Enhancement of imidization of poly(amic acid) through forming poly(amic acid)/organoclay nanocomposites

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Abstract

The imidization kinetics of nanocomposites of poly(amic acid) and organoclay were analyzed with in situ Fourier Transform Infrared spectra at several temperatures. The poly(amic acid) studied consisted of pyromellitic dianhydride and 4,4′-oxydianiline. It was found that by dispersing a small amount of organoclay in nanometer scale in the poly(amic acid), both the imidization temperature and the imidization time of the poly(amic acid) can be reduced dramatically. In specific, when two parts of exfoliated silicate layers of organoclay was dispersed in the poly(amic acid), the imidization temperature was lowered by 50°C (250°C versus 300°C) for achieving a complete imidization. Additionally, the imidization time of the poly(amic acid) at 250°C can be reduced to 15 min when the amount of organoclay increased to seven parts.Using a first-order reaction to model the imidization kinetics of poly(amic acid)/organoclay, a 20% drop in the activation energy for imidization of PMDA-ODA/organoclay (7 phr) was obtained as compared to that for imidization of neat PMDA-ODA. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Imidization; Organoclay; Activation energy

1. Introduction

Aromatic polyimides are one of the most frequently used polymers in microelectronics. Polyimides are employed in high-temperature insulators and dielectrics owing to their high electrical and temperature properties [1,2]. A well-developed synthetic method of polyimides is the two-step method. This method consisted of the synthesis of poly(amic acid) from the reaction of diamines and dianhydrides as the first step and the latter step being subsequent thermal imidization of poly(amic acids). The conversion of poly(amic acid) to polyimide is most commonly accomplished by thermal treatment of the poly(amic acid) in the solid state. A high imidization temperature, e.g., 300°C–400°C, is usually used to provide the adequate chain mobility required for a high degree of imidization. If a relatively mild reaction temperature could be employed, several side reactions might be avoided for poly(amic acid).

Polyimide-clay nanocomposites were synthesized by Toyota's group [3,4] and Lan et al. [5] from poly(amic acid) and montmorillonite. These polyimide-clay contained only a few percentages of dispersed montmorillonite and exhibited good gas barrier and low thermal expansion properties as compared to that of the neat polyimide. Moreover, montmorillonite is composed of stacked silicate sheets and has previously been used as a catalyst [6,7]. Other than the above-mentioned enhanced properties of polyimide-clay, we wonder if montmorillonite can be used as a catalyst for converting poly(amic acid) to polyimide. In other words, we want to investigate whether the imidization condition (temperature or time) of poly(amic acid) can be reduced in the presence of montmorillonite dispersed in the nanometer scale in the poly(amic acid). As a first-order kinetic equation was almost exclusively used to treat imidization kinetics [8–13] data, this study will give a comparison of kinetic parameters in PMDA-ODA and PMDA-ODA/organoclay based on a first order kinetic equation.

Pure montmorillonite is hydrophilic. A modification of montmorillonite with organics is needed to become hydrophobic for being compatible with polymer molecules. We termed the organics modified montmorillonite as organoclay.

2. Experimental

Source clay Swy-1 (Wyoming Na$^+$-montmorillonite) was obtained from the Clay Minerals Depository at the University of Missouri, Columbus, MO, USA.

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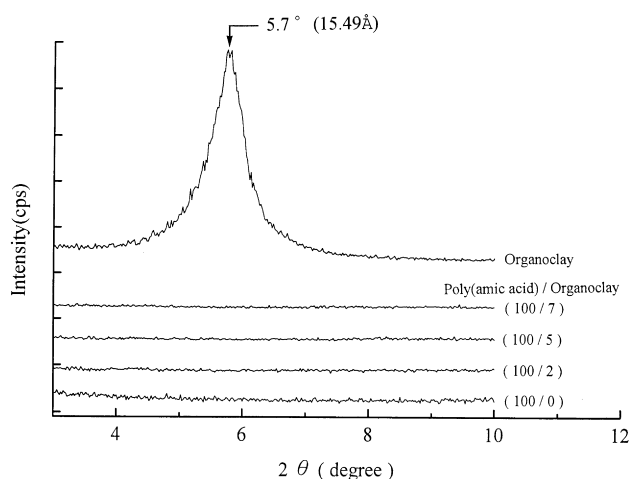*E-mail address:* khwei@cc.nctu.edu.tw (H.-L. Tyan).

Fig. 1. The X-ray diffraction curves of organoclay and poly(amic acid)/ organoclay nanocomposites.

P-phenylenediamine was obtained from ICI. By screening Swy-1 Na$^+$-montmorillonite with a sieve of 325-mesh to remove impurities, one obtained a clay having a cationic exchange capacity of 76.4 meq/100 g. Ten grams of the screened montmorillonite was gradually added to a previously prepared solution of *P*-phenylenediamine (1.08 g dissolved in 1000 ml of 0.01 N HCl) solution and was vigorously stirred for 3 h at 60°C. After the treatment, the montmorillonite suspension was repeatedly washed with de-ionized water. The filtrate was titrated with 0.1 N AgNO$_3$ until there was no AgCl precipitates to ensure a complete removal of chloride ions. Then, the filter cake was placed in a vacuum oven at 80°C for 12 h drying. The dried cake was ground and screened with a 325-mesh sieve. The powder obtained was termed organoclay.

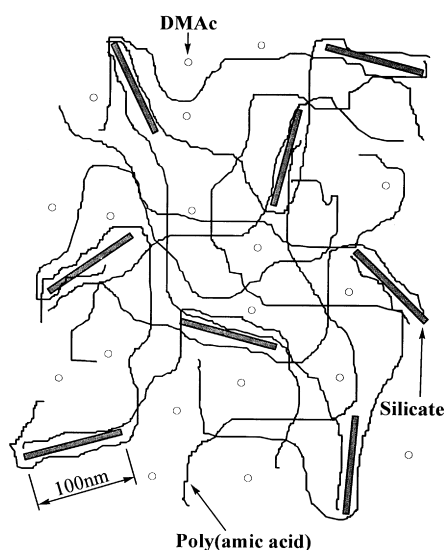Poly(amic acid) (PAA) was synthesized by putting

Fig. 2. The dispersion of the aromatic diamine modified silicate layers in poly(amic acid) and DMAc.

0.015 mol of 4,4′-oxydianiline (ODA) into a three-neck flask containing 32.92g N, N-dimethylacetamide (DMAc) under nitrogen purge at 25°C. After ODA was completely dissolved in DMAc, 0.015 mol of pyromellitic dianhydride (PMDA), which was divided into three batches, was added to the flask batch-by-batch with a time interval of 30 min between batches. After all PMDA was dissolved in DMAc, the mixtures in the flask were stirred for one hour, and a viscous poly(amic acid) solution was obtained. Different concentrations of organoclay in DMAC were prepared by putting 0.125, 0.314 and 0.439 g of organoclay in 17.83 g DMAc respectively and by mixing each of them for 12 h. These organoclay suspensions were then mixed with PAA to obtain PAA/organoclay/DMAc. The final solid content (excluding organoclay) in PAA/organoclay/DMAc is 11%.

The samples for FTIR studies were prepared by spin-coating of PAA on KBr discs at 3000 rpm. Then the KBr discs containing PAA were put in vacuum oven at 30°C for 48 h. The dried PAA/KBr discs were put in hot cell in Nicolet Ominc 3 FTIR spectrometer, and the samples were heated at 150°C, 200°C, 230°C and 250°C, respectively. The in situ FTIR spectra of the heated samples were therefore obtained at different time. X-ray diffraction study of the samples was carried out by Mac Science M18 X-ray diffractometer (50 kV, 250 mA) with copper target and Ni-filter at a scanning rate of 4°/min. The samples for Transmission Electron Microscopy (TEM) study were first prepared by putting PMDA-ODA/organoclay films into epoxy capsules and by curing the epoxy at 70°C for 24 h in vacuum. Then the cured epoxies containing PMDA-ODA organoclay were microtomed with Leica Ultracut Uct into 90 mm thick slices, and a layer of carbon about 3 nm thick was deposited on these slices that being on mesh 200 copper nets for TEM observation. The type of TEM used is JEOL-200 FX, and its accelerated voltage was 200 kV. The thermal and the thermal-gravimetric analyses of PMDA-ODA/ organoclay were carried out with Model DSC 2910 and TGA 2950 by Du Pont, respectively, at a heating rate of 20°C/min.

3. Results and discussion

The X-ray diffraction curves of organoclay and poly(amic acid)/organoclay were shown in Fig. 1. In Fig. 1, a strong peak at $2\theta = 5.7°$ displayed by organoclay represented the diffraction from the (0 0 1) crystal surface of the *P*-phenylenediamine intercalated silicate layers of organoclay. The corresponding d-spacing in the silicate layers was 15.49 Å. Moreover in Fig. 1, all cases of poly(amic acid)/organoclay, from 2 to 7 phr organoclay, there were no organoclay peak appearing in their X-ray diffraction curves. This indicated that these silicate layers of organoclay were exfoliated and dispersed in poly(amic acid)/DMAc. This is a direct evidence that poly(amic acid)/organoclay/DMAc formed nanocomposites. A schematic drawing of the dispersion of
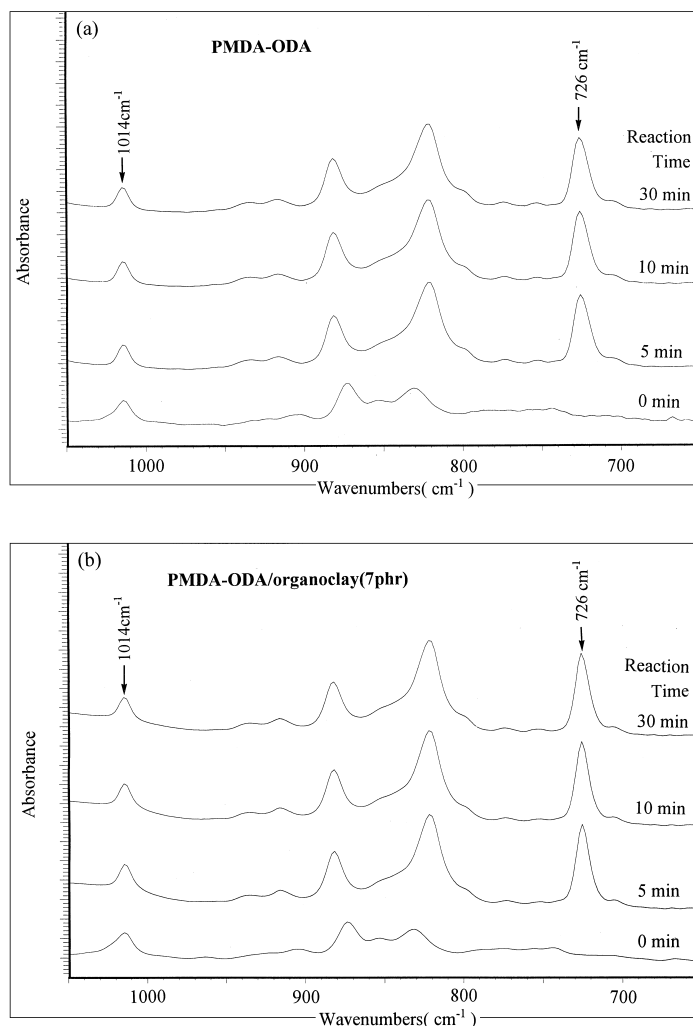
Fig. 3. The FTIR spectra of (a) PMDA-ODA (b) PMDA-ODA/organoclay(7 phr) imidized at 250°C for different time.

the aromatic diamine modified silicate layers in poly(amic acid)/DMAc is presented in Fig. 2.

The FTIR spectra of PMDA-ODA and PMDA-ODA/organoclay (7 phr) at 250°C for different time were shown in Figs. 3a and b, respectively. For following the kinetics of imidization, there are four characteristic adsorbance peaks in the spectra of poly(amic acid) can be chosen. The $726 \, cm^{-1}$ peak was caused by the bending of the cyclic imide ring (C = O), and the $1380 \, cm^{-1}$ peak resulting from the stretching of the imide ring. The $1720 \, cm^{-1}$ and the $1780 \, cm^{-1}$ peaks were resulted from the stretching of the asymmetric C = O and the stretching of the symmetric C = O, respectively [14,15]. As the $1720 \, cm^{-1}$ peaks were easily interfered by the anhydride and groups [16,17] produced during the heating of poly(amic acid), the $726 \, cm^{-1}$ peak was chosen for monitoring the extent of imidization because of its reproducibility and a minimized interference by DMAc [8,18]. In order to compare the samples that were imidized at different temperatures, the $1014 \, cm^{-1}$ absorbency peak was taken as the internal standard for normalizing the variations in the thickness of

poly(amic acid) films [19,20]. Here, we chose two cases to demonstrate how the imidization kinetics was obtained from their FTIR spectra. The first case discussed was PMDA-ODA. When PMDA-ODA was heated for 5 min at 250°C, the intensity of the $726 \, cm^{-1}$ peak increased dramatically, but only increased gradually after 10 min heating as shown in Fig. 3a. In addition in Fig. 3a, the intensity of the $1014 \, cm^{-1}$ peak was relatively constant throughout the heating, indicating its reliability as a reference peak. PMDA-ODA/organoclay (7 phr) was chosen as the second case. In the FTIR spectra of PMDA-ODA/organoclay (7 phr), the intensity of the $1014 \, cm^{-1}$ peak was about the same during the heating, as displayed in Fig. 3b. The intensity of the $726 \, cm^{-1}$ peak remained unchanged when more than 10 min heating was carried out at 250°C. This implied that the imidization of PMDA-ODA/organoclay (7 phr) has become saturated. Additionally, the general features of the FTIR spectra of PMDA-ODA/organoclay (7 phr) are very similar to that of PMDA-ODA. This indicated that the presence of silicate layers did not cause any structure change in PMDA-ODA.
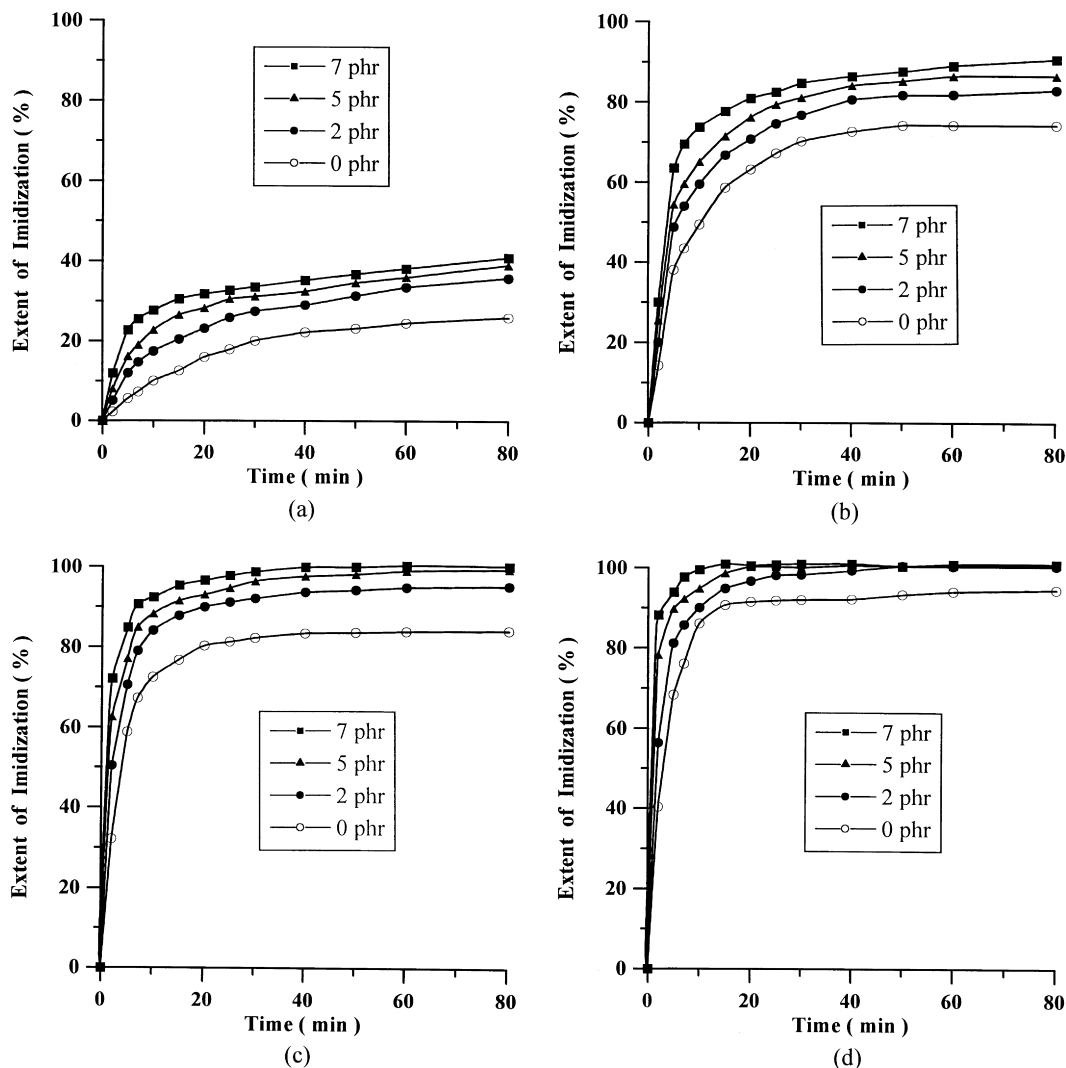
Fig. 4. The extent of imidization in percentage for different PMDA-ODA/organoclay at (a) 150°C (b) 200°C (c) 230°C and (d) 250°C for different time.

The extent of imidization can be defined by the following equation.

$$P_{T°C}(\%) = [(A_{726}/A_{1014})_{T°C}/(A_{726}/A_{1014})_{300°C}] \times 100\%, \quad (1)$$

where $P_{T°C}$ is the extent of imidization in percentage, A_{726} and A_{1014} are the intensities of the 726 cm^{-1} and the 1014 cm^{-1} absorbency peak. As the peak area was more likely affected by absorbency peaks caused by other functional groups, the peak intensity was chosen for comparison [8,16,18] in this study.

The extent of imidization of PMDA-ODA/organoclay, calculated based on Eq. (1), at 150°C, 200°C, 230°C and 250°C for different times are shown in Fig. 4. In Fig. 4a, the extent of imidization ($P_{150°C}$) of PMDA-ODA increased with reaction time at 150°C initially, but reached the inception point of a plateau at 22%, and become 25% after 80 min. When the silicate layers of organoclay were dispersed into PMDA-ODA, the extent of imidization of PMDA-ODA/organoclay increased with the amount of organoclay. For example, when the amount of organoclay

is 7 phr, the value of $P_{150°C}$ was 34% after 30 min heating and become 40% after 80 min reaction time as displayed in Fig. 4a. A relative 60% increase in the extent of imidization was obtained comparing the case of PMDA-ODA to that of PMDA-ODA/organoclay (7 phr). Moreover, in the cases of PMDA-ODA/organoclay, the value of $P_{150°C}$ reached a plateau much faster than that in the case of PMDA-ODA. This indicated that not only the extent of imidization but also the kinetics of imidization increased owing to the presence of dispersed silicate layers of organoclay.

When the reaction temperature was raised to 200°C, the values of $P_{200°C}$ were 72% and 90% for PMDA-ODA and PMDA-ODA/organoclay (7 phr) after 80 min heating, respectively, as shown in Fig. 4b. The values of $P_{230°C}$ were 85% and 98% for PMDA-ODA and PMDA-ODA/ organoclay (7 phr) after 80 min heating, respectively, as shown in Fig. 4c. At 250°C, the value of $P_{250°C}$ was 94% for the PMDA-ODA case after 80 min reaction time. However, the value of $P_{250°C}$ became 100% for the PMDA-ODA/organoclay (7 phr) only after 15 min reaction
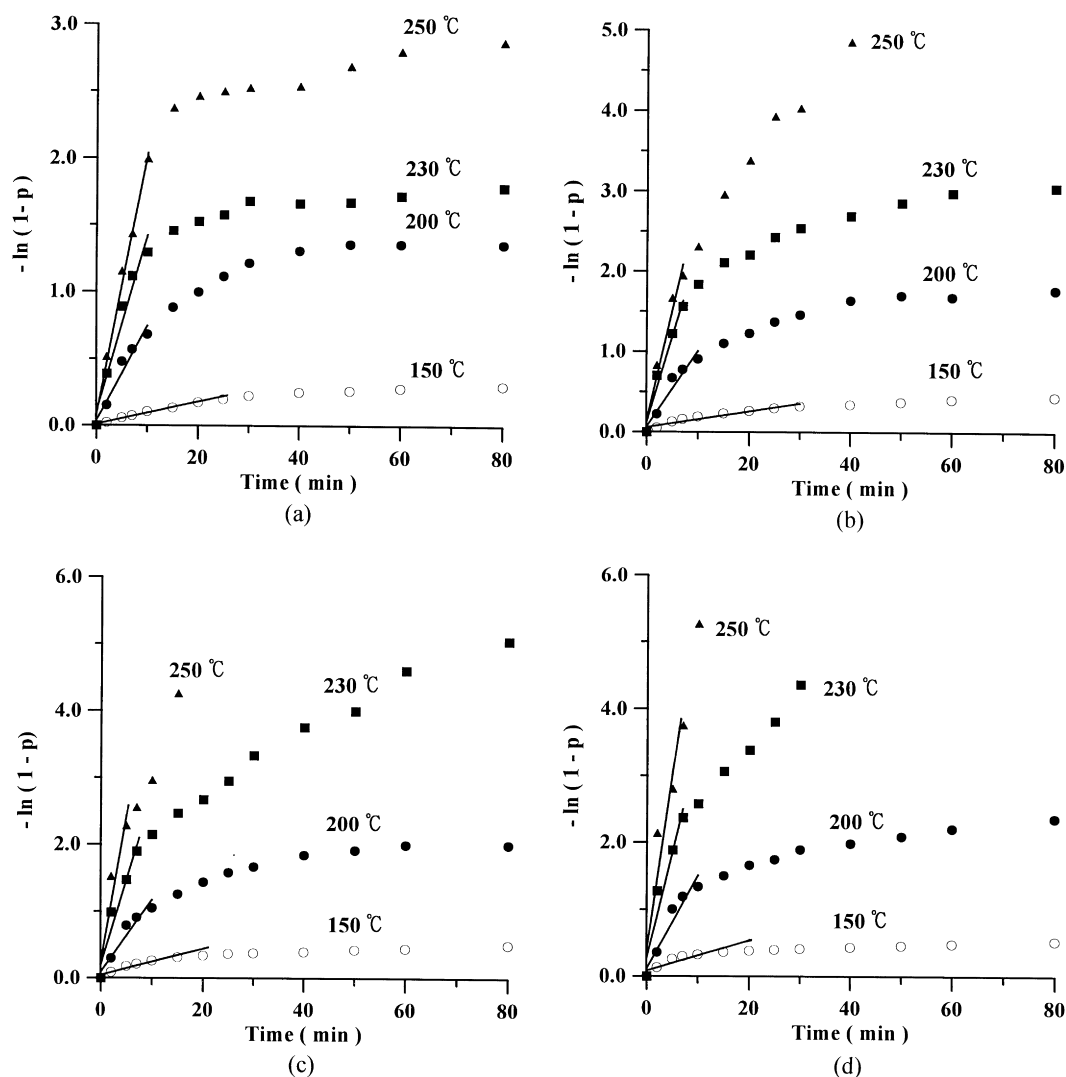
Fig. 5. The $-\ln(1-p)$ versus reaction time curves of (a) PMDA-ODA (b) PMDA-ODA/organoclay (2 phr) (c) PMDA-ODA/organoclay (5 phr) and (d) PMDA-ODA/organoclay (7 phr).

time. Even in the cases of 2 and 5 phr organoclay, the reaction times of PMDA-ODA/organoclay to reach 100% imidization were 50 and 20 min, respectively at 250°C. This fact undoubtedly lead to the conclusion that a strong enhancement of imidization and imidization kinetics occurred in the system of poly(amic acid)/organoclay nanocomposites. Specifically, a 50°C drop (250°C versus 300°C) in the imidization temperature of PMDA-ODA can be achieved for 2 phr of organoclay in PMDA-ODA. Moreover, the imidization time of PMDA-ODA can be reduced by 35 min at 250°C when 7 phr organoclay was added to the system as compared to the 2 phr organoclay case.

In previous studies, the initial imidization kinetics of poly(amic acid) was predominantly modeled with a first-order reaction [8,9,11]. Here, we adopted a first order reaction to model the kinetics of imidization. A first order kinetics can be expressed by the following

equation

$$-\ln(1-p) = kt, \tag{2}$$

where p is the extent of reaction at a reaction temperature T, k is the rate constant and t is the reaction time. The $-\ln(1-p)$ versus time curves of PMDA-ODA, PMDA-ODA/organoclay (2 phr), PMDA-ODA/organoclay (5 phr), PMDA-ODA/organoclay (7 phr) at various reaction temperatures were displayed in Fig. 5. In Fig. 5a, in the PMDA-ODA case, the straight lines were plotted based upon Eq. (2). At low temperature, 150°C, a straight line fitted the actual data points quite well within 20 min reaction time. At 200°C, 230°C and 250°C, the suitable reaction time for a first-order kinetics was reduced to 10 min. Similar behaviors of PMDA-ODA/organoclay (2 phr), PMDA-ODA/organoclay (5 phr) and PMDA-ODA/organoclay (7 phr) can be found as shown in Fig. 5b–d. This means that
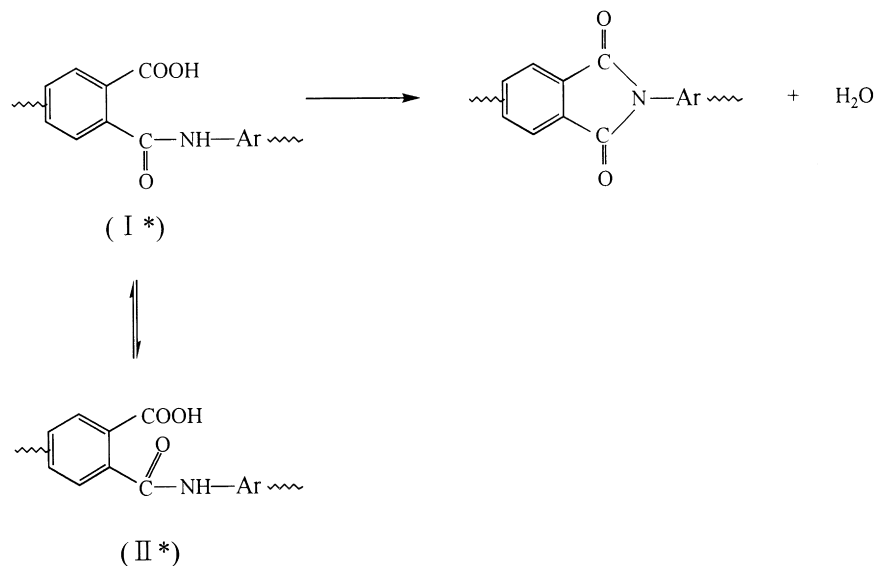
Fig. 6. The mechanism of the ring closure of poly(amic acid) in forming polyimide.

Table 1
Rate constants and preexponential factors for various contents of organoclay

PMDA-ODA/Organoclay	K				A (min^{-1})
	150°C	200°C	230°C	250°C	
100/0	7.74×10^{-3}	6.43×10^{-2}	1.31×10^{-1}	1.96×10^{-1}	7.67×10^{5}
100/2	1.09×10^{-2}	9.41×10^{-2}	1.72×10^{-1}	2.78×10^{-1}	1.75×10^{5}
100/5	2.02×10^{-2}	1.08×10^{-1}	2.45×10^{-1}	4.39×10^{-1}	9.48×10^{4}
100/7	2.68×10^{-2}	1.40×10^{-1}	3.17×10^{-1}	5.11×10^{-1}	8.08×10^{4}

the first-order reaction model was suitable for describing the imidization kinetics of PMDA-ODA as well as PMDA-ODA/organoclay at short reaction times. At longer reaction times, the imidization reaction slowed down. This is owing to the fact that after the extent of imidization increased, the glass transition temperature and the stiffness of the molecular chain of PMDA-ODA increased, and therefore a reduction in the speed of ring
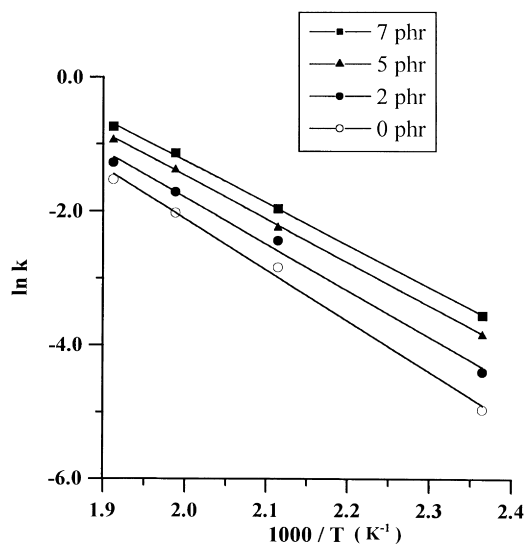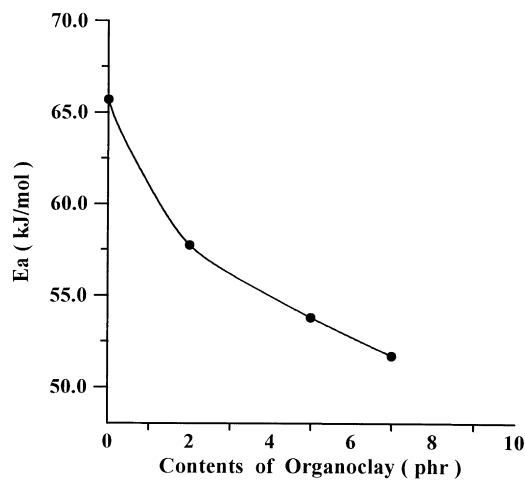

Fig. 7. Arrhenius plot of lnk versus1000/T for various compositions of PMDA-ODA/organoclay.

Fig. 8. The activation energy of a first-order imidization of PMDA-ODA/organoclay at different compositions.
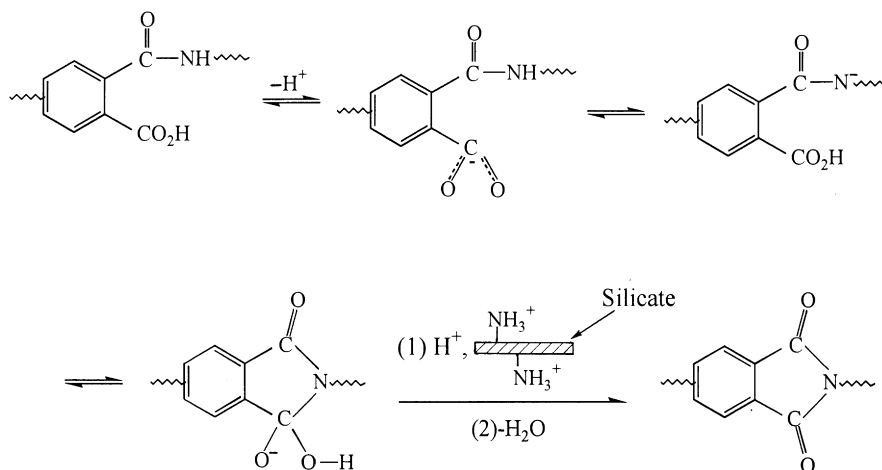
Fig. 9. A possible reaction mechanism for involving silicates layers in the imidization process.

closer of PAA. Moreover, the high speed of forming PMDA-ODA resulted from a favorable conformation [21] of poly(amic acid) (I*) in the beginning of the reaction as shown in Fig. 6. Later, the equilibrium shifted the other conformation of poly(amic acid) (II*) to the first conformation (I*), and therefore delayed the speed of the imidization.

The rate constants of the first order reaction kinetics were given in Table 1. In Table 1, the addition of organoclay to poly(amic acid) indeed resulted an increase in the rate constant calculated based upon Eq. (2). The rate of imidization increased with the amount of organoclay in PMDA-ODA. Specifically, at 150°C, the rate of imidization in PMDA-ODA/organoclay (7 phr) was almost three times of that in PMDA-ODA. In other temperatures, the rate of imidization in PMDA-ODA/organoclay (7 phr) was at

least two times of that in PMDA-ODA. Using the Arrhenius expression in Eq. (3), one can obtain the activation energy and the pre-exponential factor for PMDA-ODA containing different amount of organoclay.

$$k = A\exp(-E_a/RT), \tag{3}$$

where A is the pre-exponential factor, R is the gas constant, and E_a is the activation energy. The activation energy can be obtained by plotting ln k vs. 1000/T for various compositions of PMDA-ODA/organoclay as displayed in Fig. 7. In Fig. 7, the slopes of these lines were equal to $-E_a/R$, and the activation energy for each case was therefore determined. The activation energy for the imidization of PMDA-ODA was found to decrease with the amount of organoclay in PMDA-ODA as demonstrated in Fig. 8. In particular, a 20% reduction in the activation energy for the imidization
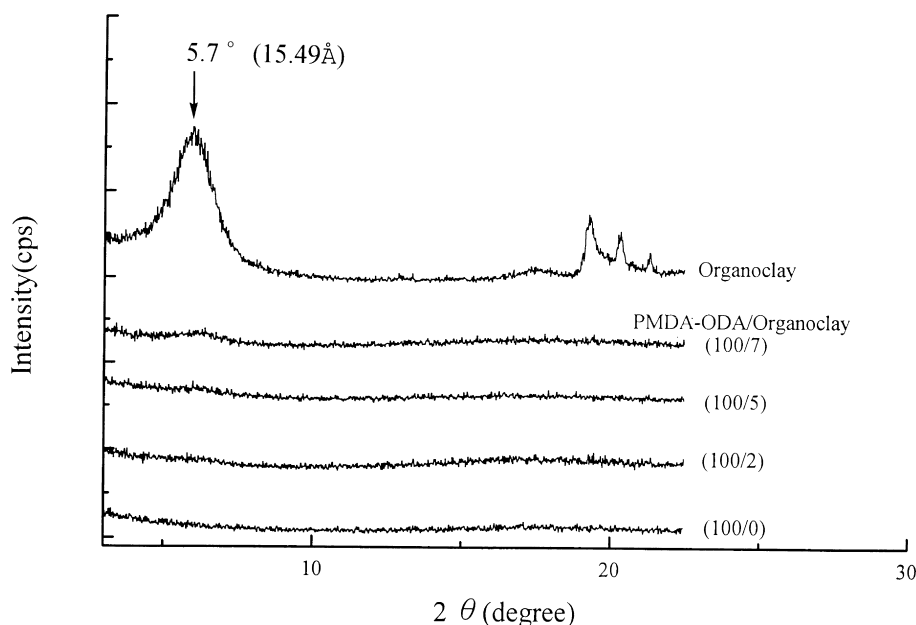

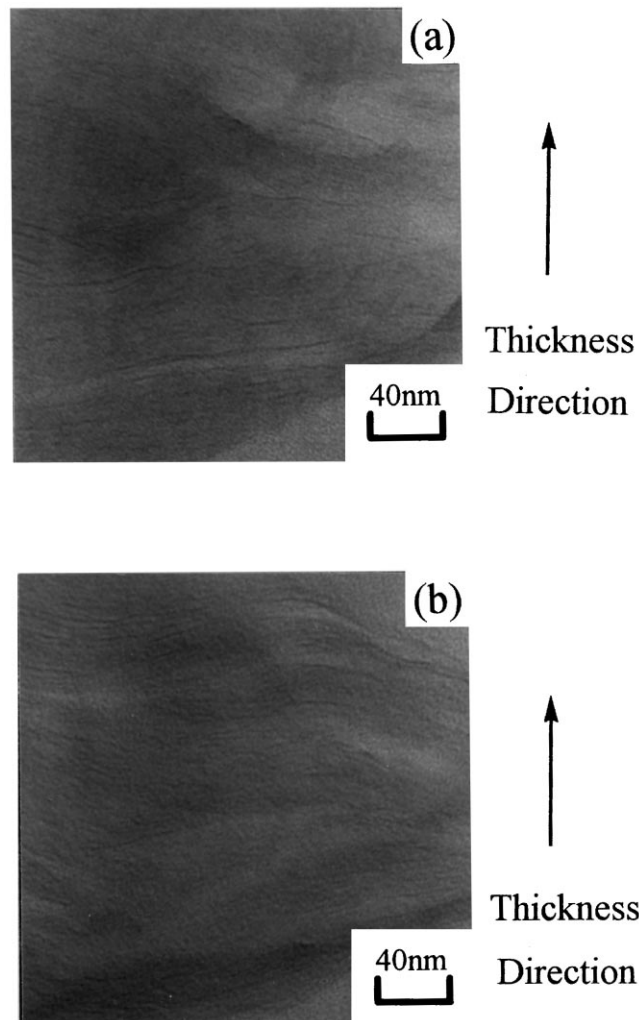Fig. 10. The X-ray diffraction curves of different PMDA-ODA/organoclay.

Fig. 11. TEM photographs of the cross section views of (a) PMDA-ODA/organoclay (5 phr) (b) PMDA-ODA/organoclay (7 phr).
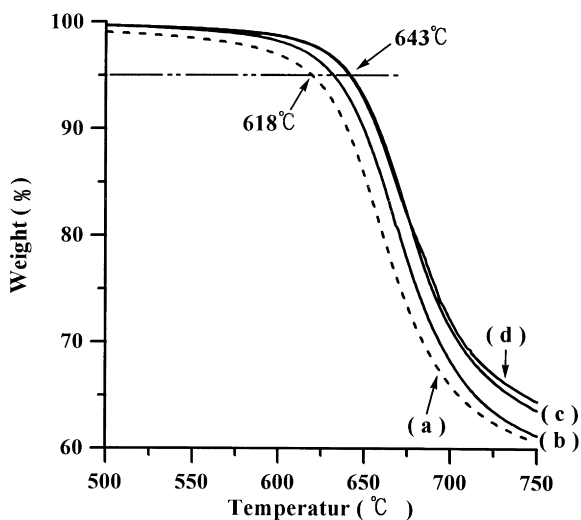

Fig. 12. The t.g.a. curves of (a) PMDA-ODA (b) PMDA-ODA/organoclay (2 phr) (c) PMDA-ODA/organoclay (5 phr) (d) PMDA-ODA/organoclay (7 phr).

of PMDA-ODA was obtained when 7 phr organoclay was added to PMDA-ODA. The pre-exponential factors determined by Eq. (3) for each case were also given in Table 1. From the above results, it was apparent that when a small amount of organoclay was dispersed in nanometer scale in poly(amic acid), both the imidization temperature and the imidization time of poly(amic acid) can be reduced dramatically. This implies that the dispersed organoclay play the role of catalyst during the imidization of poly(amic acid).

A possible imidization mechanism of poly(amic acid) involving organoclay is displayed in Fig. 9. In Fig. 9, the silicate layers of organoclay were exfoliated in poly(amic acid), and therefore the exfoliated silicate layers provided large surface areas as active sites [7] for promoting the dehydration and the imide ring closure reaction. The X-ray diffraction curves of PMDA-ODA/organoclay that were imidized at 250°C for one hour are shown in Fig. 10. In Fig. 10, the organoclay peak at $2\theta=5.7°$ did not appear, indicating PMDA-ODA/organoclay becoming nanocomposites. A further evidence of organoclay dispersed in
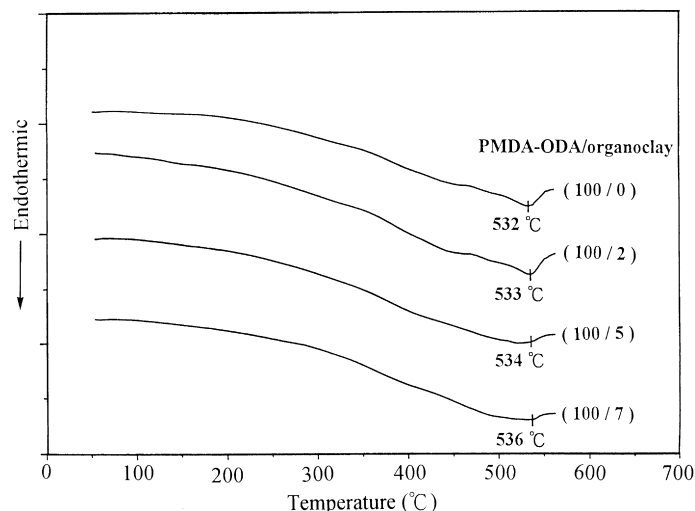
Fig. 13. The d.s.c. curves of different PMDA-ODA/organoclay.

PMDA-ODA in nanometer scale can be provided by TEM study. In Figs. 11a and b, the TEM photographs of the cross section views of PMDA-ODA/organoclay (7 phr) were presented, respectively. The thickness of silicate layers of organoclay (darker lines) was about 1 nm. The silicate layers were parallel to the surface of the films, and were dispersed homogeneously in PMDA-ODA. The distances between the silicate layers of organoclay in PMDA-ODA ranged from 4 to 15 nm, which are far larger than the original silicate layers distance of 1.5 nm. This is a strong evidence that the organoclay is exfoliated.

The thermal gravimetric analysis curves of different PMDA-ODA/organoclay are presented in Fig. 12. In Fig. 12, the heat degradation temperatures (at 5% weight loss) for PMDA-ODA, PMDA-ODA/organoclay (2 phr), PMDA-ODA/organoclay (5 phr) and PMDA-ODA/organoclay (7 phr) are 618, 632, 641, and 643°C, respectively. Therefore, the inclusion of dispersed organoclay in PMDA-ODA increased the thermal stability of the PMDA-ODA. The d.s.c. curves of PMDA-ODA/organoclay at the second heating are displayed in Fig. 13. There were no obvious glass transition temperatures present for PMDA-ODA and PMDA-ODA/organoclay. For neat PMDA-ODA, there is a melting peak at 532°C, whereas, the melting peaks become broader as the amount organoclay increased. This indicated that the presence of organoclay might reduce the crystallization of PMDA-ODA as the silicate layers retarded the mobility of polymer molecules during crystallization.

4. Conclusion

By dispersing a small amount of organoclay in nanometer scale in poly(amic acid) consisting of pyromellitic dianhydride and 4,4' oxydianiline, both the imidization temperature and the imidization time of the poly(amic acid) can be reduced dramatically. In specific, when two

parts of exfoliated silicate layers of organoclay was dispersed in poly(amic acid), the imidization temperature can be lowered by 50°C (250°C versus 300°C) for achieving a complete imidization. Additionally, the imidization time of poly(amic acid) at 250°C can be reduced to 15 minutes when the amount of organoclay increased to seven parts.

Using a first-order reaction to model the imidization kinetics of poly(amic acid)/organoclay, a 20% drop in the activation energy for imidization of PMDA-ODA/organoclay (7 phr) was obtained as compared to that for the imidization of neat PMDA-ODA. The thermal degradation temperature of PMDA-ODA/organoclay (7 phr) was about 25°C higher than that of neat PMDA-ODA.

Acknowledgements

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