

Investigation of Thermal Degradation and Flammability of Polyamide-6 and Polyamide-6 Nanocomposites

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ABSTRACT: In this paper, polyamide-6 and polyamide-6 nanocomposites were prepared by direct melt intercalation technique. The thermal degradation behavior of both polyamide-6 and polyamide-6 clay nanocomposites has been studied. The apparent activation energy of the nanocomposites is almost the same with that of pure polymer under nitrogen, but the apparent activation energy of the nanocomposites is greatly enhanced in air atmosphere. This increasing trend coincides with the thermal analysis and the cone calorimeter results,

which may suggest that the polymer/clay nanocomposites have a higher thermal stability and lower flammability. The kinetic analysis also indicates that the pyrolytic degradation and the thermal oxidative degradation of PA6 and PA6/OMT nanocomposites are two kinds of different reaction models. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2297–2303, 2007

Key words: polyamide; nanocomposites; thermogravimetric analysis; activation energy

INTRODUCTION

Polyamide resins are important engineering resins manufactured in large quantities for fiber, film, and plastic applications. Polyamide 6 (PA6) accounts for a majority of the commercial polyamide production and application. Flame retardancy of polyamide 6 is mostly required in electric industries, with typical applications in electrical connectors, terminal blocks, small electrical housings, clip fasteners, switch components, wire ties, and many other industrial parts.¹

Polymer layered silicate nanocomposites have attracted a great deal of interest over the last few years as a result of the potentially superior properties. Numerous studies have shown that a very low percentage of layered silicates can lead to a significant enhancement of many properties, such as stiffness, strength, flame retardancy, gas barrier properties, ionic conductivity, thermal stability, and tunable biodegradability. Work from the Toyota research laboratories sparked a large interest in PA-6 based silicate nanocomposites. Their papers describe PA-6 nanocomposites made by an *in situ* polymerization

process with superior strength, modulus, heat distortion temperature, and water and gas barrier properties with respect to pure PA-6.²

The thermal degradation of polymers has been at the center of thermal analysis studies for many years. Thermogravimetric analysis (TGA) is a common method to study the kinetics of polymer degradations. Kinetic analysis may effectively assist in probing degradation mechanisms as well as in predicting the thermal stability of polymers. These goals are accomplished only when using proper methods for kinetic evaluations. In this article, we report the preparation of PA6/clay nanocomposites (PA6/OMT) by direct melt intercalation technique by blending PA6 and organophilic clay. Their flammability was studied with the cone calorimeter, while the thermal degradation behavior was examined under different atmospheres.

EXPERIMENTAL

Materials

Polyamide 6 (PA6, 1003NW8) was supplied as pellets by UBE Company (Japan). The original purified sodium montmorillonite (MMT, with a cation exchange capacity of 122 mequiv/100 g) and organophilic montmorillonite (OMT) were kindly provided by Ke Yan Company (Hefei, China). OMT was prepared from MMT by ion exchange reaction using hexadecyltrimethylammonium bromide (C16) in water according to the reported method.³

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Preparation of PA6/clay nanocomposites

Samples of PA6/OMT were prepared by melt-mixing the PA6 with 5 wt % OMT at 245°C using a twin-roll mill (XK-160, made in Jiangsu China) for 10 min to yield hybrids.

Evaluation of dispersibility of the clay in PA6 resin matrix

The dispersibility of the silicate layers in the PA6 was evaluated using the X-ray diffractometer (XRD). The thin films (1 mm) of the nanocomposites were pressed at 245°C for the XRD measurements to evaluate the dispersibility of the silicate layers in the PA6 matrix. X-ray diffraction experiments were performed at room temperature by a Japan Rigaku D/max-rA X-ray diffractometer (30 kV, 10 mA) with Cu ($\lambda = 1.54178 \text{ \AA}$) irradiation at the rate of 2°/min in the range of 1.5°–10°.

Thermogravimetric and kinetic analysis

TGA was carried out using a STA 409C from NETZSCH GmbH (Germany). The samples of PA6 and PA6/OMT nanocomposites, about 10 mg, were investigated at heating rates at 5, 10, 15, and 20°C/min, in the temperature range 20–700°C. We used nitrogen and air as a purge gas at the flow rate of 50 mL/min. The temperature and the weight scales of the TGA instrument were calibrated using high-purity standards (Indium, Nickel, Zinc, Aluminum, and Gold) over a specific range of heating rates with a calibration parameter of their respective melting points.

Thermal kinetic analysis was carried out with the help of the software of Origin and NETZSCH Thermokinetics.

Cone calorimeter

Cone calorimeter experiments were performed at an incident heat of 40 kW/m². Peak heat release rate (HRR), mass loss rate (MLR), ignition time (t_i), and specific heat of combustion data were reproducible to within 10% when measured at 40 kW/m². The cone data reported here were the averages of three replicated experiments.

KINETIC METHODS

Model-free methods

Several measurements have been run on one sample at different heating rates. A model-free approximation of the activation energy can be made. It is used to gain first insights into the reaction process.

Friedman proposed to apply the logarithm of the conversion rate $d\alpha/dt$ as a function of the reciprocal

temperature.⁴ The Friedman lines exhibit a slope that is proportional to the activation energy.

The Kissinger method has been used to determine the activation energy from plots of the logarithm of the heating rate versus the inverse of the temperature at the maximum reaction rate in constant heating rate experiments.⁵

The Flynn–Wall–Ozawa method is one of the integral methods that can determine the activation energy without knowledge of reaction order. It is used to determine the activation energy for given values of conversion. The activation energy for different conversion values can be calculated from $\log\beta$ versus $1/T$ plot.⁶

Model-fitting methods

Different models were evaluated to describe the total mass loss of the experiments at various heating rates. There is a set of ordinary differential equations (ODE) for each model. The simultaneous numerical solution of the ODE system and the estimation of the kinetic parameters by the least squares (LSQ) method were calculated. The kinetic parameters were fitted running the optimization routine and the ODE solver simultaneously, according to the technique of multivariate regression. The task of nonlinear regression is the iterative calculation of the minimum sum of least squares. The multivariate analysis bases on the assumption that the kinetic parameters have to be identical for all experimental conditions in the modeled parameter range. This constraint facilitates the choice of an appropriate model considerably and improves the model validity. Fundamentally, multi-step processes can only be analyzed with nonlinear regression. But nonlinear regression proves to be advantageous for one-step processes as well, because it provides a considerably better quality of fit as compared to multiple linear regressions.⁷

RESULTS AND DISCUSSIONS

Dispersibility of PA6/OMT hybrids

Figure 1 shows the XRD patterns of the MMT, OMT, and PA6/OMT nanocomposites. The peaks correspond to the (001) plane reflections of the clays. The average basal spacing of MMT increases by organic modification from 1.3 to 2.2 nm, when original MMT was modified by C16. These increased spacing suggests that the chain of C16 intercalate into the gallery of MMT and expand it. PA6/OMT has broadened d001 peak at 3.3 nm, 1.1 nm gallery height increases compared to that of OMT, which indicates an intercalated-exfoliated structure.

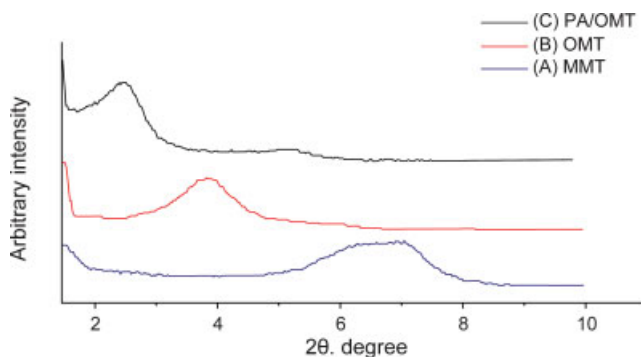


Figure 1 XRD patterns (A) MMT, pristine sodium montmorillonite; (B) OMT, modified clay; (C) PA/OMT nanocomposites. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Flammability

The HRR plots for pure PA6, nanocomposites (PA6/OMT) at 40 kW/m² are shown in Figure 2. When 5 wt % OMT is present, the ignition time decreases from 100 to 85 s. After ignition, the HRR of the nanocomposites increases at same rate as that of pure PA6. At the time of 115–210 s, the heat release rate of the nanocomposites keeps in a flat tendency, and then reaches its peak of 597 KW/m² at the time of 215 s. But the HRR of pure polymer rises regularly to a maximum of 1118 KW/m² at the time of 215 s and then decreases sharply. Reduction of the HRR peak is a typical feature of polymer layered silicate nanocomposites, as reported by Gilman.⁸ The lower flammability of polymer/clay nanocomposites is not due to retention of a large fraction of fuel, but in the form of carbonaceous char, in the condensed phase.

The intercalated PA-6 nanocomposites, prepared via melt blending, does not bond the MMT treatment to the polymer. This may reduce the ignition time. An additional effect may be due to processing. Decomposition products generated during processing may supply volatile fuel early in the Cone experiment and shorten the ignition time.⁹

The presence of OMT in PA may also accelerate the speed of thermal decomposition in the early stage, and so the ignition time has been shortened. The intumescent char is more likely to be formed on the surface the nanocomposites (PA6/OMT) when heated. The char will then shield the inner of material from the external thermal radiation, and make the temperature of the surface rise highly, resulting in the earlier thermal decomposition on the surface.

The formation of a protective barrier in the case of PA6 clay nanocomposites in fire conditions may also correspond to the reduction in the peak heat release rate, by the formation of protective floccules on the sample surface, which shield the PA6 from the external thermal radiation and heat feed back from the flame, thus acting as a thermal insulation layer.¹⁰

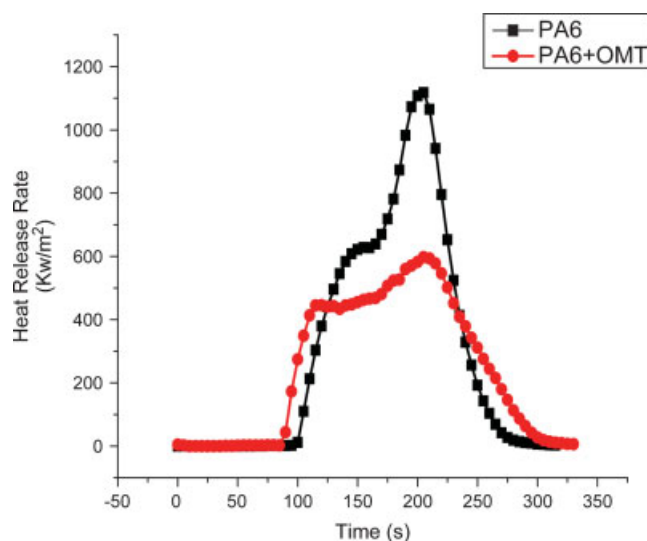


Figure 2 HRR data for a pure PA6 and PA6/OMT. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Pyrolytic degradation of PA6 and PA6/OMT nanocomposites

The TGA for PA6 and PA6/OMT nanocomposites was made in nitrogen at all heating rates. One of the comparisons of the test results is shown in Figure 3. Under pyrolytic conditions, PA6 and PA6/OMT nanocomposites degrade in one step. The thermal stability of the nanocomposites is not enhanced relative to that of virgin PA6. The onset temperature of the degradation for the nanocomposites has been reduced from 363.5°C for the virgin polymer to 350.7°C, and the melting point of the PA6/OMT nanocomposites has been reduced from 213.9°C for the virgin polymer to 205.1°C. On the other hand, the yield of charred residue at 520°C for the PA6/

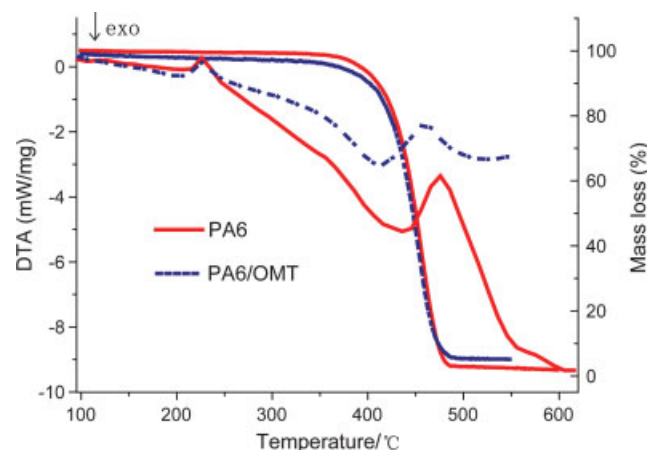


Figure 3 TG/DTA analysis results of (1) PA6 and (2) PA6/OMT under N₂ at 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

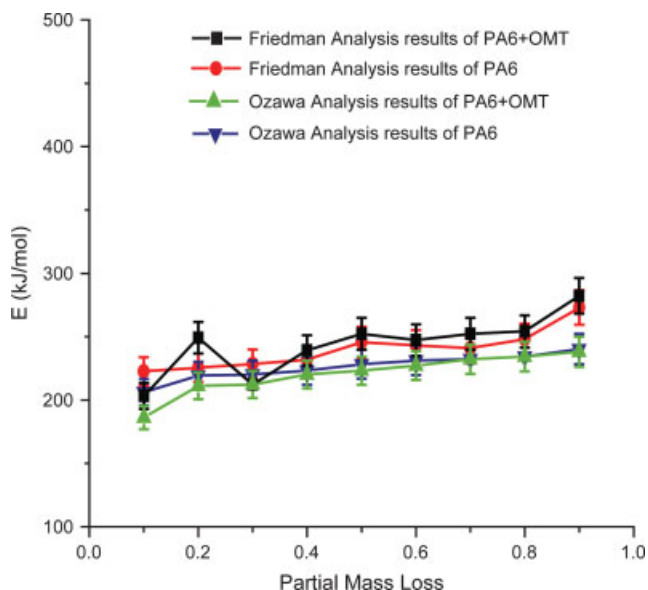


Figure 4 Comparison of the Friedman and Flynn–Wall–Ozawa analysis to PA6 and PA6/OMT under N_2 . [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

OMT nanocomposites has been enhanced from 2.73% for the virgin polymer to 7.25%.

The models that describe the total mass loss of the samples were calculated using the thermogravimetric results. Model-free analysis, including the Friedman analysis, Kissinger analysis, and Flynn–Wall–Ozawa analysis, for the thermal decomposition reactions can yield the apparent activation energy with the extent of reaction. Figure 4 is the Friedman analysis results and Ozawa analysis results of PA6 and PA6/OMT under nitrogen, while Table I is the Kissinger analysis results of these polymers.

It is clearly observed that the activation energy values (E) computed using all these model-free methods agree on the similar change trend that the activation energies of the thermal degradation for the nanocomposites are almost the same with those of the pure polymer. And the plot with constant activation energy is seriously indicated by the presence of a single-step process. To check whether the single step model with n th-order kinetics (F_n), $A \rightarrow B$ of F_n type, is sufficiently reliable for technical applications, best fits were evaluated for the two data sets with multiple linear regression. The applicability of F_n models is demonstrated in Figure 5 and 6, which

TABLE I
Activation Energies of PA6 and PA6/OMT under N_2
Obtained by the Kissinger Method

Sample	Activation energy, E (kJ/mol)	Correlation coefficient
PA6	217	0.9986
PA6/OMT	216	0.9971

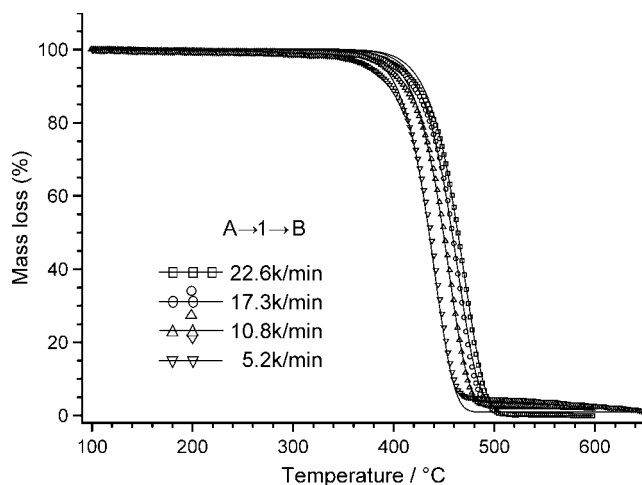


Figure 5 Global model for the thermal decomposition of PA6 under N_2 .

confirms that the data sets can be described fully by a single n th-order reaction models. The results for kinetic parameters are given in Table II.

Comparing values for the activation energies for the pyrolytic degradation of the PA6 and PA6/OMT nanocomposites, via both the model free and model fitting method, we find that there is a similar tendency for invariability of the apparent activation energy of the nanocomposites and the virgin polymer. This stable tendency coincides with the thermal analysis result. But from the result of cone calorimeter experiments, the flame retardancy of PA6/OMT do increase, which may not result in the thermal stability. For further analysis, we will conduct the research of thermo-oxidative degradation of the material.

Thermo-oxidative reaction of PA6 and PA6/OMT nanocomposites

The TGA) for PA6 and PA6/OMT nanocomposites was made in air at all heating rates. One of the

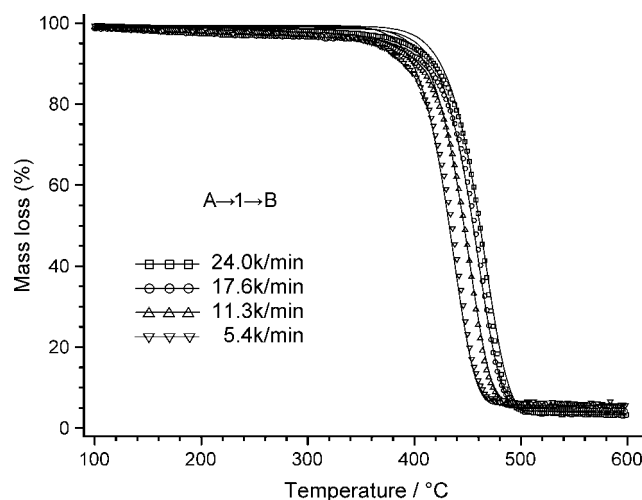


Figure 6 Global model for the thermal decomposition of PA6/OMT under N_2 .

TABLE II
Kinetic Data for the Decomposition of PA6 and PA6/OMT under N₂ using the Multiple Linear Regression

Parameter	PA6	PA6/OMT
logA	13.5	13.1
E (kJ/mol)	216.7	210
n	1.0	1.0
Correlation coefficient	0.9995	0.9986

logA, logarithm of the pre-exponential of reaction step; E (kJ/mol), apparent activation energy; n, reaction order.

results is shown in Figure 7. Under thermo-oxidative conditions, PA6 and PA6/OMT nanocomposites degrade in two steps. The onset temperature of the degradation for the nanocomposites has been increased from 347.6°C for the virgin polymer to 372.0°C, and the yield of charred residue at 630°C for the PA6/OMT nanocomposites has been enhanced from 0.83% for the virgin polymer to 6.27%. Under air atmosphere, the flame retardancy of PA6/OMT nanocomposites is enhanced as the result of the higher thermal stability and higher charred residue of nanocomposites. From the thermal analysis, we may assume that the thermo-oxidative reaction of PA6 and PA6/OMT nanocomposites is a two-step reaction, which will be proved later by the thermal kinetics.

The apparent activation energy with the extent of reaction is calculated with the Friedman analysis. Figure 8 and 9 are the Friedman analysis results of PA6 and its nanocomposites under air.

The Friedman plot with multiple peaks or inconstant activation energy may be indicated of the pres-

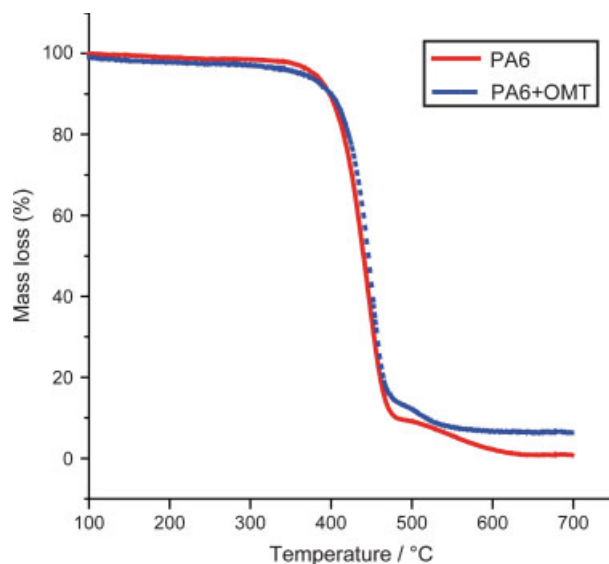


Figure 7 TGA results of PA6 and PA6/OMT under air at 10°C/min. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

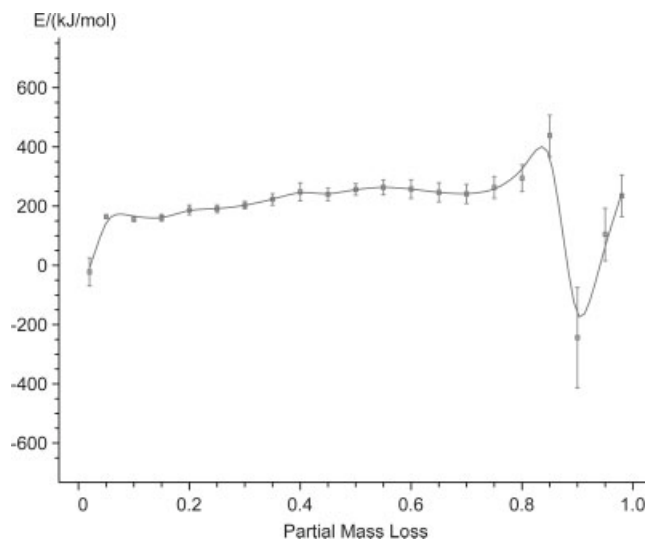


Figure 8 Plot of activation energy versus conversion rate of PA6 under air.

ence of a multiple-step process. The reaction model of the thermal oxidation decomposition reactions of the PA6 and its nanocomposites under air can be developed by the model-fitting method. The first reaction step F_n , the n th-order reaction model, and the second reaction step (R3), three-dimensional phase boundary reaction, were analyzed with multivariate nonlinear regression (MULTIVAR-NLR). The reaction type could best be modeled via two successive reactions $A \rightarrow B \rightarrow C$ of F_n type and R3 type. The results for the best fit of the samples are shown in Figures 10 and 11. The kinetic parameters of the thermal oxidation decomposition reactions of PA6 and its nanocomposites are presented in Table III.

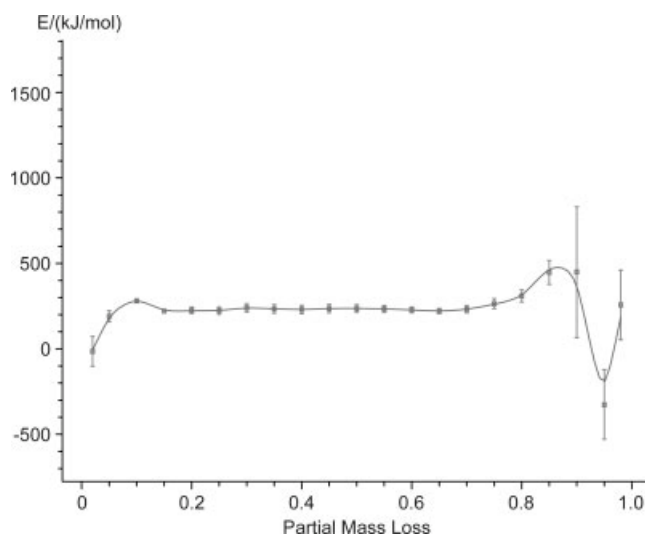


Figure 9 Plot of activation energy versus conversion rate of PA6/OMT under air.

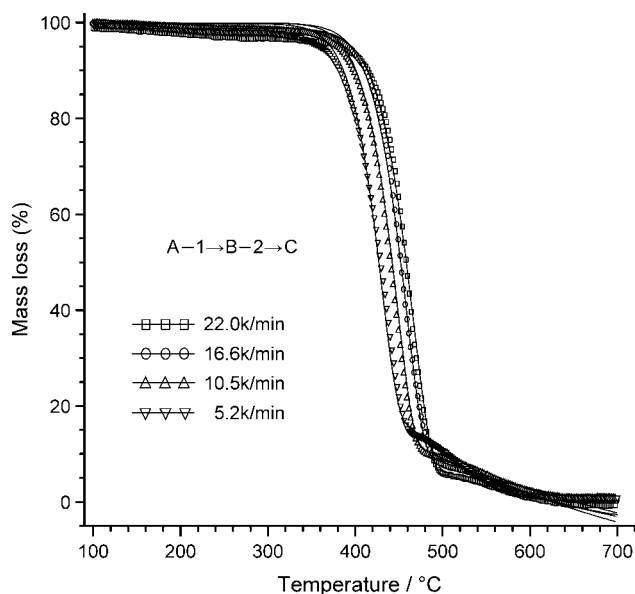


Figure 10 Global model for the thermal oxidative decomposition of PA6 under air.

Comparing values for the activation energies for the thermo-oxidative reaction of PA6 and PA6/OMT nanocomposites, via both the Friedman and multivariate nonlinear regression method, we find that there is an obvious tendency for the increase of the apparent activation energy of the nanocomposites. Oxygen plays a major role in the stabilization process of PA6/OMT, by oxidation of the clay surface. Clay particles tend to aggregate and stack against each other after the degradation of the organic treat-

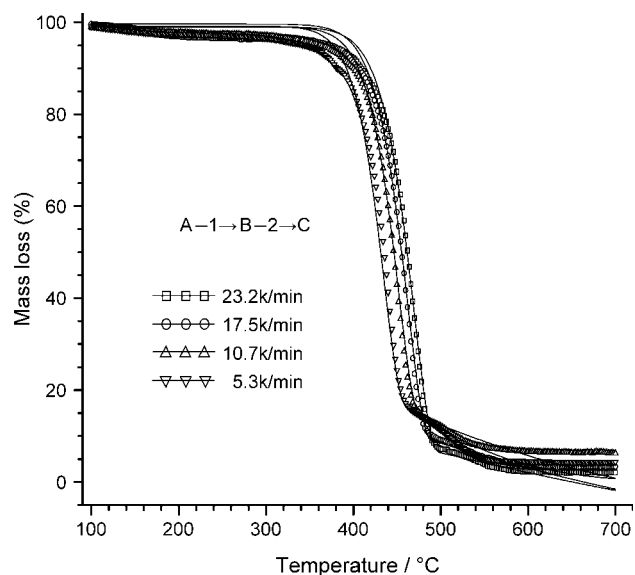


Figure 11 Global model for the thermal oxidative decomposition of PA6/OMT under air.

TABLE III
Kinetics Data of PA6 and PA6/OMT Obtained by the Multivariate Nonlinear Regression

Parameter	PA6	PA6/OMT
$\log A$	10.3	11.2
E_1 (kJ/mol)	171	184
n	0.74	0.75
$\log A$	-3.5	-2.4
E_2 (kJ/mol)	0.04	15
Foll. React	0.74	0.84
Correlation coefficient	0.9995	0.9986

$\log A$, logarithm of the pre-exponential of reaction step; E (kJ/mol), apparent activation energy; n , reaction order; Foll. react., successive reaction faction.

ment on the clay surface making them more hydrophilic and less compatible with the resin.¹¹

DISCUSSION

Under an inert atmosphere, there is a similar tendency for invariability of the apparent activation energy of the nanocomposites and the virgin polymer. But increasing tendency of activation energy of nanocomposites in air atmosphere coincides with the thermal analysis results, which indicate that polymer/clay nanocomposites have a higher thermal stability and lower flammability than the pure polymer. Oxygen plays an important role in the stabilization process of PA6/OMT by oxidation of the clay surface.

The two results of the thermo-oxidative reaction and pyrolytic degradation should both be considered when comparing the thermal kinetics results with the result of cone calorimeter experiments. Since the cone calorimeter is a well ventilated fire, which means that the oxygen availability is nearly stoichiometric. However, the ventilation of the fire does not mean that the decomposition of the materials in the pyrolysis zone is thermo-oxidative. If the material burns with a stable flame above the whole surface, a rather anaerobic pyrolysis takes place in the condensed phase with all the oxidation occurring in the gas phase. Thus, the mass loss, the pyrolysis products, the fire residues, etc. of a fire and also a cone calorimeter experiment corresponds to a decomposition of the material under an inert atmosphere and air.

CONCLUSIONS

From the investigation of the activation energies for the pyrolytic degradation and the thermo-oxidative reaction of PA6 and PA6/OMT nanocomposites, via both model-free and model-fitting method, we find that there is no tendency for the increase of the apparent activation energy of the nanocomposites under nitrogen, but the apparent activation energy

of the nanocomposites is greatly enhanced in air atmosphere. This increasing trend coincides with the thermal analysis and cone calorimeter result, although this may suggest that the polymer/clay nanocomposites have a higher thermal stability and lower flammability. But the activation energy may not be the only reason for the thermal analysis and cone calorimeter result. The kinetic analysis also indicates that the pyrolytic degradation and the thermal oxidative degradation of PA6 and PA6/OMT nanocomposites are two kinds of different reaction model. The pyrolytic degradation reaction of the polymer is a one-step reaction model of n th-order, whereas the thermal oxidative degradation reaction of the polymer is a two-step following reaction model: $A \rightarrow B \rightarrow C$ of the n th-order reaction model and the three-dimensional phase boundary reaction.

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