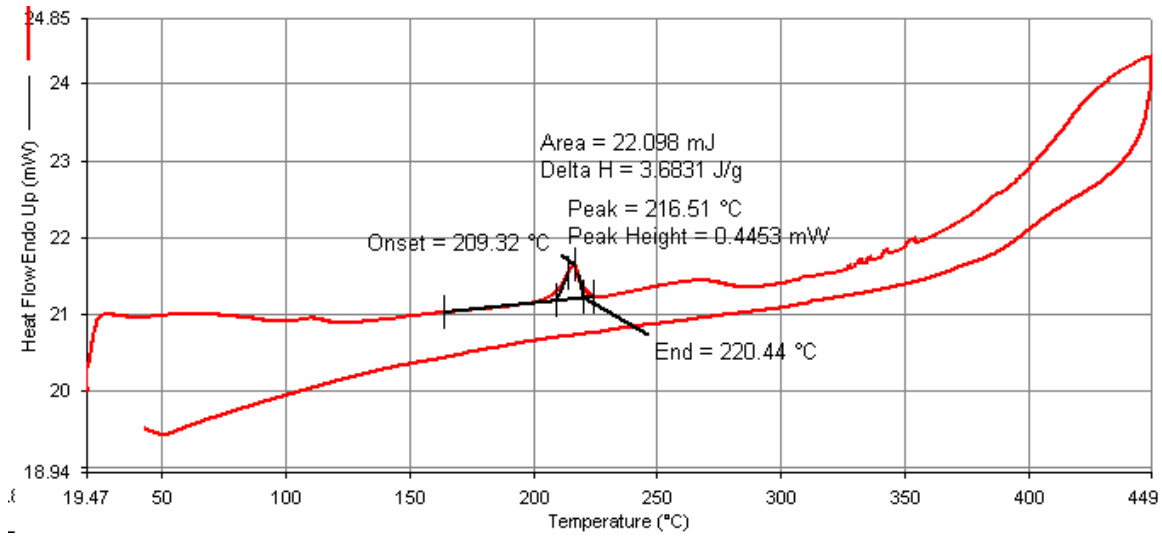


Figure 7 DSC thermogram of CN85/PA6 blend

Figure 8 show the thermogram of CN75/PA6 blend. It has one peak which represents it's T_m at 215.2°C. Heat of enthalpy of CN75/PA6 blend is slightly higher (4.5960 J/g) than CN85/PA6.

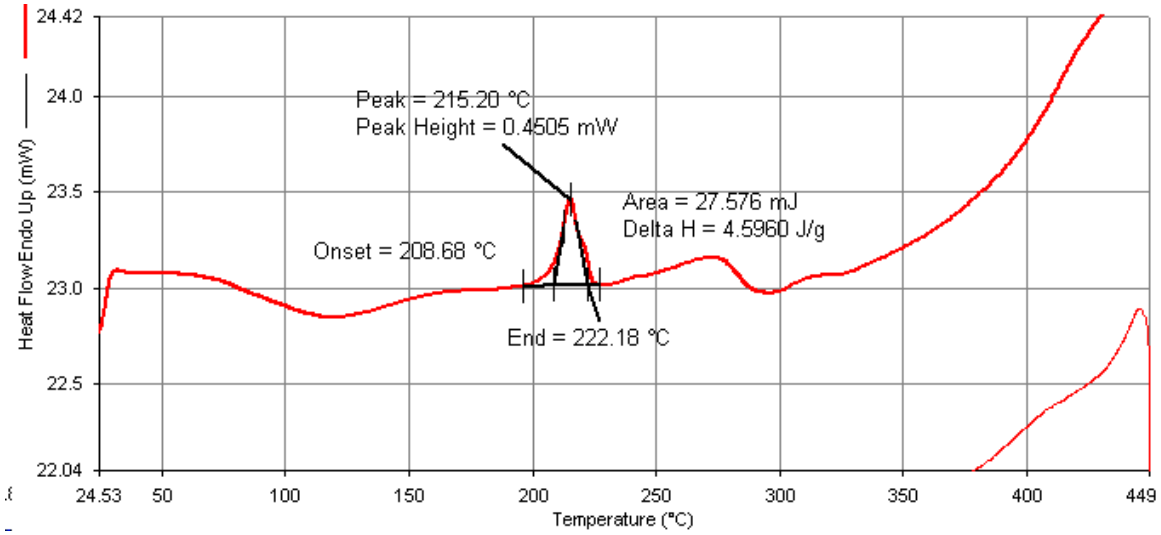


Figure 8 DSC thermogram of CN75/PA6 blend

The DSC heating thermograms of CN56/PA6 blends are presented in Figure 9. It is clear that CN56/PA6 thermograms posses two sharp melting peaks. The first melting peak occurs at 215.8 °C while the second peak is at 257.8 °C. The ΔH_m for this blend is calculated as the sum of low and high of temperature melting enthalpies which is sum of melting enthalpy of two peaks which is 14.7842 J/g.

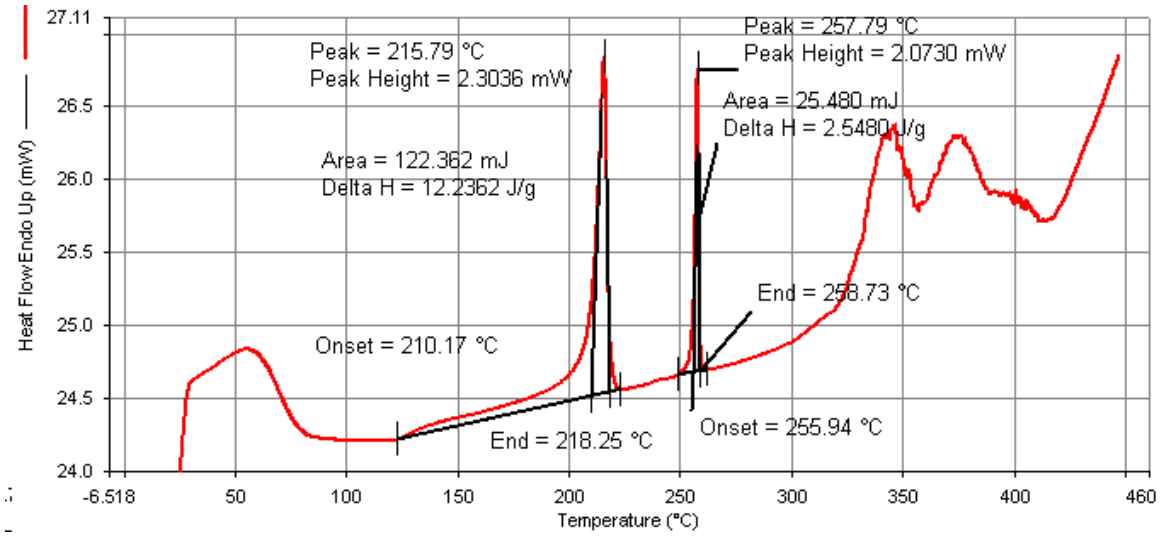


Figure 9 DSC thermogram of CN56/PA6 blend

Figure 10 shows thermogram for CN46/PA6 blend. It also comprise of double melting peak where the first one at 215.5 °C and another at 257.5 °C. For this blend, it has lower enthalpy than CN56/PA6 which is 8.9196 J/g.

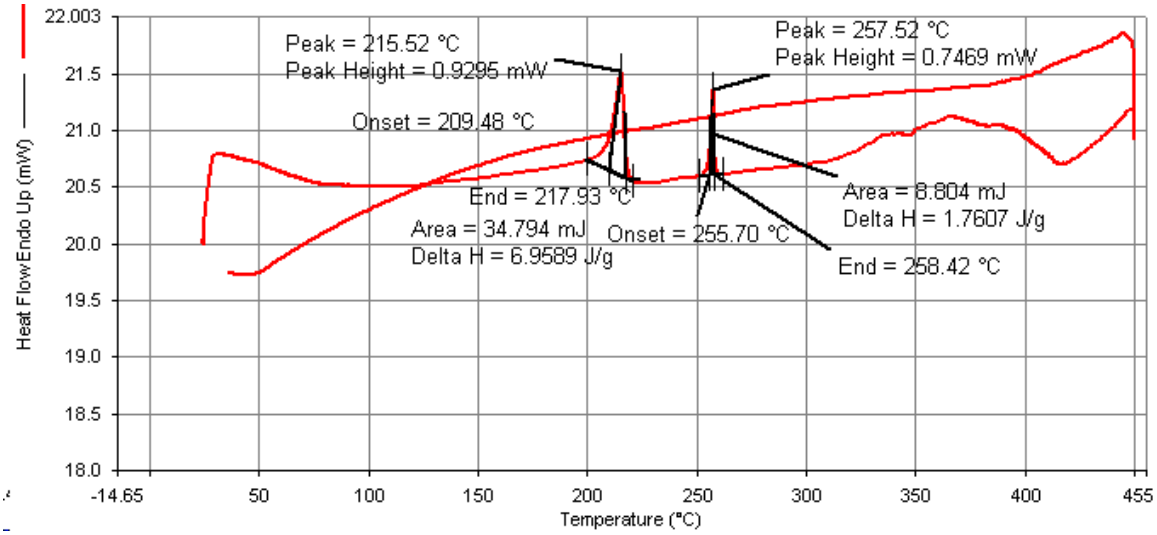


Figure 10 DSC thermogram of CN46/PA6 blend

Some representative values of T_m and ΔH_m upon heating are summarized in Table 3 for pure chitosan and PA6 and its blends. From Table 3, it can be seen that T_m of blends is lower (except for CN56/PA6 and CN46/PA6) than T_m of pure chitosan or PA6. This indicates that diluents effect due to the influence of interaction of both macromolecules is probably by hydrogen bonds [11, 18]. He *et al.* [11] also stated that when two polymers are miscible in the melt, the chemical potential of the crystallizable polymer is decreased due to the addition of the second component. This will lead to a reduction in the equilibrium melting temperature [12].

Table 3 Values of T_m and ΔH_m upon heating by DSC

Type of Film (% DD)	**T_m (^oC)**		**ΔH_m (J/g)**
	Low	High	
Pure chitosan	-	270.7	4.7551
PA6	-	220.3	3.7619
CN85/PA6	-	216.5	3.6831
CN75/PA6	-	215.2	4.5960
CN56/PA6*	215.8	257.8	14.7842
CN46/PA6*	215.5	257.5	8.7196

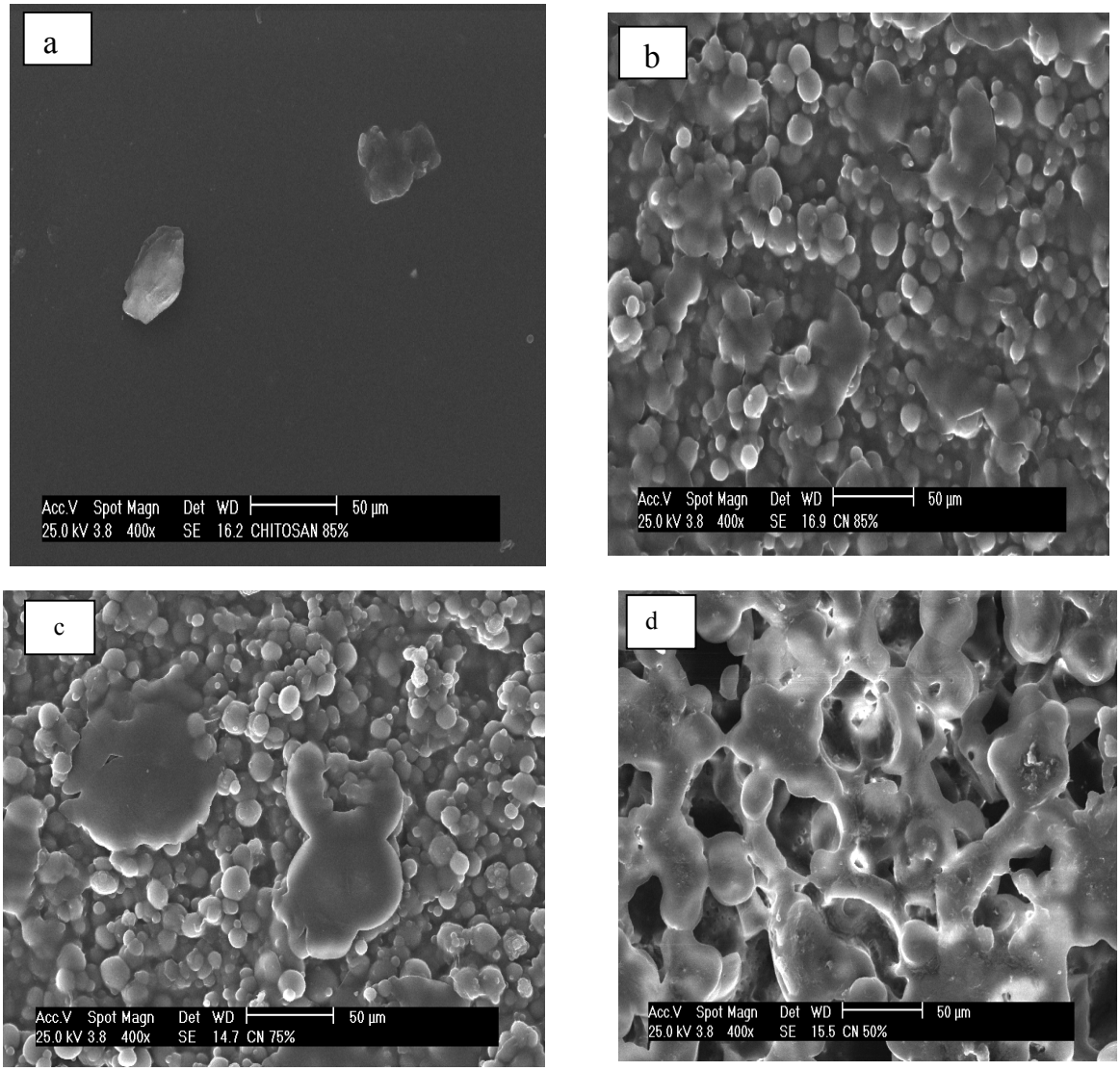
*Double melting point; ΔH_m reported as the sum of low and high temperature melting enthalpies

Table 3 shows that CN85 and CN75 which has higher DD give one sharp peak compared to CN56/PA6 and CN46/PA6 which has two peaks. This could indicate that blends with higher DD will contribute towards good compatibility between chitosan and PA6. While for CN56/PA6, two peaks were observed clearly; peak at low temperature (215.8°C) is due to the thermal decomposition of PA6 and at higher temperature (257.8 °C) is from decomposition of chitosan. A similar thermal transition behavior was observed in the CN46/PA6 blends.

In conclusion, DSC analyses suggested partial miscibility between PA6 and chitosan blend. The blends show higher energy liberation during decomposition due to the higher amount of energy is released in the blends during decomposition which is definitely related to the presence of some stronger bonding in the blending as proven by FTIR results.

3.2.3 Scanning Electron Microscopy (SEM) Analysis

SEM photographs of pure chitosan and blends are shown in Figure 11.



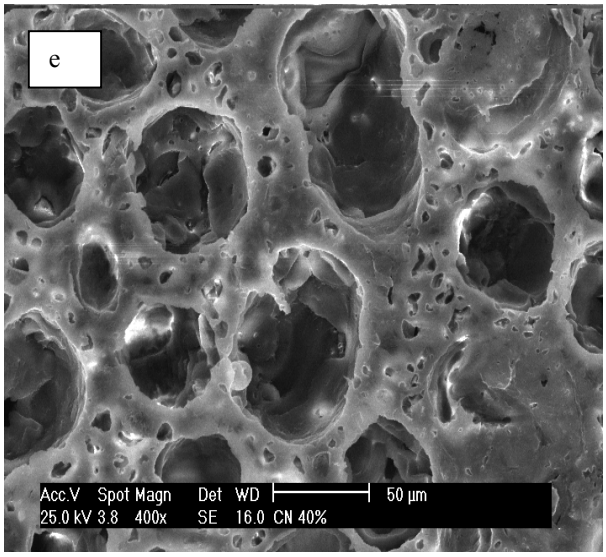


Figure 11: SEM photographs of a) pure chitosan; b) CN85/PA6; c) CN75/PA6; d) CN56/PA6 and e) CN46/PA6 at 400x magnification

The surface of a pure chitosan film shows that its surface is very smooth and homogenous. This film also displayed a flat dense surface (Figure 11a). However, when chitosan and PA6 were blended together, the smoothness surfaces gradually disappear and the flat dense surface became undulating. The photographs in Figure 11 (b) and (c) shows that a scattered round plaque likes structure which occur due to the immiscibility of the two polymers. Whereas the presences of holes can be observed on the blends surface as shown in Figure 11 (d) and (e) which correspond to the degradation of chitosan. The CN46/PA6 blend also displays more and larger holes as compared to CN56/PA6. All the photographs show phase separation occuring in blend. Similar observation also found in work done by Dufresne *et al*. [12] which concluded that phase separation happen during the formation of films from the casting and evaporation of PA6 and chitosan blend solution [13].

It was noted that the degree of deacetylation of chitosan affected the compatibility as well as the surface structure of blends which can be seen from the SEM photographs. As the DD increased, it can be seen that the surface structure of blends are finer and no appearance of holes. It also can indicate the increase of compatibility between polymers. It might be attributed to the higher amino group content in chitosan with higher DD which might interact with the functional group of PA6. Similar observations of increasing compatibility with increasing DD of chitosan was reported by Zakaria *et al*. [18] when studying the effect of DD of chitosan on PA66 blends.

4.0 CONCLUSION

These studies have successfully demonstrated the process of deacetylation of chitin to chitosan by autoclaving method. Using solution blending technique, blends of chitosan and PA6 were successfully fabricated. Characterizations of the chitosan blends have proven the existence of hydrogen bonding which is essential to the compatibility and miscibility of the blend. From FTIR analysis, the shifting of carbonyl band of amide group to the lower frequency indicated that these two polymers can form hydrogen bonding between them. DSC analysis revealed that ΔH_m of blends is lower than the respective original polymer

itself. SEM analysis showed that the surface morphology of blend is rough with scattered round plaques like structure which may be due to the immiscibility of the polymers especially when using lower DD chitosan. Results also imply that blends are more compatible with increased degree of deacetylation of chitosan. This compatibilization is caused by the formation of hydrogen bond between chitosan and PA6. Chitosan with higher DD will have more amino group which will contribute towards the formation of hydrogen bonding. The blends prepared can give new material which can be further developed to expand its application in future such as biomedical devices.

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