Nonisothermal Decomposition Kinetics of Nylon 1010/POSS Composites

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ABSTRACT: The thermal stability of nylon 1010/polyhedral oligomeric silsesquioxane (POSS) composites prepared by melt blending was investigated with thermogravimetric analysis. The octavinyl POSS (vPOSS) and epoxycyclohexyl POSS (ePOSS) were used, and it was found that nylon/vPOSS composites have higher integral procedure decomposition temperature and char yield at 800°C than nylon/ePOSS composites. The Doyle–Ozawa (model-free) and Friedman (model-fitting) methods were used to characterize the nonisothermal decomposition kinetics of nylon 1010 and its composites. The activation energy (E_a), reaction order (n), and the natural logarithm of frequency factor of nylon 1010 were 267 kJ/mol, 1.0, and 47 min^{-1}, respectively, in nitrogen. After the addition of POSS, the E_a of nylon 1010 considerably increased, whereas n had less change. The E_a steadily increased with increasing conversion and with increasing heating rate. The lifetime of nylon 1010 and its composites decreased with increasing temperature. At a given temperature, POSS significantly prolonged the lifetime of nylon 1010. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 17–23, 2009

Key words: nylon; kinetics; POSS; nonisothermal decomposition

INTRODUCTION

Thermal stability and decomposition kinetic parameters are important information for polymer materials,[1] providing an understanding on the applicability and thermal decomposition process of the polymers at high temperature. A number of researches were focused on the thermal stability of thermoplastic resins,[2–5] thermotropic liquid crystalline polymer, and also energetic materials. The decomposition kinetic parameters of polymers depend on the components,[6,7] environmental conditions,[8] calculating methods, etc.

Recently, polymer/polyhedral oligomeric silsesquioxane (POSS) composites have drawn great attention.[9–11] POSS is a kind of structurally well-defined compound composed of a silicone-oxygen single bond with the general formula of $(RSiO_{1.5})$ (Fig. 1). POSS was incorporated into polymers by copolymerization,[12] grafting,[13] and melt blending.[14] Polymer/POSS composites have higher heat distortion temperature and better oxygen aging resistance and mechanical properties in comparison with virgin polymers. The thermal stability and flame retardancy are attractive topics for polymer/POSS composites. POSS was found to significantly improve the thermal stability of silicone resin.[15,16] The incorporation of metal-functionalized POSS into polypropylene could improve the thermal stability and considerably reduce the heat release rate of polypropylene.[17,18] However, to our knowledge, less attention has been paid to the thermal decomposition kinetics of polymer/POSS composites.

Nylon 1010, a condensation polymer of decanedioic acid and decamethylenediamine, is a prominent member of the nylon class of semicrystalline polymers. It is a widely used commercial engineering plastic because of its better toughness at low temperature and lower water absorption ratio in comparison with nylon 6. In this article, POSS with vinyl or epoxy groups were employed to prepare the nylon/POSS composites through melt blending. The epoxy groups can react with both of the carboxylic[19] and amine groups of nylon, whereas the vinyl groups cannot react. The effect of POSS with different functional groups on the thermal stability of nylon 1010 would be investigated. The nonisothermal decomposition kinetic parameters would be calculated by employing different methods, from which the life time (t_f) of nylon in different temperatures could also be predicted.
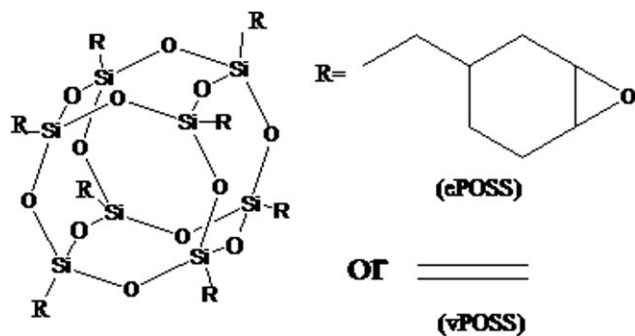
Figure 1 Schematic diagram of POSS. R is epoxycyclohexyl or vinyl group in this work.

EXPERIMENTAL

Materials

Nylon 1010 was produced by Shanghai Salient Chemical (Shanghai, China). The octavinyl POSS (vPOSS, OL1160) and epoxycyclohexyl POSS (ePOSS, EP0408) were obtained from Hybrid Plastic, Hattisburg, USA.

Sample preparation

Nylon 1010 pellets were vacuum-dried at 80°C for more than 12 h. A solution of ePOSS in chloroform was mixed with nylon 1010 pellets, and the mixture was dried to remove chloroform. The nylon/ePOSS mixture or nylon/vPOSS (2 and 5 wt % to the nylon 1010 weight) were mixed in the mixing chamber of a HAAKE Rheometer RC9000 at 210°C and a rotor speed of 60 rpm for 8 min. The composites obtained were compression-molded at 210°C for 20 min, and then cold-pressed for 10 min to get samples for testing.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out in a Perkin-Elmer TGA7 (USA). A sample of 3–5 mg was loaded into a platinum crucible, which was heated from ambient to 800°C under a nitrogen flow of 20 mL/min at a heating rate of 5, 10, 20, or 40°C/min.

Determination of thermal stability

The initial decomposition temperature (IDT) was determined by the temperature of 5% weight loss of the sample from a thermogravimetric (TG) thermogram.[20] The temperature at maximum rate of weight loss (T_{max}) was taken from the peak value of a differential thermogravimetric (DTG) thermogram. The integral procedure decomposition temperature (IPDT), which is usually used to evaluate the ther-

mal stability of materials, was calculated from the following equation[20]:

$$\text{IPDT } (^{\circ}C) = A^* K^* (T_f - T_i) + T_i \tag{1}$$

where A^* is the area ratio of total experimental curve defined by the total TGA thermogram, K^* is the coefficient of A^*, T_i is the initial experimental temperature, and T_f is the final experimental temperature. A representation of S_1, S_2, and S_3 for calculating A^* [$A^* = (S_1 + S_2)/(S_1 + S_2 + S_3)$] and K^* [$K^* = (S_1 + S_2)/S_1$] is shown in Figure 2.

### Determination of kinetic parameters

Friedman,[21] Horowitz–Metzger,[22] Coats–Redfern,[23] Kissinger,[24] and Doyle–Ozawa[25–27] methods can be used for calculating nonisothermal decomposition kinetic parameters. As model-fitting methods,[28] the first three methods are used to calculate E_a and A at a single given heating rate[4,8,29] without considering the effects of testing temperature or conversion on the decomposition kinetics. As model-free methods,[28] the last two methods can give E_a as a function of temperature or conversion by using several different heating rates without any assumption on the decomposition model, and thus reveal thermal decomposition mechanisms by determining the dependency of E_a on conversion.[25,30] The kinetic parameters depend on the selected methods as well as testing environment. In this article, the Friedman and Doyle–Ozawa methods were used to evaluate E_a, reaction order (n), and frequency factor (A).

Doyle–Ozawa method

The Doyle–Ozawa method is described by the following equation:

$$\ln \beta = \ln\left(\frac{A E_a}{R F(\alpha)}\right) - 5.331 - 1.052 \frac{E_a}{RT} \tag{2}$$
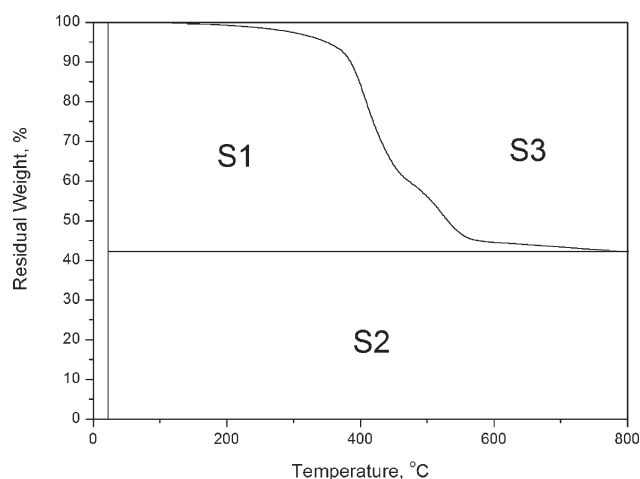
Figure 2 Schematic representation of S_1, S_2, and S_3 for A^* and K^*.

where α is the conversion, β is the heating rate, R is the universal gas constant [8.3136 J/(mol K)], and T is the absolute temperature (K). For a specific α, $F(\alpha)$ is a constant and thus $\ln\beta$ is linearly proportional to $1/T$. E_a is calculated from the slope of the fitted straight line of $\ln\beta$ versus $1/T$.

Friedman method

The Friedman method is described by the following equation:

$$\ln(A) = \ln\left(\frac{d\alpha}{dt}\right) - n\ln(1-\alpha) + \frac{E_a}{RT} \qquad (3)$$

Since

$$\frac{d\alpha}{dt} = \beta\frac{d\alpha}{dT} \qquad (4)$$

Hence

$$\ln(A) = \ln\left(\beta\frac{d\alpha}{dT}\right) - n\ln(1-\alpha) + \frac{E_a}{RT} \qquad (5)$$

By plotting $\ln(d\alpha/dt)$ or $\ln(1-\alpha)$ against $1/T$, a straight line could be obtained with a slope of $-E/R$ or E/nR, respectively. Thus, n can be obtained by the ratio of the two calculated slopes. The $\ln A$ can be calculated from the intercept of the fitted line between $[\ln(d\alpha/dt) - n\ln(1-\alpha)]$ and $1/T$.

RESULTS AND DISCUSSION

Thermal stability

POSS shows a competition between evaporation/sublimation and decomposition when heated in nitrogen.[18] The vPOSS has a T_{max} of 331°C and a residual amounting to 10% [Fig. 3(a)], which is much lower than the vPOSS inorganic fraction amount (66%) owing to its sublimation. The ePOSS has a better thermal stability than vPOSS as regards both T_{max} and the residual weight. The residual weight of ePOSS (46%) is much higher than the ePOSS inorganic fraction amount (29%), which can be attributed to the entrapment of carbon in the structure. The nylon 1010 has a T_{max} of 471°C and exhibited a complete weight loss at 800°C. The thermal stability of nylon/vPOSS composites should be worse than that of nylon 1010 as regards T_{max}, provided that there are no chemical or physical interactions between vPOSS and nylon 1010. Actually, the nylon/vPOSS (ePOSS) composites have better thermal stability than nylon 1010 [Fig. 3(b,c)]. In case of nylon/vPOSS composites, the improvement of thermal stability is mainly attributed to the following reasons. First, the sublimation of vPOSS can be restricted or retarded due to the POSS entrapment in the nylon 1010 matrix. Similar phenomenon was reported in polypropylene/octamethyl-POSS composites.[31] Second, the
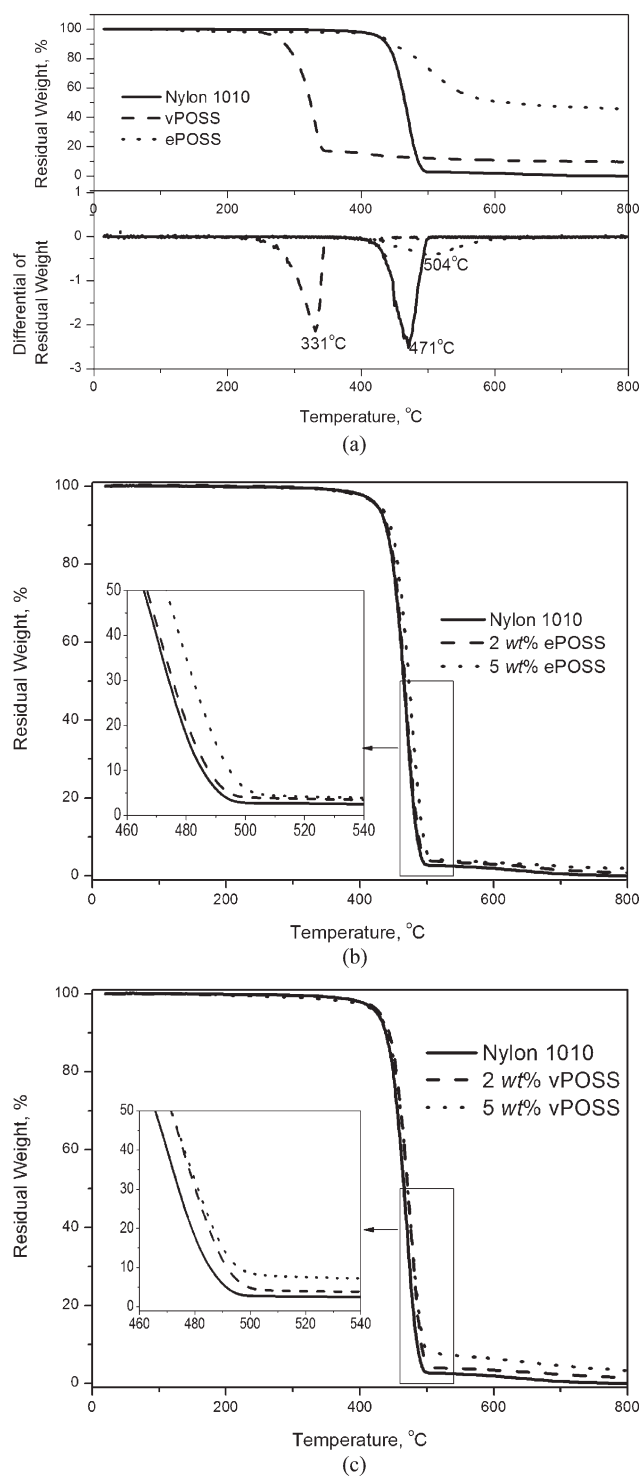
Figure 3 Thermograms of POSS and nylon/POSS composites with a heating rate of 20°C /min: (a) nylon and POSS; (b) nylon and nylon/ePOSS composites; and (c) nylon and nylon/vPOSS composites.

left vPOSS can form a ceramic-like layer at high temperature. Such layer can act as a physical thermal shield to limit the gas diffusion at the interfaces[31,32] and thus to retard the decomposition of nylon 1010. In case of nylon/ePOSS composites, besides the

TABLE I
The Thermal Stability Parameters of Nylon 1010 and Nylon/POSS Composites
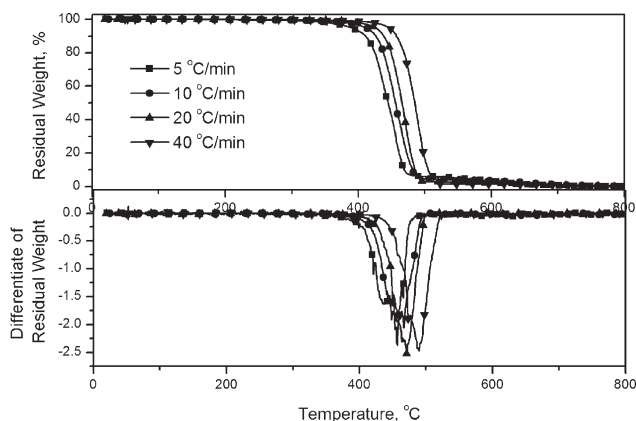
	A^*	K^*	IDT (°C)	IPDT (°C)	Char[a] (%)	Char[b] (%)
Nylon 1010	0.57	1.00	425.7	465.7	0	0
2 wt % ePOSS	0.57	1.01	423.9	475.1	0.82	0.89
5 wt % ePOSS	0.59	1.03	430.0	493.0	1.89	2.18
2 wt % vPOSS	0.58	1.03	432.2	490.3	1.58	0.19
5 wt % vPOSS	0.59	1.06	426.6	510.8	3.41	0.46

[a] The actual char yield.
[b] The calculated char yield.

shielding effect of ceramic-like layer, chain extension of nylon 1010 by reacting ePOSS with carboxylic and/or amine groups may also improve the thermal stability of nylon.

IPDT is used to evaluate the thermal stability of materials. The nylon/POSS composites have higher IPDT but nearly the same IDT compared with nylon 1010 (Table I). With increasing POSS content, the IPDT of nylon 1010 is further increased. The char yield of nylon 1010 at nitrogen is zero for all the organic contents that can be converted into gaseous products. The char yield of vPOSS and ePOSS at 800°C are 9.7% and 45.8%, respectively. Thus, the theoretical char yield of nylon/POSS composites can be calculated according to the component of composites. The actual char yield of nylon/ePOSS composite at 800°C is near to the value calculated. In case of nylon/vPOSS composites, the actual char yield is much higher than the calculated value, which is attributed to the formation of ceramic layer. The ceramic layer can retard the decomposition of nylon due to its shielding effect as mentioned earlier. In addition, the char at 800°C should contain silicon dioxide and some carbonaceous material. The nylon/vPOSS composites have higher char yield than nylon/ePOSS composites at the same POSS content. It is probably because the vPOSS has higher inorganic fraction than ePOSS, and also the sublimation of vPOSS is restricted.

Determination of kinetic parameters

Doyle–Ozawa method

The TG and derivative TG (DTG) curves of nylon 1010 at different heating rates are shown in Figure 4. All the TG curves show one single weight-loss stage because of the primary polyamide chain scission occurring either at C(O)—NH or NH—CH$_2$ bonds.[33] Using TG data, lnβ was plotted as a function of $1/T$ at a specific α (Fig. 5). Good linearity is obtained for all the samples, suggesting that the experimental data can be well described by Doyle–Ozawa method. The E_a was calculated from the slope of the fitted line at different heating rates. The nylon/POSS composites have much higher E_a than nylon 1010 (Table II). The E_a of nylon/vPOSS (100/5) is more than 50% higher than that of nylon 1010. All the E_a values increase with increasing α. A similar phenomenon occurred in the decomposition of poly(ethylene terephthalate).[34] Nonisothermal decomposition usually involves nuclei, nucleation growth, and gas diffusion mechanisms.[34] The increase of E_a with increasing α should be attributed to the change of controlling mechanism with the progress of decomposition, from nuclei to nucleation growth, and the nucleation growth has a higher E_a than the nuclei.[30]

Figure 4 Thermograms of nylon 1010 with heating rates of 5, 10, 20, and 40°C/min.
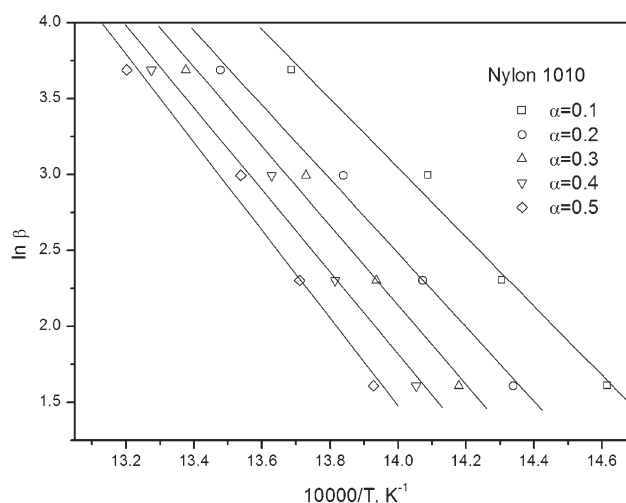
**Figure 5** Plots of lnβ versus $1/T$ according to Doyle–Ozawa method for nylon 1010 at different α.

TABLE II
The Kinetic Parameters of Nylon 1010 and Nylon/POSS Composites Obtained from Nonisothermal Decomposition by Using Doyle–Ozawa Method

	α	E_a/R (×10³)	R_{cc}[a]	E_a(kJ/mol)
Nylon 1010	0.1	22.8	0.994	180
	0.2	24.4	0.996	193
	0.3	26.1	0.993	207
	0.4	27.0	0.991	214
	0.5	28.9	0.990	229
	Average	25.9		204
2 wt % vPOSS	0.1	27.3	0.992	216
	0.2	29.0	0.999	229
	0.3	29.1	0.999	230
	0.4	29.5	0.999	233
	0.5	30.2	0.999	239
	Average	29.0		229
5 wt % vPOSS	0.1	36.1	0.999	286
	0.2	38.9	0.999	308
	0.3	40.1	0.999	317
	0.4	42.0	0.999	332
	0.5	44.5	0.995	352
	Average	40.3		319
2 wt % ePOSS	0.1	26.3	0.999	208
	0.2	31.0	0.991	245
	0.3	32.4	0.981	256
	0.4	33.0	0.983	261
	0.5	34.5	0.995	273
	Average	31.4		249
5 wt % ePOSS	0.1	32.0	0.993	253
	0.2	33.4	0.996	264
	0.3	35.1	0.997	277
	0.4	34.1	0.998	269
	0.5	38.8	0.999	307
	Average	34.7		274

[a] R_{cc} is the correlation coefficient of the linear-fit analysis.

Friedman method

Friedman method is based on the relationship of α and T by employing a single heating rate. The $\alpha \sim T$ and $(d\alpha/dT) \sim T$ curves calculated by the original TG curves are shown in Figure 6. Because the fitted lines of different samples overlapped each other, the experimental data were offset in both X and Y directions to obtain a distinct view (Fig. 7). According to eq. (3), it is the slope of fitted line rather than the absolute values of X and Y that is used to calculate the kinetic parameters. Therefore, the offset values of X and Y are omitted here. The E_a of nylon 1010 decomposition is 267 kJ/mol (Table III), which is slightly higher than that obtained by Doyle–Ozawa method (204 kJ/mol) because of the the different data treatments. The n stays around 1.0 at different heating rates, indicating that the nonisothermal decomposition of nylon 1010 is a first-order reaction. POSS dramatically increases the E_a and ln$A$ of nylon 1010 but has little effect on the n of nylon 1010. Although POSS can dramatically enhance the thermal stability of nylon 1010 by increasing E_a, it does not change the reaction order. The E_a of all the com-
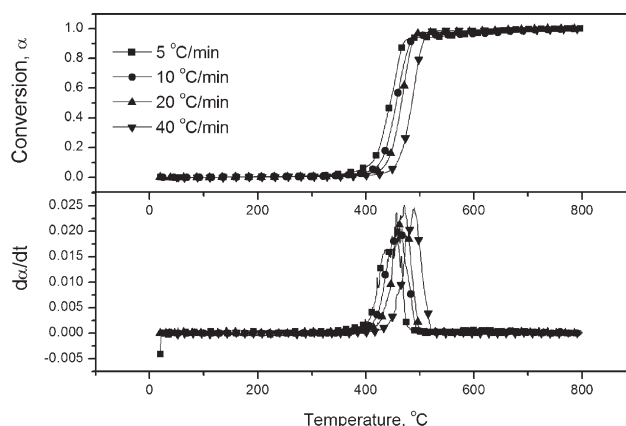

Figure 6 $\alpha \sim T$ curves of nylon 1010 at heating rates of 5, 10, 20, and 40°C/min.

posites increase with increasing heating rates. Such dependency of E_a on the heating rates is in agreement with other researchers' results and is attributed to the different controlling mechanisms in decomposition.[8,29,35] At low heating rates, the diffusion of the degradation products hardly affects the kinetics of the decomposition process and the E_a values are relatively low. With increasing heating rates, the decomposition of the polymer may become faster than the diffusion of the decomposition products through the polymer melt. The decomposition kinetics is under diffusion control and thus the observed kinetic parameters increase with increasing heating rate.[29]

Determination of lifetime (t_f)

A major application of calculating thermal decomposition kinetic parameters is to estimate the t_f of the polymer. It provides a simple and convenient way for quality-control experiments by using an
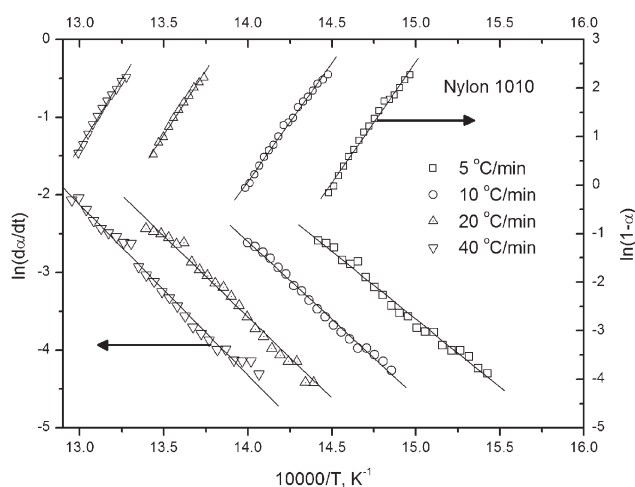
Figure 7 Friedman plots of ln($d\alpha/dt$) or ln(1-α) vs 1/T for the direct calculation of E_a or n value of nylon 1010 in nitrogen at different heating rates (the plots shown here have been offset in both X and Y directions).

	β (K/min)	E_a/R ($\times 10^3$)	R_{cc}	E_a/nR ($\times 10^3$)	R_{cc}	n	E_a (kJ/mol)	$\ln A$ (min^{-1})	R_{cc}
Nylon 1010	5	27.9	0.976	30.2	0.979	0.93	232	42	0.983
	10	32.0	0.995	30.5	0.990	1.05	266	44	0.994
	20	33.4	0.995	33.6	0.990	0.99	278	50	0.998
	40	35.1	0.995	34.3	0.990	1.03	292	51	0.998
	Average	32.1		32.1		1.00	267	47	
2 wt % vPOSS	5	31.9	0.990	30.1	0.999	1.06	265	48	0.993
	10	36.0	0.998	37.6	0.997	0.96	300	48	0.997
	20	35.8	0.996	35.6	0.992	1.01	298	49	0.998
	40	33.4	0.999	32.2	0.991	1.04	278	51	0.999
	Average	34.3		33.9		1.02	285	49	
5 wt % vPOSS	5	35.9	0.994	29.6	0.999	1.21	298	50	0.994
	10	33.3	0.997	24.9	0.998	1.34	277	52	0.999
	20	36.6	0.999	34.0	0.992	1.07	304	53	0.999
	40	38.3	0.998	38.2	0.990	1.00	319	54	0.999
	Average	36.0		31.7		1.16	299	52	
2 wt % ePOSS	5	27.2	0.996	28.6	0.993	0.95	226	42	0.992
	10	31.8	0.994	32.8	0.999	0.97	264	46	0.996
	20	34.1	0.994	31.1	0.981	1.10	283	50	0.996
	40	36.8	0.994	34.2	0.993	1.07	306	52	0.999
	Average	32.5		31.7		1.02	270	47	
5 wt % ePOSS	5	29.7	0.997	29.1	0.996	1.02	247	47	0.999
	10	35.4	0.998	34.8	0.996	1.02	294	49	0.996
	20	38.1	0.992	37.3	0.991	1.02	317	52	0.997
	40	37.9	0.994	36.0	0.985	1.05	315	54	0.994
	Average	35.3		34.3		1.03	293	50	

accelerating aging process.[29] The t_f at the service temperature can be extrapolated from the thermal decomposition kinetics at high temperature. The t_f of polymer is usually defined to be the time when sample suffers a 5% weight loss. The t_f predication is based on the following equation:

$$\frac{d\alpha}{dt} = k(1-\alpha)^n = A \exp\left(-\frac{E_\alpha}{RT}\right)(1-\alpha)^n \qquad (6)$$

where k is the reaction rate constant. By integrating eq. (6), the t_f with a specific α can be interpreted as follows:

$$t_f = [1-(1-\alpha)^{1-n}]\frac{\exp(E_a/RT)}{A(1-n)} \quad \text{when } n \neq 1 \qquad (7)$$

$$\text{or } t_f = \frac{-\ln(1-\alpha)}{A}\exp(E_a/RT) \quad \text{when } n = 1 \qquad (8)$$

The t_f can be obtained when α equals 0.05.

The nonisothermal decomposition of nylon 1010 and its composites is a first-order reaction according to the Friedman method. Therefore, the t_f of nylon 1010 is predicated by using eq. (8). The t_f of nylon 1010 is dramatically prolonged by the addition of POSS especially at low temperatures (Table IV). Such prolonging effect becomes less obvious as the temperature goes up. The t_f is greatly affected by E_a and A. According to eq. (8) either the increase of E_a or the decrease of A can significantly prolong the t_f at a certain temperature. The t_f of the nylon/vPOSS (100/5) composite is longer than that of the nylon/vPOSS (100/2) at 100, 200, and 300°C but the latter has a longer t_f than the former at higher temperatures (350 and 400°C). A similar phenomenon is observed between nylon 1010 and nylon/ePOSS (100/2) composite. From eq. (6), it can be easily concluded that the higher the E_a, the faster is the

TABLE IV
Estimated Lifetime (t_f) of Nylon and Nylon/POSS Composites Based on the Kinetic
Parameters Under Nonisothermal Decomposition in Nitrogen

Temperature (°C)	100	200	300	350	400
Nylon 1010, min	5.76×10^{15}	7.15×10^7	5.10×10^2	5.68	0.12
2 wt % vPOSS, min	1.76×10^{17}	6.42×10^8	2.06×10^3	17.0	0.29
5 wt % vPOSS, min	9.69×10^{17}	1.32×10^9	2.22×10^3	14.3	0.20
2 wt % ePOSS, min	7.91×10^{15}	8.08×10^7	5.07×10^2	5.38	0.11
5 wt % ePOSS, min	8.80×10^{17}	1.82×10^9	4.05×10^3	28.9	0.43

increase of k with increasing temperature. Thus with increasing temperature, the t_f of sample with higher E_a always decreases much faster. The t_f listed in Table IV are merely theoretical values calculated from the kinetic parameters according to eq. (8). The degradation in reality can be affected by many factors such as photodegradation, mechanical, chemical degradations, etc. Therefore, the real t_f of nylon 1010 in its service condition will be definitely shorter than the values listed in Table IV.

CONCLUSIONS

The thermal behavior of nylon 1010 and nylon/POSS composites was investigated. The nonisothermal decomposition of nylon 1010 only included a single weight-loss stage, which is attributed to the primary polyamide chain scission. POSS could increase the IPDT and char yield of nylon 1010. The char yield of nylon/octavinyl POSS composites was much higher than the calculated values because of the shielding effect of a ceramic-like layer formed at high temperatures.

The Doyle–Ozawa and Friedman methods were used to calculate the nonisothermal kinetic parameters. The results according to Doyle–Ozawa method showed that the E_a of nylon 1010 was significantly increased after the addition of POSS, and the E_a gradually increased with increasing conversion. Friedman's method showed that the nonisothermal decomposition of nylon 1010 was a first-order reaction and the addition of POSS increased the E_a of nylon 1010 but had less effect on the reaction order. The E_a gradually increased with increasing heating rate. The lifetime (t_f) of nylon 1010 and its composites was calculated through the kinetic parameters. POSS considerably prolonged the t_f of nylon 1010, especially at low temperatures.

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