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합성 열안정제에 의한 나일론 4의 분해거동

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Degradation Behavior of Nylon 4 in the Presence of Newly Synthesized Thermal Stabilizers

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초록: 힌더드 아민기를 포함하고 있는 헤테로환을 가지며 알킬사슬 길이가 서로 다른 세 종류의 나일론 4 열안정제를 합성하였다. 힌더드 아민기를 이용하여 라디칼에 의한 열분해를 방지하고, 열안정제와 나일론 4의 아마이드기 간 수소결합을 조절하여 나일론 4의 열적 특성에 미치는 영향을 확인하였다. 안정제의 알킬사슬의 수가 4개일 때 수소결합이 가장 최적화되는 것으로 등온 TGA 결과를 통해서 확인하였다. 또한 시판중인 나일론 6의 열안정제를 사용하여 나일론 4에 대한 열안정성을 비교 실험한 결과, 합성 열안정제가 나일론 4의 열안정성을 실질적으로 향상시킨 것을 확인하였다.

Abstract: Three kinds of thermal stabilizers for nylon 4 were synthesized to incorporate both hindered amine groups and methylene units with various lengths. It is expected that the hindered amine groups play a role in the capture of degradation-triggering species. Considering sequence rules, hydrogen bonding formed between nylon 4 and the stabilizers is optimized to alter the lengths of the methylene units in the stabilizers. As a result, it was found that a tetramethylene unit in the stabilizer is an optimal length for hydrogen bonding in terms of isothermal thermogravimetric analysis (TGA). Considering the slight and often negligible improvement of thermal stability of nylon 4 containing commercially-available nylon 6 stabilizers, retardation of thermal degradation has been substantially improved upon.

Keywords: nylon 4, thermal stability, TGA, thermal stabilizers.

Introduction

Nylon 4, also known as polypyrrolidone or polybutyrolactam, is a highly promising polymer for many years since it was firstly synthesized in 1953. The main advantage of this polymer stems from its hydrophilic nature, which provides desirable moisture regain. Thus, physical properties of nylon 4 such as those affecting static interaction, hygroscopic properties, and dyeing properties are similar to those of natural cotton, while mechanical properties such as modulus, strength, and elongation at break are comparable to those of nylon 6.[1]

2-Pyrrolidone, a monomer for nylon 4 can be obtained from bio-mass resources and, thus, nylon 4 is relatively biodegradable.[2] Though nylon 4 shows a high melting temperature of about 260 ºC and good mechanical properties, its commercial use has been limited, presumably due to its lack of thermal stability, of which melting temperature is lower than decomposition temperature.[3] Therefore, there is significant commercial interest in improving the thermal stability of nylon 4.

In order to overcome the poor thermal stability of nylon 4, a variety of investigations have been focused on the modification of chain ends, because it is generally accepted that degradation is initiated by depolymerization from the chain end.[3a,4] Additives for enhancing thermal stability have also

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been investigated for practical use.[5] Additionally, alternative approaches have been sought to address this shortcoming. In particular, copolymers of nylon 4 and nylon 6 have been developed for this purpose.[1b,6]

However, since the degradation mechanism of nylon 4 has not been clearly understood, thermal stabilizers for nylon 4 can be conjectured bearing the degradation mechanism of nylon 6 in mind. Herein, nylon 4 was polymerized from 2-pyrrolidone and thermal stabilizers, based on hindered amine groups linked with various lengths of methylene units, were synthesized to optimize the effect of hydrogen bonding. The thermal properties of nylon 4 containing stabilizers were investigated by both dynamic and isothermal TGA and were compared with commercially available nylon 6 stabilizers produced by Ciba.

Experimental

Materials and Characterization. 2-Pyrrolidone, sodium, and acetic anhydride used for polymerization of nylon 4 were purchased from Aldrich and were used as received. 4-Amino-2,2,6,6-tetramethyl-piperidine, adipoyl chloride, suberoyl chloride, sebacoyl chloride, and triethylamine were purchased from Aldrich and were used without further purification. Thermal stabilizers for nylon 6: Irganox 168, Irganox 1010, and Irganox 1098, were kindly provided by Ciba. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-300 spectrometer (Korea Basic Science Institute). FTIR spectra were obtained from Bruker Tensor 27. TGA was carried out on a Mettler-Toledo Thermal Analyzer. Elemental analysis was performed on an Elemental Analyzer EA 1108 (Fisons Instruments). The viscosity of nylon 4 was measured in a m-cresol solution to determine viscosity average molecular weight (M_v). The intrinsic viscosity was measured with an Ubbehlode viscometer. Using Mark-Houwink equation, $[\eta] = K[M_v]^a$, where K and a are equal to 3.98×10^{-4} dL/g and 0.77, respectively, M_v was calculated.[7]

Polymerization of Nylon 4. The polymerization of nylon 4 was accomplished according to the previously reported method.[7] Briefly, the synthetic method is as follows. Monomer, 2-pyrrolidone (555 g, 6.52 mol) was added to a four-neck flask equipped with a magnetic stirrer, a drying tube, and a vacuum apparatus in an oil-bath at 50 °C. Water, which was contained in 2-pyrrolidone, was removed by evacuation for 30 min under reduced pressure. Sodium (4.49 g, 0.19 mol) was cut by a slice and was immediately added, and allowed to react with monomer 2-pyrrolidone while vigorous stirring for 1 h under reduced pressure. The polymerization was initiated by adding acetic anhydride (9.99 g, 0.097 mol). The mixture was stirred under reduced pressure in an oil bath at 50 °C. The polymerization was carried out for 36 h. After the reaction, the mixture was solidified and maintained for another 4.5 days. The polymer was dissolved in formic acid and precipitated in acetone. The crude nylon 4 was then washed with methanol and dried *in vacuo* at 50 °C for 24 h (yield 326 g, 55 %). $[\eta]$ = 1.00, M_v = 26100.

Synthesis of N1,N6-bis(2,2,6,6-tetramethylpiperidin-4-yl)adipamide (HA). 4-Amino-2,2,6,6-tetramethylpiperidine (2 mL, 11.7 mmol) and triethylamine (3.24 mL, 23.4 mmol) were added into a flask containing methylene chloride (30 mL) and stirred at room temperature. A solution of adipoyl chloride (1.04 mL, 5.7 mmol) in methylene chloride (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 12 h at room temperature. After the reaction, the mixture was washed with water and the organic layer was dried over magnesium sulfate. After evaporation of the methylene chloride, the product was purified by recrystallization in ethanol. Yield 1.63 g (68%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.5 (s, 1H), 4.2-4.4 (m, 2H), 2.2 (t, 4H), 1.8 (s, 2H), 1.25 (d, 8H), 1.15 (s, 24H), 0.95 (q, 4H) ppm. ^{13}C NMR ($CDCl_3$) δ = 171.5, 48.2, 45.7, 36.3, 33.7, 29.1, 24.7 ppm. FTIR (KBr, cm^{-1}): 3253 (N-H), 2850 (aliphatic C-H), 1631 (amide C=O), 1548 (amide N-H bending). Anal. Calcd for $C_{24}H_{46}N_4O_2$: C, 68.20; H, 10.97; N, 13.26. Found: C, 68.89; H, 10.12; N, 12.98.

Synthesis of N1,N8-bis(2,2,6,6-tetramethylpiperidin-4-yl)octanediamide (HB). The synthetic procedures and purification steps are the same as those for **HA**, and the only difference lies in the use of suberoyl chloride (1.04 mL, 5.7 mmol). Yield 1.85 g (72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.3 (s, 1H), 4.2-4.4 (m, 2H), 2.2 (t, 4H), 1.7 (s, 2H), 1.25 (d, 8H), 1.15 (s, 24H), 0.94 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$) δ = 172.5, 47.2, 45.7, 36.7, 33.8, 29.0, 28.4, 25.5 ppm. FTIR (KBr, cm^{-1}): 3252 (N-H), 2853 (aliphatic C-H), 1631 (amide C=O), 1548 (amide N-H bending). Anal. Calcd for $C_{26}H_{50}N_4O_2$: C, 69.29; H, 11.18; N, 12.43. Found: C, 68.98; H, 11.10; N, 12.16.

Synthesis of N1,N10-bis(2,2,6,6-tetramethylpiperidin-4-yl)decanediamide (HC). The synthetic procedures and purification steps are the same as those for **HA**, and the only difference lies in the use of sebacoyl chloride (1.36 mL, 5.7 mmol). Yield 1.94 g (71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ = 5.3 (s, 1H), 4.2-4.4 (m, 2H), 2.2 (t, 4H), 1.7 (s, 2H), 1.25 (d,

8H), 1.15 (s, 24H), 0.94-1.01 (m, 12H) ppm. ^{13}C NMR ($CDCl_3$) δ = 172.3, 47.4, 45.8, 36.9, 33.8, 29.1, 29.0, 28.7, 25.7 ppm. FTIR (KBr, cm^{-1}): 3250 (N-H), 2857 (aliphatic C-H), 1631 (amide C=O), 1548 (amide N-H bending). Anal. Calcd for $C_{28}H_{54}N_4O_2$: C, 70.24; H, 11.37; N, 11.70. Found: C, 70.16; H, 11.30; N, 11.82.

Preparation of Nylon 4 Containing Stabilizers. Nylon 4 was dissolved in 2,2,2-trifluoroethanol by 5 wt%. An appropriate amount of stabilizer was added to the solution which was then stirred for 2 h. The solution was poured into ethanol, washed with methanol and acetone, and was finally dried *in vacuo* at 35 °C overnight.

Results and Discussion

Nylon 4 was prepared via ring-opening polymerization of 2-pyrrolidone at 50 °C using sodium and acetic anhydride, as catalyst and initiator, respectively (Scheme 1). It was difficult to obtain relative molecular weight using GPC due to very narrow choice of solvents, and thus viscosity was measured to determine the viscosity average molecular weight, which was found to be 26100. The chemical structure of nylon 4 was confirmed by NMR and FTIR spectroscopy as indicated in Figure 1. Protons at methylene groups were found at 1.5 to 3.2 ppm and protons of amide (N-*H*) at 7.35 ppm in the NMR spectrum. Strong carbonyl characteristic band can be found at 1630 cm^{-1} along with a characteristic band of N-H at 3297 cm^{-1} in the IR spectrum. Thus it can be concluded that the polyamide was successfully prepared.

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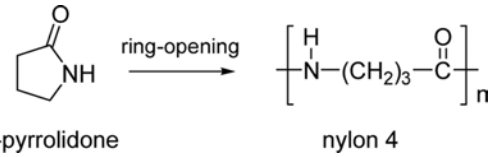
To endow thermal stability to polyamides against thermal degradation, various kinds of thermal stabilizers are commercially available.[8] However, selection of thermal stabilizer strongly depends on the requirements of the application and



Scheme 1. Ring-opening polymerization of nylon 4.

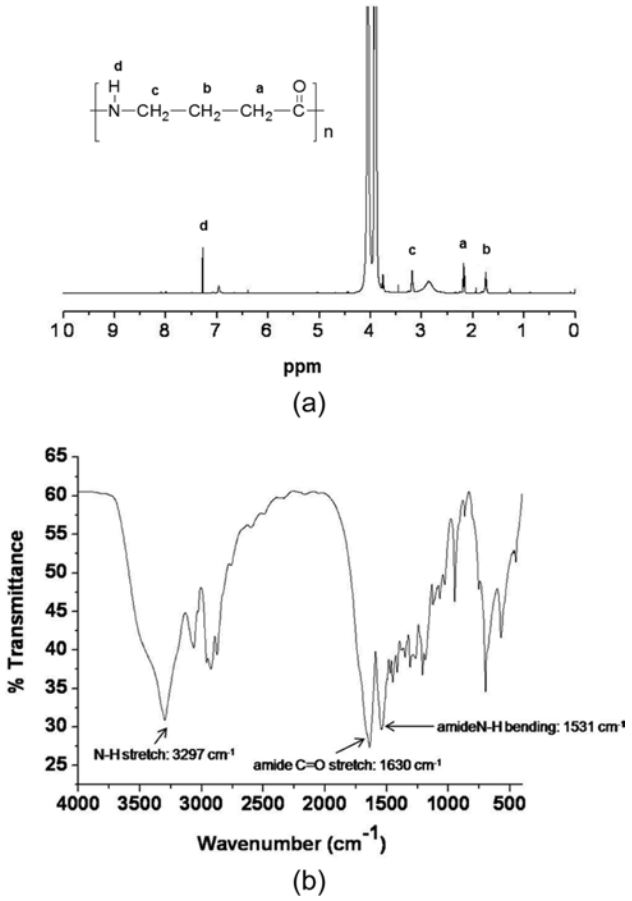
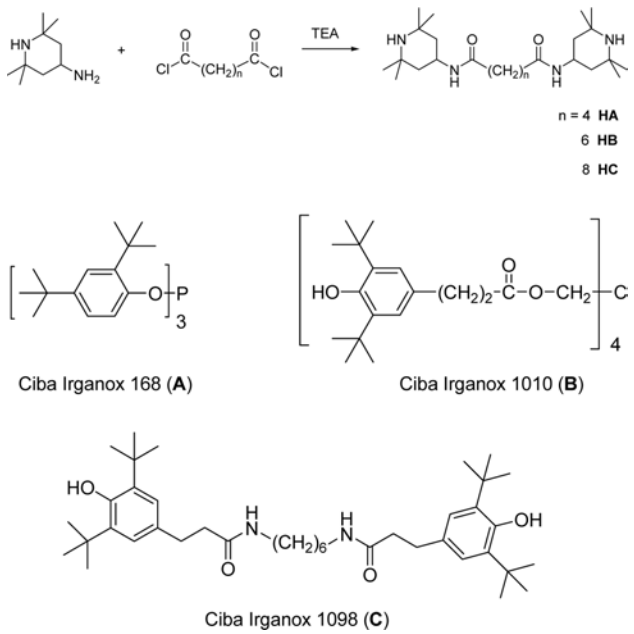


Figure 1. (a) ^{1}H NMR (solvent: 2,2,4-trifluoroethanol); (b) FTIR spectra of nylon 4.

the polymer to be used. To design thermal stabilizers for nylon 4, the sequence rule of intermolecular hydrogen bonding is a primary concern and, thus, three kinds of hindered amine derivatives with different lengths of methylene units were conjectured.[9] The synthesis is simple and straightforward, involving the reaction of hindered amine and corresponding diacid chloride as shown in Scheme 1. To compare the relationship between the chemical structures of stabilizers and thermal property of nylon 4, the effects of conventional thermal stabilizers for nylon 6 on the thermal property of nylon 4 were also investigated. The chemical structures of thermal stabilizers for nylon 6 including Irganox 168, Irganox 1010, and Irganox 1098 are illustrated in Scheme 2.

The chemical structures of three thermal stabilizers were confirmed by elemental analysis, NMR, and FTIR. Similar chemical shifts with different integration of methylene linkages were observed in the ^{1}H NMR spectra of HA, HB, and HC as shown in Figure 2.



Scheme 2. Synthesis of thermal stabilizers for nylon 4 and commercially available thermal stabilizers for nylon 6 or nylon 66.

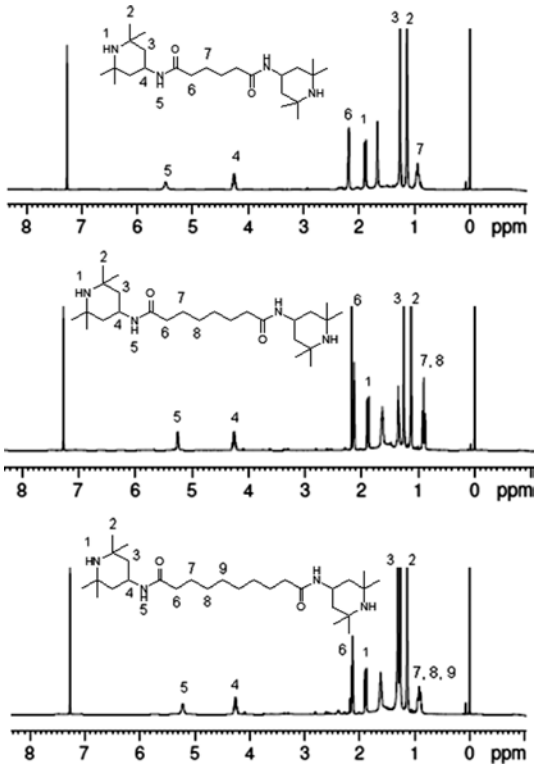


Figure 2. ^{1}H NMR spectra of thermal stabilizers (upper to bottom: HA, HB, and HC; solvent $CDCl_3$).

Protons of hindered amine and amide groups can be observed at 1.7 and 5.3 ppm, respectively. As shown in FTIR spectra in Figure 3, characteristic bands of stretching vibration for N-H group and for C=O group can be found at 3500 to 3400 cm^{-1} and 1631 cm^{-1}, respectively. The characteristic band of methylene linkage was observed around 3000-2900 cm^{-1}. Thus it can be concluded that the thermal stabilizers were successfully synthesized as expected.

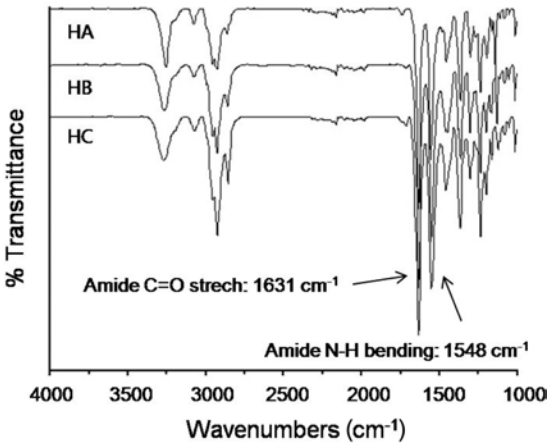


Figure 3. FTIR spectra of thermal stabilizers (KBr pellet).

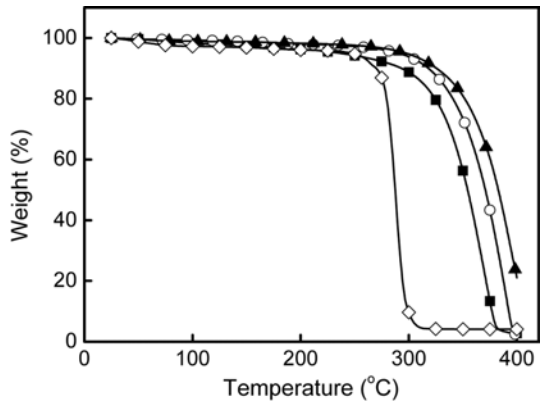


Figure 4. TGA decomposition curves of nylon 4 (◇) and thermal stabilizers of HA (■), HB (○), and HC (▲) under nitrogen atmosphere. Heating rate: 10 °C/min.

Figure 4 shows the TGA thermograms of pure nylon 4 and the newly synthesized thermal stabilizers at a heating rate of 10 °C/min. The onset decomposition temperatures (T_d) of HA, HB, and HC were determined to be 320, 325, and 333 °C, respectively. Considering the fact that the thermal decomposition temperature of nylon 4 is starting from 260 °C, the T_d's of the thermal stabilizers indicates that the synthesized stabilizers can be applied for improving the stability of nylon 4 in terms of higher T_d than that of nylon 4. Decomposition temperatures of nylon 4 and the stabilizers at 5 and 10% are tab-

Table 1. Thermal Degradation Behavior of Nylon 4, HA, HB, and HC (°C)

	Nylon 4	HA	HB	HC
Onset T_d	273	320	325	333
5% T_d[a]	247	251	291	298
10% T_d[b]	270	293	318	326

[a]Decomposition temperature at 5% weight loss. [b]Decomposition temperature at 10% weight loss.

Table 2. Preparation and Their Abbreviations of Nylon 4 Samples with Thermal Stabilizers

Sample names	Composition[a]
N4-HA	Nylon 4 + 0.5 wt% HA
N4-HB	Nylon 4 + 0.5 wt% HB
N4-HC	Nylon 4 + 0.5 wt% HC
N4-A	Nylon 4 + 0.5 wt% Irganox 1010
N4-B	Nylon 4 + 0.5 wt% Irganox 1098
N4-C	Nylon 4 + (0.5 wt% Irganox 1098 + 0.5 wt% Irganox 168)

[a]Weight percent is with respect to the weight of nylon 4.

ulated in Table 1.

Each thermal stabilizer or mixture of commercial stabilizers is incorporated into nylon 4 via a solution blending method in 2,2,2-trifluoroethanol solution to remove the thermal history of each sample. The content of stabilizer in nylon 4 was of 0.5 wt% (with respect to the weight of nylon 4) as shown in Table 2.

According to the dynamic thermogravimetric analysis as shown in Figure 5 and Table 3, both commercial stabilizers and synthesized stabilizers had negligible effects on increase in the decomposition temperature of nylon 4. This implies that the thermal stabilizers do not affect the thermal stability of nylon 4 above 270 °C, regardless of the number of methylene linkage, indicating that the hydrogen bonds between nylon 4 and the thermal stabilizers do not cooperate to protect nylon 4 from decomposition. As illustrated in Table 3, all samples decompose by 5% prior to approaching onset T_d, due to the moisture content in nylon 4.

In contrast, it should be noted that isothermal analysis clearly shows the improvement of thermal properties of nylon 4, as shown in Figure 6. Noticeable difference in thermal degradation of nylon 4 in the presence and absence of the stabilizers are not observed at the temperature of 210 °C, which is

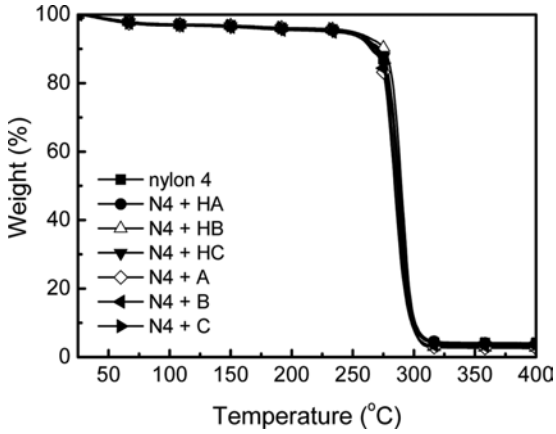


Figure 5. TGA decomposition curves of nylon 4 and nylon 4 containing various stabilizers under nitrogen atmosphere. Heating rate: 10 °C/min.

Table 3. Thermal Decomposition Temperatures (°C) of Nylon 4 with Thermal Stabilizers

	Nylon 4	N4-HA	N4-HB	N4-HC	N4-A	N4-B	N4-C
Onset T_d	273	274	276	274	270	272	273
5% T_d[a]	247	249	248	245	248	233	250
10% T_d[b]	270	271	275	270	265	264	268

[a]Decomposition temperature at 5% weight loss. [b]Decomposition temperature at 10% weight loss.

much lower than the melting temperature of nylon 4 (Figure 6(a)). For the case of isothermal analysis at 250 °C as can be seen in Figure 6(b), all samples show retarded degradation compared to pristine nylon 4 without stabilizers, irrespective of using commercial or synthesized stabilizers.

It should be emphasized that the decomposition of nylon 4 at 270 °C is significantly retarded with the use of stabilizer HA as shown in Figure 6(c). Thus, it can be concluded that the decomposition rate at 270 °C was noticeably improved in the presence of HA (methylene units of 4) with higher char residue content of nylon 4. Compared to other newly synthesized stabilizers with different lengths of methylene units (6 and 8), the sequence rule of hydrogen bonding between nylon 4 and the synthesized stabilizers plays a role in stabilizing effect of nylon 4. Because the new stabilizers have amide bond in their structures, intermolecular hydrogen bonding will occur between nylon 4 and the stabilizer. This time, compact interaction between them plays a key role in stabilization of nylon 4. It is likely that the more compact interaction between nylon 4 and HA facilitates the capture of degradation-triggering species.[10]

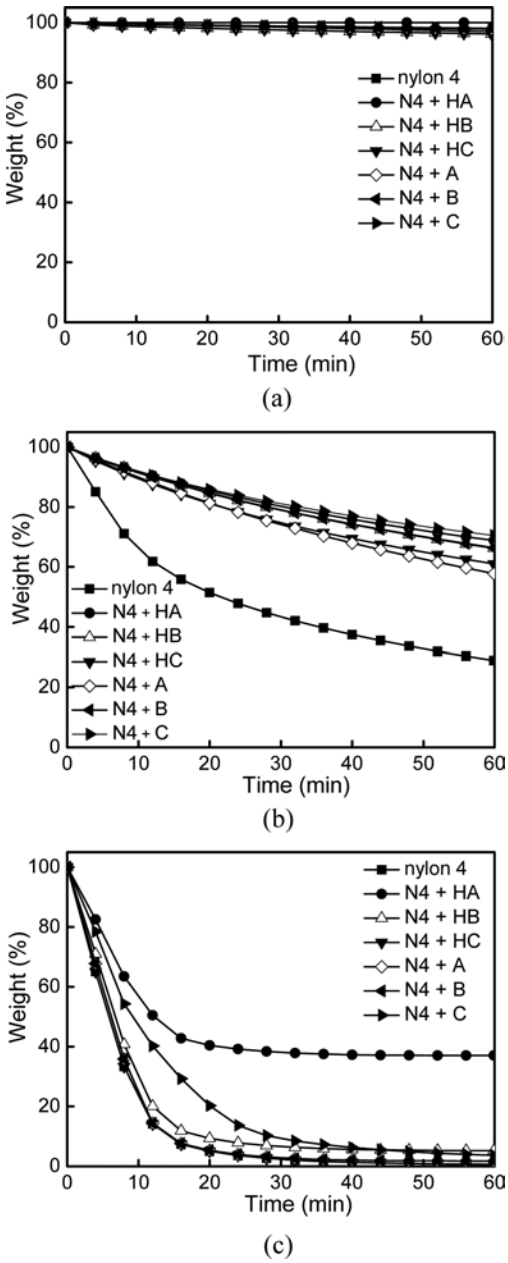


Figure 6. Isothermal TGA thermal decomposition curves of nylon 4 in the presence and in the absence of stabilizers at (a) 210 ºC; (b) 250 ºC; (c) 270 ºC.

Conclusions

We investigated the thermal stability of nylon 4 via the addition of newly synthesized hindered amine stabilizers. To attain this goal, nylon 4 was prepared via ring-opening polymerization of 2-pyrrolidone. Three kinds of thermal stabilizers were synthesized to retard the degradation of nylon 4 which is known to be considerably vulnerable near its melting temperature. Among them, stabilizer with four methylene units which are incorporated into nylon 4 showed significant retardation of the thermal degradation of nylon 4 at 270 ºC according to the isothermal TG analysis.

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