A Kinetic Study of Thermal Degradations of Chitosan/Polycaprolactam Blends

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Abstract: We have used FT-IR spectra to explain the effects of hydrogen bonding between chitosan and polycaprolactam (PA6). A dynamic mechanical analysis study suggested that the optimum chitosan and PA6 miscibility under the conditions of this experiment were obtained at a blending ratio of 40:60. We studied the thermal degradation of chitosan blended with PA6 (chitosan/PA6) by thermogravimetric analysis and kinetic analysis (by the Ozawa method). Dry chitosan and PA6 exhibited a single stage of thermal degradation and chitosan/PA6 blends having >20 wt% PA6 exhibited at least two stages of degradation. In chitosan/PA6 blends, chitosan underwent the first stage of thermal degradation; the second stage proceeded at a temperature lower than that of PA6, because the decomposition product of chitosan accelerated the degradation of PA6. The activation energies of the blends were between 130 and 165 kJ/mol, which are also lower than that of PA6.

Keywords: thermal degradation, chitosan, blended, polycaprolactam, kinetic analysis, activation energy.

Introduction

Chitin is a biodegradable polymer with the main chain structure (β-(1-4)D-glucopranose) like cellulose. The crucial difference is that, in the C-2 position, the hydroxyl is replaced by the acetamide and forms [β-(1-4)-2-acetamido-2-deoxy-]-D-glucopranose], which is the major structure of chitin. Chitosan is obtained by the deacetylation of chitin,[1-3] since chitin is hard to deacetylate completely, chitosan is classified into several types, according to molecular weight and its capacity to be deacetylated. Chitosan contains cations, and so can suppress the growth of microorganisms and bacteria that possess anions, so chitosan is classified as a bio-polymer.[4] Chitosan can absorb enzymes, anionic polysaccharides, and metal ions, as well as associate with food processing wastewaters. Hence it also has applications in separation and purification processes. Much of this information has been reviewed in the literature.[5-7]

Polycaprolactam (PA6) has a wide range of applications in plastics and textiles, and exhibits favorable mechanical properties. Unfortunately, polycaprolactam is not biodegradable. The reactive amine side groups within chitosan can physically cross-link with other polar polymers, so the natural polymer (chitosan) is blended with the synthesized polymer (PA6) to yield a biodegradable polymer blend with improved

mechanical properties. The chitosan/polycaprolactam blends will be applied to fiber spinning,[8] nonwoven,[9] antiseptic fabric,[10] dialysis membrane,[11] packaging materials[12] and medical materials.[13] This polymer blend offers greater economic advantages.[14]

The applications of polymer and polymer blend generally depend on their mechanical properties; however, their thermal characteristics must also be considered.[15] The temperature of the thermal degradation of polymers must be determined before they can be used in thermal applications. Some investigations have discussed the thermal behaviors of chitosan and chitosan derivatives, including chitosan,[16] chitosan Schiff bases,[17] chitosan-metal ion complex,[18] chitosan/poly(3-hydroxybutric acid) blends[19] and chitosan-lactic/glycolic acid.[20] Thermal analysis techniques include pyrolysis-mass spectrometry, scanning differential calorimetry (DSC) and thermogravimetry analysis (TGA). Polyamide and its blends, such as PA6 and PA66,[21] PA6-polypropylene blends[22] and PA6/EPDM[15] blends have been similarly analyzed. However, chitosan blended with PA6 (chitosan/PA6) polymer blend exhibits deficient thermal degradation characteristics.

This investigation first used FT-IR to observe the hydrogen bond effect between chitosan and PA6. Simultaneously, the results of DSC and of dynamic mechanical analysis (DMA) were utilized to evaluate the miscibility of blends. By the results of DMA, we obtained an optimum blend ratio of chitosan/PA6 blend. The degradation of polymer blends with various chitosan/PA6 contents was examined by ther-

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mogravimetric analysis (TGA) and the Ozawa method to evaluate the activation energy of degradation.[23,24]

Experimental

Materials. Polycaprolactam with an weight average molecular weight of 3.0×10^4 was purchased from Aldrich Co., USA; 84.5% deacetylated chitosan with an weight average molecular weight of 1.5×10^5 was obtained from Fluka Co., Switzerland, and 99% pure formic acid was purchased from Acros Co., USA.

Preparation of Membrane. Chitosan and polycaprolactam were dissolved in formic acid solution during blending, before being and then heated to 65 °C for four 4 hrs. The blending ratios of the polycaprolactam varied from 10% to 90% (wt%). The blended solution was spread on a glass plate and then heated in a vacuum oven to form a 0.07-0.15 mm thick membrane. The membrane was submerged in a 2 M sodium hydroxide solution to neutralize it; soaked in deionized water for 24 hrs; settled at room temperature, and dried naturally. Table I lists the blend ratios and each sample codes.

Measurement. FT-IR measurements were taken using a PIKE 6141 spectrophotometer; and scanned ten times ranging from 500 to 4500 cm^{-1} at room temperature. FT-IR measurements were used dried samples.

DSC measurements were taken using a Perkin Elmer Pyris 1 DSC, on samples with mass of about 5 mg, at heating rate of 10 °C/min; samples were tested in the nitrogen gas condition, and testing temperature ranging from 30 to 275 °C.

DMA measurements were conducted using a Perkin Elmer DMA 7e, with heating rate of 5 °C/min, testing temperature ranging from -150 to 150 °C frequency of 1 Hz. Moreover, the dimensions of the testing sample were thickness 0.07-0.15 mm, width 5 mm and length 10 mm.

TGA measurements were conducted using a Perkin Elmer TGA 1, on samples with masses of about 5 mg, at heating rates of 5, 10, 20 and 40 °C/min; samples were tested in the nitrogen gas condition, and testing temperature ranging from 30 to 750 °C.

Results and Discussion

FT-IR. Figure 1 shows the shifted FT-IR spectra of chitosan, PA6 and the chitosan/PA6 membrane; the spectra present the amide group of chitosan; the intensity and frequency of the absorption peak, which displays the characteristics of
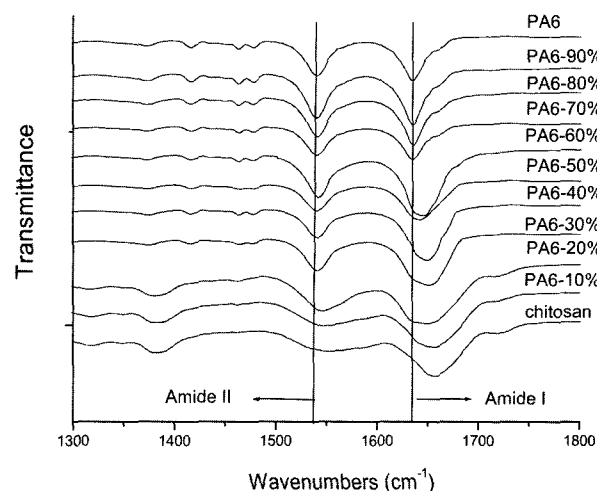

Figure 1. FT-IR spectra of chitosan/PA6 blended membranes.

alternation and transition, indicate a certain degree of inter-relationship between PA6 and chitosan. The absorption peak of chitosan in the amide band in Figure 1 appears at 1657 cm^{-1} while that of PA6 appears at 1632 cm^{-1}. The absorption peak of chitosan in the amide II band appears at 1557 cm^{-1} and that of PA6 appears at 1541 cm^{-1}. After PA6 is added, the frequency of the absorption peak of chitosan in the amide I band declines approximately 25 cm^{-1}. The frequency shift in the amide II band was similar, but less than that of chitosan/PA6 blends in the amide I band. Generally, the frequency of the absorption peaks in the amide I and amide II bands shift downward, and no any new absorption peak being generated as the PA6 content increased; also indicating that the hydrogen bond formed between chitosan and PA6.[25]

DSC. Figure 2(a) shows DSC scan of chitosan, an endothermic peak centered around 100 °C can be assigned to the evaporation of adsorbed water. The sample was held at 100 °C for 10 min and cooling to room temperature, and then started DSC scan. We did not find the endothermic peak on DSC curve (as shown in Figure 2(b)). The DSC curve of chitosan does not indicate any endothermic transition between room temperature and 250 °C, that assigns the lack of any crystalline or any other phase change during the heating process. Sreenivasan[18] suggested that the strong endothermic peak around 270 °C was due to the oxidative degradation of chitosan. Thus, the endothermic peak centered around 287 °C in Figure 2(b) ought to the thermal degradation of the sample.

Table I. Samples Blend Ratios

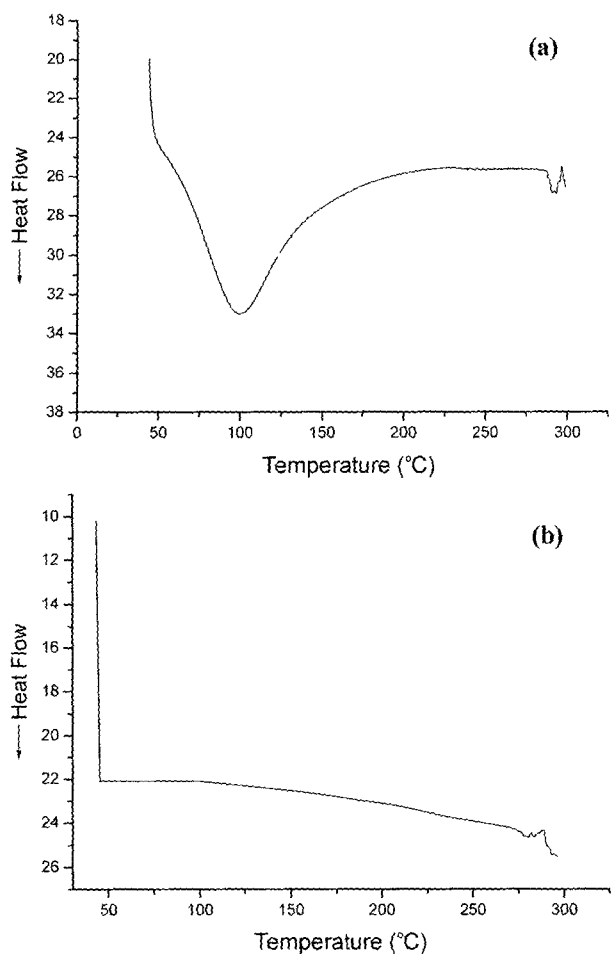| Sample Code	Chitosan	PA6-10%	PA6-20%	PA6-30%	PA6-40%	PA6-50%	PA6-60%	PA6-70%	PA6-80%	PA6-90%	PA6
Chitosan Content	100 wt%	90 wt%	80 wt%	70 wt%	60 wt%	50 wt%	40 wt%	30 wt%	20 wt%	10 wt%	0 wt%
PA6 Content	0 wt%	10 wt%	20 wt%	30 wt%	40 wt%	50 wt%	60 wt%	70 wt%	80 wt%	90 wt%	100 wt%

Figure 2. (a) DSC curve of chitosan obtained at a heating rate of 10°C/min and (b) DSC curve of dry chitosan obtained at a heating rate of 10°C/min in an atmosphere of nitrogen.

Figure 3. DSC curves of polycaprolactam and chitosan/polycaprolactam blended samples obtained at a heating rate of 10°C/min in an atmosphere of nitrogen.

Chitosan and polycaprolactam possess polar groups, thus the water is adsorbed onto the polymers while hydrogen bond forming. Therefore, all samples were dried at 100°C for 10 min then cooling to room temperature before DSC scan.

Figure 3 displays DSC scan of polycaprolactam and chitosan/polycaprolactam blended samples. From Figure 3, the endothermic peak of adsorbed water evaporation was disappeared. We observed only one endothermic peak on each blended samples, the temperature of the endothermic peak corresponds to the T_m of polycaprolactam. Before the endothermic peak of T_m, no any slope change was observed. It is probably owing to DSC scan condition unavailable to examine for the T_g of samples.

Basically, the temperature of endothermic peak was shifted toward low temperature with increasing of chitosan content. Above-mentioned results can be used to explain chitosan interfere the crystallization of polycaprolactam, both in reducing the size of crystalline and broadening the distri-
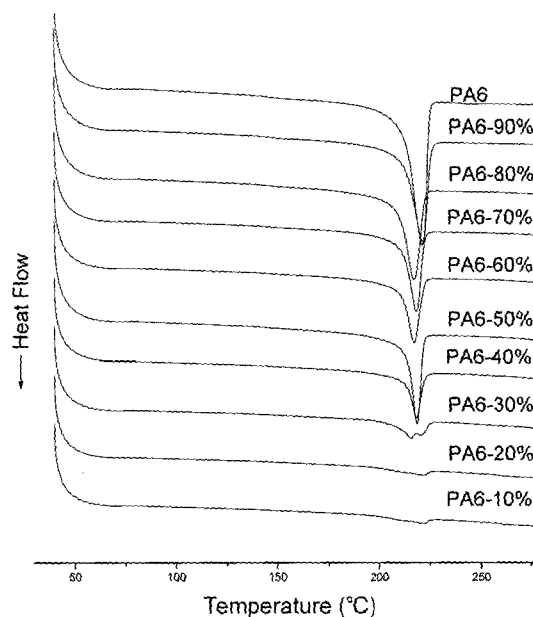
bution of crystalline. The hydrogen bond formed between molecular chains in the two compositions restricted the crystallization of polycaprolactam. Besides, the steric hindrance formed by the molecular chains of chitosan also restricts the movement of polycaprolactam chains, and then causes the difficulties of crystallization. If the former effect plays as the main reason, miscibility between chitosan and polycaprolactam exist.

Because DSC results can't be used to evaluate the miscibility of chitosan/polycaprolactam blends precisely, further evaluations for the same miscibility by DMA will be discussed in the next part.

DMA. For miscibility testing without the influence of humidity, all samples were dried at 100°C for 10 min in a vacuum oven for humidity removal. To prevent humidity penetrating into samples, a sealed type cooling tank was used to avoid liquid nitrogen bringing humidity into test samples. The samples were placed on the clamp, the temperature was increased to 100°C rapidly, and held for 5 min, then decreased to -150°C rapidly. The dry nitrogen gas rate (20 cm³/min) was continuously added to the system at the position occupied by the sample during testing.

Figure 4 illustrates the relationship between the tan δ and temperature under this test condition. From Figure 4, the three peaks of PA6, namely the γ peak, β peak and α peak, from low to high temperature, were at -130, -62 and 78°C, respectively. PA6 has three loss peaks, representing the motion of the methylene group between the amide groups, the partial motion of the amide group and the segment motion of the main chain, from low to high temperatures.
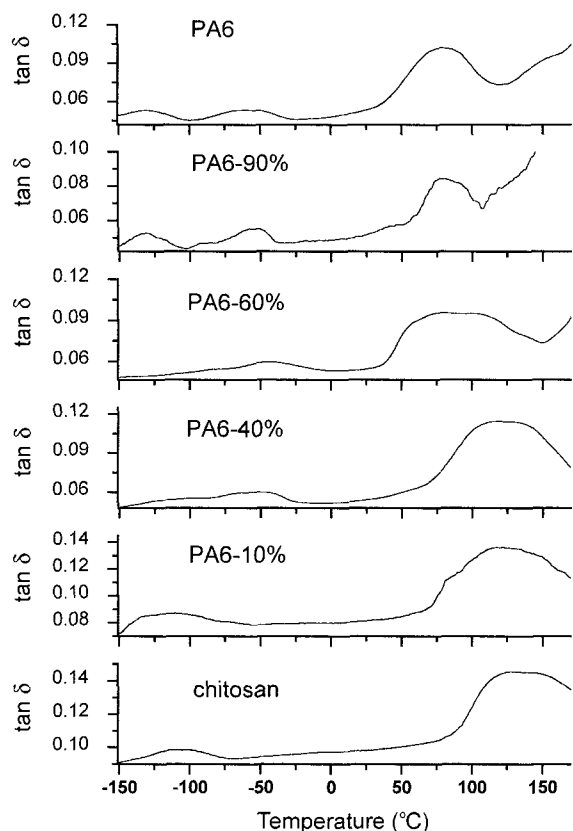
Figure 4. Loss tangent (tan δ) of "dried" samples in dry condition.

Chitosan has two loss peaks, namely: the γ peak occurring at -110 °C, resulting from vibrations of the polysaccharide, and the α peak at approximately 130 °C, resulting from motion of main chains.

This investigation found that, under the condition, the α peak of the blends shifts toward high temperature with increasing chitosan content. This phenomenon is attributed to the hydrogen bond generated between chitosan and PA6. This hydrogen bond restricts the molecular chain motion, thus making the α peak to shift toward high temperature. The β peak of PA6-90% shifted toward high temperature and narrowed, and a shoulder of the β peak appeared at the low temperature that corresponded to the γ peak of chitosan. The α peak of PA6-90% increased slightly, but a shoulder appeared around 100 °C, indicating that chitosan and PA6 had not only an inter-relation but also a phase separation. The same situation occurred for the PA6-60%, for which the temperature of the α peak extended from 53 to 108 °C, corresponding to the temperature of the α peak of PA6 and chitosan, respectively, and demonstrating that the phase separation also existed in PA6-60%.

The temperature range of the two peaks of the PA6-10% appeared, corresponding to the γ peak and the α peak of chitosan. A shoulder of PA6-10% appeared around 80 °C that

corresponded to the α peak of PA6, indicating that, molecule chain motion of PA6 and chitosan both existed in the blend, implying the occurrence of phase separation. PA6-40%, at low temperature, displayed only one peak that approached the β peak of PA6, and no shoulder of α peak. Additionally, because the influence of chitosan caused the α peak to shift toward high temperature, ranging from around 105~140 °C. To sum up, PA6-40% had the highest miscibility of all blends.

TGA.

Degradation of Wet Samples: Chitosan and polycaprolactam (PA6) possess polar groups, so the water is adsorbed onto the polymers while hydrogen bond forming.[26-31] As the temperature from 30 reach to 120 °C, the TG curve indicated a degreed of 12 wt% weight loss of chitosan, implying the presence of water; the weight loss of PA6 was about 4 wt%, as indicated in Figures 5(a) and 5(b). Following the loss of water, chitosan and PA6 underwent the primary stage of degradation. The primary degradation of chitosan started at about 295 °C and completely degraded at about 720 °C. For PA6, the primary degradation was from 437 to about 510 °C. In spite of the water loss, the TG curves indicate that both polymers underwent a single stage of degradation.

After chitosan and PA6 polymers dried at 100 °C for 10 min, the TG curves indicated no weight loss of water, as shown in Figures 5(c) and 5(d). Therefore, in subsequent experiments, all samples were dried at 100 °C for 10 min to proceed thermal degradation and measure weight loss. Moreover, the dry samples were very useful in analyzing the kinetics.

Degradation of Chitosan and PA 6: The TG curve of dry PA6 in Figure 5(d) has a horizontal base line between 100 and 300 °C, implying the sample had been already completely dehydrated. However, the base line of the TG curve for dry chitosan indicated a 5 wt% weight loss between 100 and 280 °C, as shown in Figure 5(c); this weight loss is associated with deacetylation.[20,32]

The dry chitosan and PA6 exhibited a single stage of degradation, that reflected the temperature of the maximum rate of degradation (DTG curve) as shown in Figures 5(c) and 5(d). The temperature of initial degradation (T_1) of chitosan was about 287 °C and the temperature of the maximum rate of degradation (T_{1max}) was about 313 °C; finally a high char residue of about 37 wt% was produced at 720 °C. The degradation of chitosan in fact started with the amine groups, and formed an unsaturated structure.[20] Similarly, PA6 also exhibited a single stage of degradation at about 429 °C, and the temperature of maximum rate of degradation was at about 466 °C, and related to the breakage of the main chain. The degradation of PA6 was a depolymerization (a reversed reaction of cyclic polycondensation) to form a caprolatam[21,33]; finally, formed the char residual less than 0.21 wt%.

Degradation of Chitosan Blended with PA6: TGA was used herein to examine various components of blended sam-
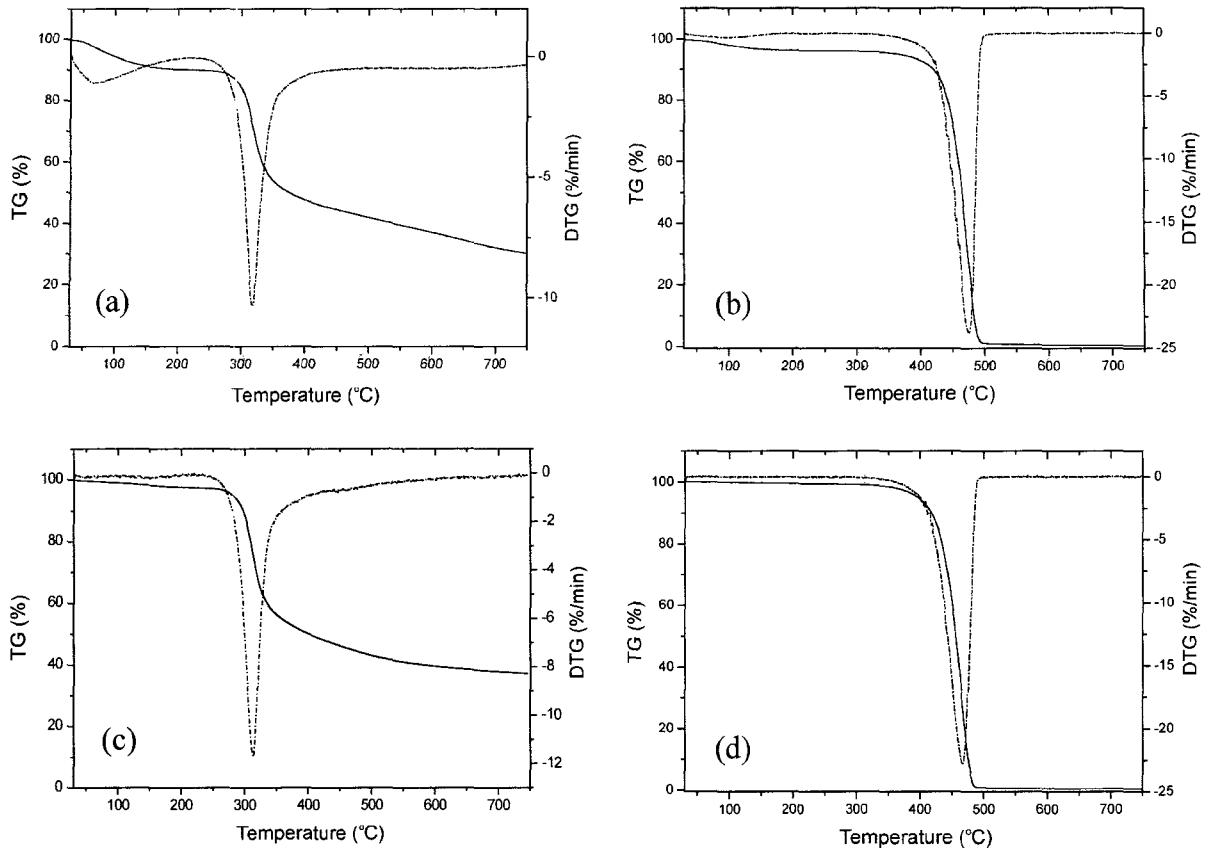
469

Figure 5. TG and DTG curves of (a) wet chitosan obtained at a heating rate of 10 °C/min in an atmosphere of nitrogen, (b) wet PA6 obtained at a heating rate of 10 °C/min in an atmosphere of nitrogen, (c) dry chitosan obtained at a heating rate of 10 °C/min in an atmosphere of nitrogen, and (d) dry PA6 obtained at a heating rate of 10 °C/min in an atmosphere of nitrogen.

ples. The TG curves of blended samples with a PA6 content of above 20 wt% clearly exhibited two stages of degradation, as shown in Figure 6. The temperature ranges of the first and second stages of degradation seem to correspond to the temperature ranges of degradation of pure chitosan and PA6, respectively. Via two peaks on the DTG curves, which were considered to indicate the temperature of the maximum rate of the first and second degradation stages. However, the TG and DTG curves of the blended samples that contain more than 30 wt% PA6 leaded the temperature of the second stage to shift toward higher temperature, as shown in Figure 6. For blended samples, the degraded substrates of chitosan seemed to affect the PA6 degradation earlier.

Qualitative Characterization of Chitosan/PA6. Table II lists the temperatures of characterization at 10 °C/min in nitrogen for all dry blended samples. Degradation process is qualitatively characterized by the onset temperature of degradation and by the temperature of maximum rate of degradation of stage I (T_1 and T_{1max}) and stage II (T_2 and T_{2max}). T_1 and T_2 of these samples are determined by extrapolating the initial temperature of degradation because of the repeatability.

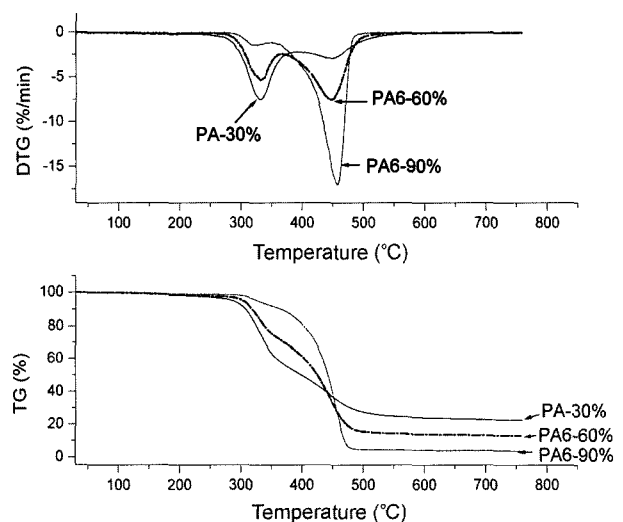The temperature of characterization of pure PA6 of clearly

Figure 6. TG and DTG curves of chitosan/PA6 of various proportions, obtained at a heating rate of 10 °C/min in an atmosphere of nitrogen atmosphere.
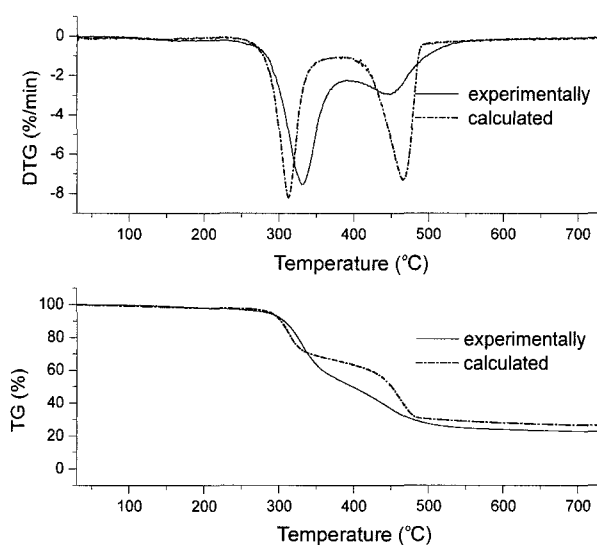
greatly exceeded that of chitosan. These chitosan/PA6 blendes exhibited two stages of degradation when the PA6

Table II. Temperature of Characterization at a Heating Rate of 10 °C/min in an Atmosphere of Nitrogen

	T_1 (°C)	T_{1max} (°C)	T_2 (°C)	T_{2max} (°C)	Char Residue
Chitosan	287	313			37.14%
PA6-10%	295	326			27.82%
PA6-20%	296	329	356	447	21.28%
PA6-30%	296	331	355	442	20.29%
PA6-40%	307	334	405	438	18.27%
PA6-50%	291	328	403	440	15.64%
PA6-60%	293	322	404	446	12.83%
PA6-70%	295	334	409	447	10.47%
PA6-80%	298	332	413	450	6.00%
PA6-90%	305	321	417	457	4.00%
PA6			429	466	0.21%

Figure 7. Experimentally determined and calculated TG and DTG curves for PA6-30% blend determined at a heating rate of 10 °C/min in an atmosphere of nitrogen.

content above 20 wt%; the samples with a PA6 content under below 20 wt% exhibited one stage of degradation. T_1 and T_{1max} of chitosan/PA6 blends with above 20 wt% PA6 content in the first stage were respectively about 300 and 330 °C, slightly exceeding those of pure chitosan. However, the T_2 of the PA6-20% and PA6-30% samples, of about 355 °C, was much lower than that of pure PA6 (429 °C). When the PA6 content in the blended samples was increased to above 40 wt%, the T_1 and T_{1max} slightly exceeded those of the pure chitosan. The T_2 and T_{2max} of the blended samples with a PA6 content of above 40 wt% were between 403~417 °C and 438~457 °C, respectively closer to the onset temperature of degradation and the temperature of maximum rate of degradation of pure PA6 than those of the blended samples with a low PA6 content. Besides, the first stage of degradation follows mainly from the degradation of chitosan; however, the degradation of chitosan may affect the second stage of degradation. Therefore, the T_2 and T_{2max} of those blended samples are lower than pure PA6, which fact may contribute to the interaction between PA6 and chitosan.

Indeed, the interaction during thermal degradation at low heating rates can be elucidated using conventional thermo-analytical techniques.[34,35] The TG/DTG curves of the blended sample in Figure 7 refer to a 10 °C/min heating rate in nitrogen. The calculated weight loss curves were determined from individual weight loss data concerning chitosan and PA 6. They are plotted in Figure 7 as dotted lines, neglecting inter-actions between components during thermal degradation. The calculated weight loss curve markedly differed by between 350~470 °C from the experimentally observed curve, which result was consistent with the second stage of degradation, as shown in Figure 7. The result indicates that the two components interacted. Similar results have been

obtained for the degradation behavior of aromatic poly-amide fiber blended with cotton fiber.[35] The T_2 and T_{2max} of those blended samples declined as the chitosan content increased and the experimental weight loss in the second stage of degradation clearly exceeded the calculated weight loss, indicating that the products of thermal degradation of chitosan in the blend affects the thermal degradation proce-dure of the PA6. Qu *et al.*[20] investigated the residual products of chitosan by IR technique. They proposed that the charac-teristic peak of amino around 1591 cm^{-1} was wide due to the formation of the unsaturated structure during degradation under high temperature. Carlos *et al.*[27] also studied the decomposition of chitosan using IR analyze and had the same results with Qu. Moreover, they discussed the degra-dation behavior of chitosan with pyrolysis-mass spectra and pointed out that the major degradation of chitosan was the breakdown involving the primary amino groups of the D-glucopyranose moieties. Furthermore, the dehydration of D-glucopyranose caused the hydrogen releasing at higher tem-perature. Those outcomes showed that the degradation of chitosan resulted in the products (such as unsaturated structure, hydrogen, amino groups etc.). Several studies have proved that the acids/bases or ions promote the thermal deg-radation of PA6.[33] The observed experimental weight loss of the blended samples is due to the products that are generated by the degradation of chitosan, accelerating the degradation of PA6. The above opinion can be supported by the activation energy, which will be discussed in the later section of kinetic analysis.

Kinetic Analysis. The thermal degradation can typically be described as a first-order reaction (whose parameter is loss of weight) if the decomposition products are volatile.

Although many methods for calculating kinetic parameters have been reviewed, nonisothermal methods are commonly believed to be able to describe thermal degradation.[36,37] Several methods can be used to evaluate the activation energy (E_a) from TGA curves, but the E_a of the process can rarely be correctly evaluated from a single TGA curve. More reliable methods involve many dynamic and isothermal curves. Ozawa[23,24] proposed a conversional method that relies on many TG curves, obtained at various heating rates. The activation energies of the samples at various degrees of conversion were analyzed using the Ozawa method, which can also be applied to describe the effect of activation energy.

Figure 8 plots the relationship between the logarithm of the heating rate ($\log_{10} B$) vs. $1/T$ for various values of α (0.1, 0.2 ⋯ 0.9) (where α, degree of conversion = weight loss at a given temperature/total weight loss of the degradation) for
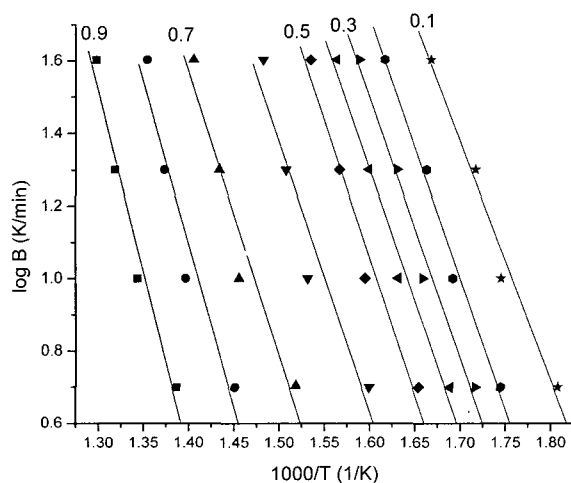

Figure 8. Dependence of logarithm of heating rate (log B) on reciprocal absolute temperature ($1/T$), according to the Ozawa method, at specified conversions (α) by the decomposition of PA6-30% blend in an atmosphere of nitrogen.

the PA6-30% sample. E_a was calculated from the isoconversion curves for each extent of conversion over the entire range of extents of conversion (10~90%). All samples in this study yielded straight lines with high correlation coefficients, such as in Figure 8 of the PA6-30% sample, so the activation energy in this study was calculated from the slope of the lines, according to the expression,

$$E_a = \text{-Slope} \times R/0.457 \tag{1}$$

where R is the gas constant.

Table III lists the E_a values of all samples at various values of α. The E_a of PA6 at various values of α was almost fully maintained about 170~179 KJ/mol, indicating that the PA6 exhibited a single stage of degradation, consistent with its TG and DTG curves. However, the E_a values of pure chitosan clearly increased with α values increase. The values of E_a did not remain constant, indicating that the sample underwent at least two stages of degradation. This result was dissimilar from that indicated by chitosan's TG and DTG curves, because the dehydrogenation of the D-glucopyranose structure caused sustained carbonization. Therefore, E_a values increased with α values and reached a maximum value at $\alpha = 0.6~0.7$, also approaching that value at the temperature of maximum rate of degradation -about 320°C. Above this temperature, the carbonization during the degradation of chitosan was slow yielded almost the maximum amount of char, as shown in Figure 2(c). When the α value was between 0.6 and 0.7, E_a suddenly increased to a very high value, indicating that more chitosan had been carbonized. Similar results were obtained for the PA6-10% and PA6-20% blends.

The E_a values of the blends increased with the values of α, as listed in Table III, in contrast to the E_a of the PA6, which remained almost content. The E_a values were similar to that of pure chitosan when the PA6 content was below 50 wt%

Table III. Activation Energies (E_a) in *KJ/mol* of Degradation of All Samples Calculated by the Ozawa Method

α \ Samples	Chitosan	PA6-10%	PA6-20%	PA6-30%	PA6-40%	PA6-50%	PA6-60%	PA6-70%	PA6-80%	PA6-90%	PA6
0.9	140.08	251.90	215.35	182.37	163.12	162.87	170.19	182.88	186.84	207.37	176.66
0.8	154.48	255.50	197.97	162.82	157.88	158.64	166.76	177.17	179.25	201.21	179.04
0.7	175.91	183.71	190.76	142.71	153.36	154.60	167.05	172.85	175.89	197.99	176.09
0.6	175.81	161.72	176.39	135.27	145.24	147.32	164.36	173.03	168.48	193.97	173.74
0.5	160.89	148.65	170.28	137.86	141.81	139.69	161.47	169.94	162.42	185.86	171.42
0.4	151.20	146.53	150.89	132.05	144.54	133.31	158.92	165.32	160.19	184.63	170.12
0.3	137.65	140.29	145.58	130.91	139.01	130.34	157.59	160.75	150.16	178.51	167.96
0.2	128.02	141.84	137.13	131.41	130.98	121.77	150.42	154.96	137.52	161.61	169.05
0.1	114.47	150.73	128.80	120.23	112.90	110.77	155.57	149.09	128.14	143.01	171.54

and α value was below 0.3. At the domain $0.3 \le \alpha \le 0.7$ the E_a values of the PA6-30%, PA6-40% and PA6-50% blends, were lower than those of pure chitosan, PA6 and other blended samples. The low E_a value of these samples indicated that the products generated by the degradation of chitosan accelerated the degradation of PA6. The acceleration of degradation with increasing PA 6 content above 60 wt% declined gradually as α value increased from 0.3 to 0.7, so E_a value increased with the PA6 content in the domain of values. This acceleration of degradation obtained from E_a values using the Ozawa method, is consistent with the results obtained from TG-DTG. Moreover, the E_a values of samples with PA6 contents of above 60 wt% at α between 0.1 and 0.6 were much higher than those of blended samples that PA6 contents of below 60 wt%. Obviously, the acceleration of degradation due to the chitosan in the blended samples was a function of the chitosan content. Furthermore, the E_a values of the blended samples with the values of α above 0.6 and PA6 contents above 60 wt% were close to that of pure PA6, indicating that the degradation the blends at high temperature were similar to that of pure PA6.

Conclusions

The FT-IR result explained the effect of the hydrogen bond between chitosan and PA6. The DMA results explained the optimum chitosan and PA6 miscibility under the conditions of this experiment were obtained at a blending ratio of 40 : 60. Chitosan and PA6 underwent a single stage of degradation; however, chitosan/PA6 blends underwent two stages of degradation with PA6 content above 20 wt%. The completely thermal degradations of chitosan and PA6, with weight losses are about 62 and 99 wt%, respectively. Subsequently, the products of the degradation of chitosan clearly accelerated the degradation of the blends with PA6 content between 30 and 50 wt%. The acceleration of degradation led to a lower temperature of degradation in the second stage for blended samples. The interaction within blended samples between chitosan and PA6 led to accelerate the second stage degradation, had already verified by the lower E_a value in this study.

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