Cyclodehydration of Poly (amic acid) to Polyimide

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Cyclodehydration of Poly (amic acid) to Polyimide

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It was observed that the cyclodehydration of PMDA-ODA or BTDA-ODA poly (amic acid) to polyimide in presence of ε-caprolactam takes place at a faster rate at lower temperature compared to the control film. It appears that the said lactam performed some catalytic function in the curing process and its influence was less in case of the PMDA based film than the BTDA based films. Also the rate of cyclodehydration of BTDA-ODA based poly (amic acid) to the corresponding polyimide is higher than the PMDA-ODA based poly (amic acid).

Keywords: Cyclodehydration; Curing; Poly (amic acid); Polyimide; Normalized peak height; ε-caprolactam

INTRODUCTION

Polyimide is generally prepared either by two step methods [1, 2] or by one step method [3]. Generally in two step method for the formation of polyimide film thermal curing is followed and for this the precursor poly (amic acid) film is cured upto 300°C or at higher temperature [4–6]. But Korshak [7] and Oba [8] *et al.*, have shown that when some catalyst like acetic acid, benzoic acid, *m*-hydroxybenzoic acid, *p*-hydroxyphenylacetic acid, and *p*-hydroxybenzenesulfonic acid is used the requirement for high temperature curing is not necessary to get a good quality polyimide film rather curing upto 200°C is quite sufficient.

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The present investigation deals with the cyclodehydration of the two poly (amic acid) (PAA) systems prepared from PMDA/ODA and BTDA/ODA to the corresponding polyimides in presence of ε-caprolactam.

It was expected that ε-caprolactam would help in cyclodehydration by absorbing the water formed as by product of imidification reaction as ε-caprolactam is hygroscopic in nature. Also the acid group of the amino acid which is formed from ε-caprolactam by absorption of water may act as an accelerator of cyclodehydration. The progress of curing was monitored by IR spectral analysis of the films cured at different temperatures.

EXPERIMENTAL

Reagents and Solvents

Pyromellitic dianhydride (PMDA), (Fluka, Switzerland) and benzophenone tetracarboxylic dianhydride (BTDA) (Gulf oil Corp., USA) were purified at first by boiling with acetic anhydride and activated charcoal and hot filtered. Next such PMDA and BTDA were further purified by recrystallization from acetic anhydride, filtered and washed with dry dichloromethane and dried in vacuum at 100°C. PMDA was vacuum sublimed to get the pure product, while BTDA was used after drying in vacuum oven as mentioned earlier. Oxydianiline (ODA), (Fluka, Switzerland) was purified by recrystallization from alcohol and water mixture in reducing atmosphere followed by drying, and vacuum sublimation twice to get a very pure ODA. The differential thermal analysis (DTA) of the purified PMDA, BTDA and ODA showed melting points at 285°C–286°C, 225°C–226°C and at 190°C–191°C which matched well with the literature data [9, 10].

The ε-caprolactam, dimethyl formamide (DMF), dichloromethane (s.d. Fine Chem, India) were purified by usual procedure [11].

Preparation of PAA and ε-caprolactam Solution

Poly (amic acid) of PMDA-ODA and BTDA-ODA was synthesized following the method mentioned elsewhere [12]. 5 g of PAA solution

(20% solid content w/w) of PMDA-ODA or BTDA-ODA in DMF was weighed accurately in a weighing bottle and to it 100 mg ε-caprolactam was added so that the ratio of PAA to ε-caprolactam became 10:1.

Film Casting

Poly (amic acid) films both control and blend of approximately 3 cm × 5 cm were cast on clean glass plate. On a glass plate four such films were doctored from two control poly (amic acids) and two ε-caprolactam added poly (amic acids). Five such plates were prepared for studying at five different temperatures (200, 250, 275, 300 and 330°C). Thickness of PAA film was so optimized that after curing the thickness of polyimide films remain in the range of 45–30 µm.

Drying and Curing (Cyclodehydration) of PAA Films

The PAA films were at first dried in vacuum at 40–50°C for 2 h to get non sticky films. Then all the films on the glass plates were inserted in an air circulating aging oven and the following curing schedule was followed

$$70°C \xrightarrow{\text{ I }} 150°C \xrightarrow{\text{ II }} 180°C \xrightarrow{\text{ III }} 200°C \xrightarrow{\text{ IV }} 250°C \xrightarrow{\text{ V }} 275°C$$
$$(30\text{min}) \quad (30\text{min}) \quad (30\text{min}) \quad (1\text{h}) \quad (1\text{h}) \quad (1\text{h})$$
$$\xrightarrow{\text{ VI }} 300°C \xrightarrow{\text{ VII }} 330°C$$
$$(1\text{h}) \quad (1\text{h})$$

Change of temperature from one stage to the next stage was made in 30 min. First glass plate containing four films was taken out from oven after its stay at 200°C for 1 h and the second glass plate containing another set of four films was taken out after its stay at 250°C for 1 h and so on. The hot glass plates were allowed to reach room temperature in a desiccator. Then the polyimide films were stripped manually from glass plate.

IR Spectroscopic Analysis

IR spectrum of all the films were recorded by a Shimadzu 270 spectrophotometer. The IR spectra of PMDA-ODA films and

BTDA-ODA films cured at 200°C for 1 h are shown in Figures 1 and 2 respectively. It is seen from these figures that peak for imide carbonyl stretching occurs at $1771-1773\,cm^{-1}$ region. The imide carbonyl peak height which is a function of imide group concentration has been utilized as a tool to monitor the progress of curing, *i.e.*, polyimide formation. Since uniformity in film thickness could not be maintained normalization of the IR peak height would eliminate the imide concentration difference due to difference in film thickness. For all the films normalized imide peak heights at $1771-1773\,cm^{-1}$ were calculated [13]. This normalized peak heights of the control film and ε-caprolactam added film were then compared for the evaluation of variation of state of cure. Similarly normalized peak heights of all other films cured at higher temperatures were calculated. All these normalized peak heights were plotted against temperature (Fig. 3).
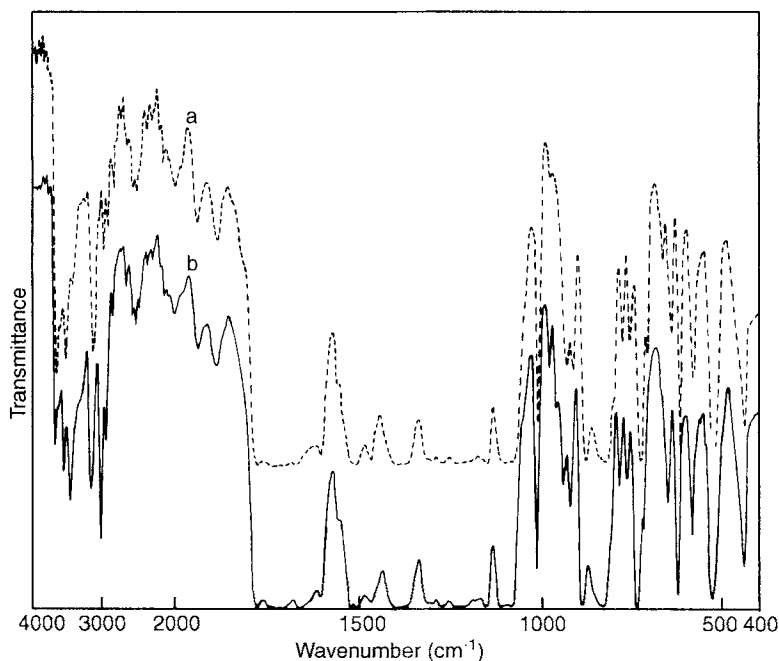

FIGURE 1 Curing of PMDA based films (a) Control and (b) ε-caprolactam added film after 1 h at 200°C.
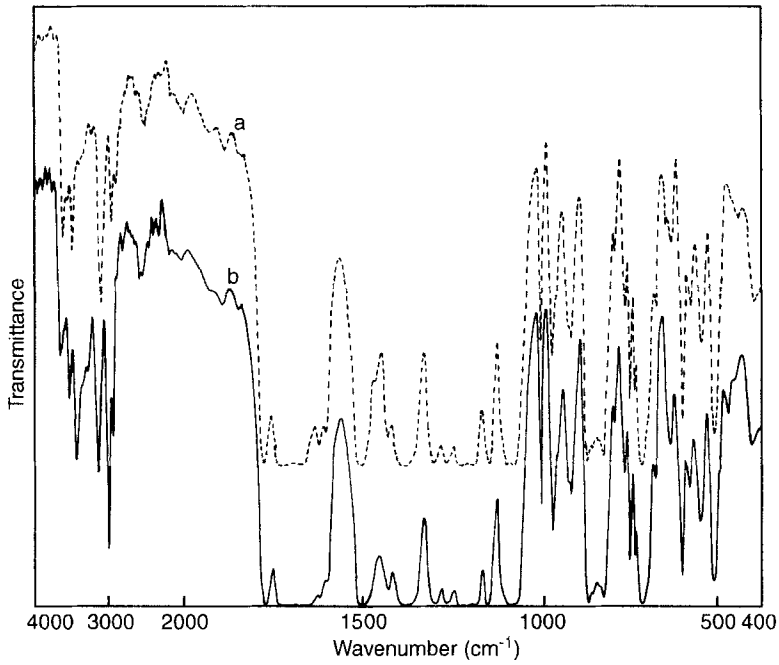
FIGURE 2   Curing of BTDA based films (a) Control and (b) ε-caprolactam added film after 1 h at 200°C.
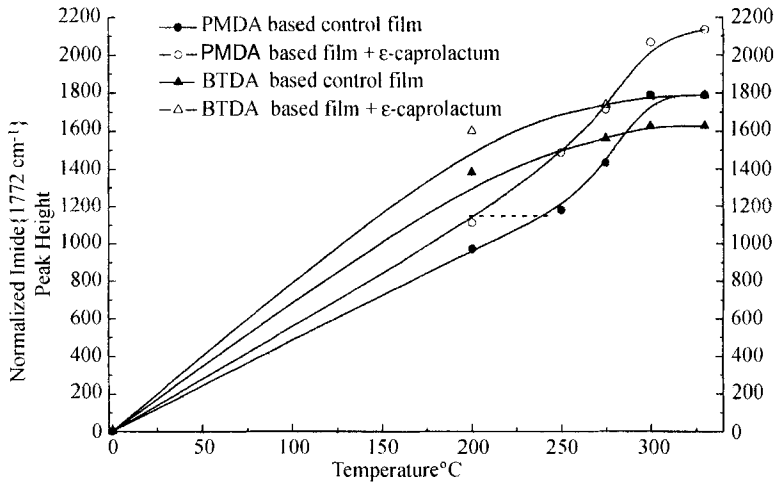

FIGURE 3   Variation of normalized imide peak height with temperature.

RESULTS AND DISCUSSION

Figures 1 and 2 show characteristic absorption of the control and ε-caprolactam added films of PMDA-ODA and BTDA-ODA based films cured at 200°C for 1 h respectively.

Variation of normalized imide peak height at 1771 cm^{-1} region with the progress of curing at progressive higher temperatures is shown in Figure 3. From Figure 3 it is observed that the normalized peak heights of the ε-caprolactam added films are higher compared to the control film and this is true for the two different systems studied. It is interesting to note from (marked with dotted line) that the temperature required to achieve a specific state of cure is higher for the control film than that of the film containing ε-caprolactam. This is true for both the polyimide systems studied. It appears that the ε-caprolactam is playing a definite role during curing while ε-caprolactam is undergoing *in situ* polymerization [14]. With the help of this normalized IR peak analysis another interesting phenomenon is observed, which is curing speed of polyimides. From Figure 3 it is evident that BTDA system undergoes rapid curing than that of PMDA system. This curing speed is further enhanced in presence of ε-caprolactam. Such comparison of curing speed may be made at any curing temperature for each of the four curves since all the films were raised to that temperature with the same heating rate.

Mechanism of Cyclodehydration

The higher state of curing is observed because of the reason that the water released (Scheme 1) during cyclodehydration is absorbed by ε-caprolactam. By absorbing water ε-caprolactam undergoes chemical transformation to amino caproic acid, which acts as a curing activator. As has been pointed out earlier such behavior is also found with other organic acids [7, 8].

The imidization is accomplished through nucleophilic attack of the amide nitrogen on the acid carbonyl carbon with elimination of water (Scheme 1) [15]. This nucleophilic attack is dependent on the availability of electron on nitrogen (*i.e.*, electron density on nitrogen). Again it is solely determined by the neighboring groups adjacent to nitrogen (Scheme 2) [16]. In Scheme 2 the carbonyl group marked '*'
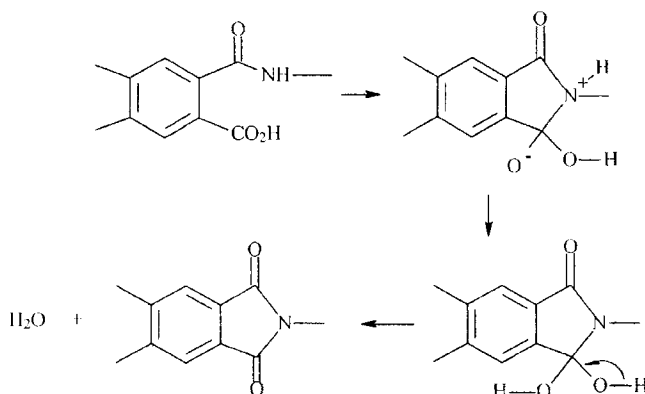
SCHEME 1   Cyclodehydration of poly (amic acid) to polyimide [15].

PMDA System   BTDA System
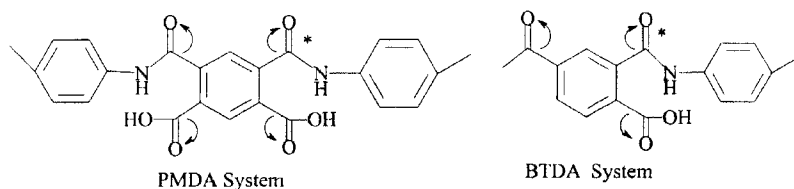
SCHEME 2   Nature of electron withdrawal from benzene ring in PMDA and BTDA based systems [16].

pulls electron both from the nitrogen and the adjacent benzene ring. In PMDA the electron density on the benzene ring is less compared to that of the benzene ring in BTDA as four and three carbonyl groups are attached with the PMDA and BTDA respectively. Therefore the ultimate electron density on nitrogen in BTDA based poly (amic acid) system is higher compared to that of the PMDA based poly (amic acid) system [16]. So the steps leading to cyclodehydration in BTDA based system is faster, *i.e.*, imide formation is faster. Another factor which would be also playing some role is the flexibility of the polymer chain. In PMDA based system at a particular temperature the formation of a 5-6-5 member rigid fused ring system is not a favorable one. But in case of BTDA based system such 5-6-5 member fused ring system is not present and as a result cyclodehydration for the formation of imide is taking place at a faster rate at a particular temperature.

CONCLUSION

Presence of ε-caprolactam enhances the cyclodehydration reaction of poly (amic acids) (both BTDA and PMDA based) at relatively lower temperature. BTDA-ODA poly (amic acid) system shows faster curing than that of the PMDA-ODA poly(amic acid) in presence of ε-caprolactam.

Acknowledgement

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