Polymer Bulletin 43, 505–510 (2000)

Polymer Bulletin

Properties of molecular composite film of poly(4,4'-diamino-2'-carbamoylbenzanilide terephthalamide)(p-PDCBTA) and poly(4,4'-diamino-2'-chlorobenzanilide terephthalamide) (P-LCI)

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Received: 31 August 1999/Revised version: 19 November 1999/Accepted: 25 November 1999

Summary

A new thermally stable, high strength and high modulus aromatic polyamide film was obtained via the formation of the molecular composite of p-PDCBTA and P-LCl. The two polymers exhibited good miscibility *identified with the measurement of dynamic mechanical property and FTIR spectra*. By the combination of drawing by 40% and subsequent heat treatment, the tensile property of the composite film could be achieved to the strength of 450 MPa and the modulus of 24 GPa, which were sustainable upto 400 °C.

Introduction

In recent years, high performance polymer blends have attracted much interests particularly for the technical viewpoint(1-9). *Amongst earlier reports in this area, Takayanagi and coworkers(7-8) have suggested, probably firstly, the concept of molecular composite that is somewhat different from simple blends. Since their suggestion, many other works have been reported on various polymeric molecular composite systems(1-6). For example,* the US Air Force studied a film formation process using the molecular composite of poly(p-phenylenebenzobisthiazole) and compatible polymers, e.g. poly(2,5(6')-benzimidazole)(9). The molecular composite of these components improved the tractability of rigid rod polymers, however, the complexity involved in preparation diminished the cost advantage of the products.

In general, liquid crystalline polymers such as *poly(p-phenylene terephthalamide) (PPTA) has comparatively high crystallinity and chain rigidity*, and thus is difficult to get good compatibility with matrix material. Chemical modifications of PPTA have thus been considered in order to overcome such difficulties. However, the matrix polymer which sustains liquid crystalline reinforcing polymer has usually poor thermal stability. Therefore, its mechanical performance at high temperature is unavoidably poor even if it has high strength and high modulus at room temperature.

This study thus aims at preparing thermally stable, high strength and high modulus aromatic polyamide film via the molecular composite of the chlorinated aromatic polyamide forming liquid crystalline phase and the aromatic polyamide having pendant carbamoyl group. The miscibility between two polymers, thermal and tensile properties of the resultant molecular compostie film were examined together with the structural change on heat treatment.

Experimental

Preparation of molecular composite film of p-PDCBTA and P-LCl

70 ml of 12% poly(4,4'-diamino-2'-carbamoylbenzanilide terephthalamide)(p-

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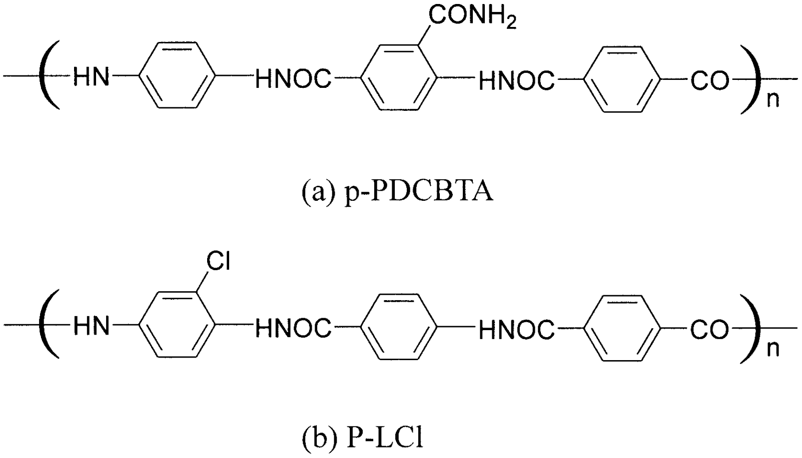
PDCBTA)*(Scheme 1(a))*(10, 11) in DMAc was mixed at room temperature with 30 ml of 12% poly(4,4'-diamino-2'-chlorobenzanilide terephthalamide)(P-LCl) *(Scheme 1(b))*(12) in DMAc. After stirring for a day the solution was cast on a glass plate, followed by the immersion in water to obtain a transparent wet film. The film was then manually drawn by 40% on an aluminium frame and vaccum-dried at 150 °C as fixed on the frame. After the cyclization at a specifed temperature, a tough and transparant molecular composite film of cyclized p-PDCBTA/P-LCl was finally obtained.



(a) p-PDCBTA

(b) P-LCl

Scheme 1. Chemical structure of (a) poly(4,4'-diamino-2'-carbamoylbenzanilide terephthalamide)(p-PDCBTA) and (b) poly(4,4'-diamino-2'-chlorobenzanilide terephthalamide)(P-LCl)

Characterization

Perkin Elmer FTIR spectrometer 1760X has been used to monitor the process of thermal cyclization of the molecular composite film. Thermal analysis was performed using the Perkin Elmer DSC/TGA Model TGA7 with a scan rate of 20 °C/min under nitrogen gas purging

Tensile property was measured by Instron Model 4204 for the films with the crosshead speed of 20 mm/min and specimen length of 30 mm. The film samples were of the width of 10 mm and thickness of 10~20 μm. Miscibility of the two polymers was examined with the Rheometrics Mechanical Spectrometer RMS-800E over the temperature range from 50 to 400 °C with frequency of 10 Hz.

The physical structural change in the film by drawing and/or thermal cyclization was monitored on Mac Science X-ray diffractometer MXP-18 operating at 40 kV and 200 mA, using the nickel filtered CuKα radiation. The scan was made from 10° to 50° with the step speed of 4 °/min and the step angle of 0.05°. In the case of the drawn film, the scanning was done along the drawing axis.

Results and discussion

Compatibility between p-PDCBTA and P-LCl

The compatibility of the two polymers was examined with rheometrical technique. Figure 1 shows that the storage modulus, E' of the P-LCl rapidly decreases in the temperature range from 180 °C to 210 °C. However, for p-PDCBTA, the first drop in E' occurs due to the thermal cyclization in the range of 200 °C to 250 °C, followed by a slight modulus increase to 300 °C. If the composite film has no compatibility, then the drop in the two moduli should be expected. The fact that uncyclized p-PDCBTA/P-LCl composite film has similar dynamic mechanical behavior to p-PDCBTA suggests that the two polymers have indeed good compatibility in molecular level.

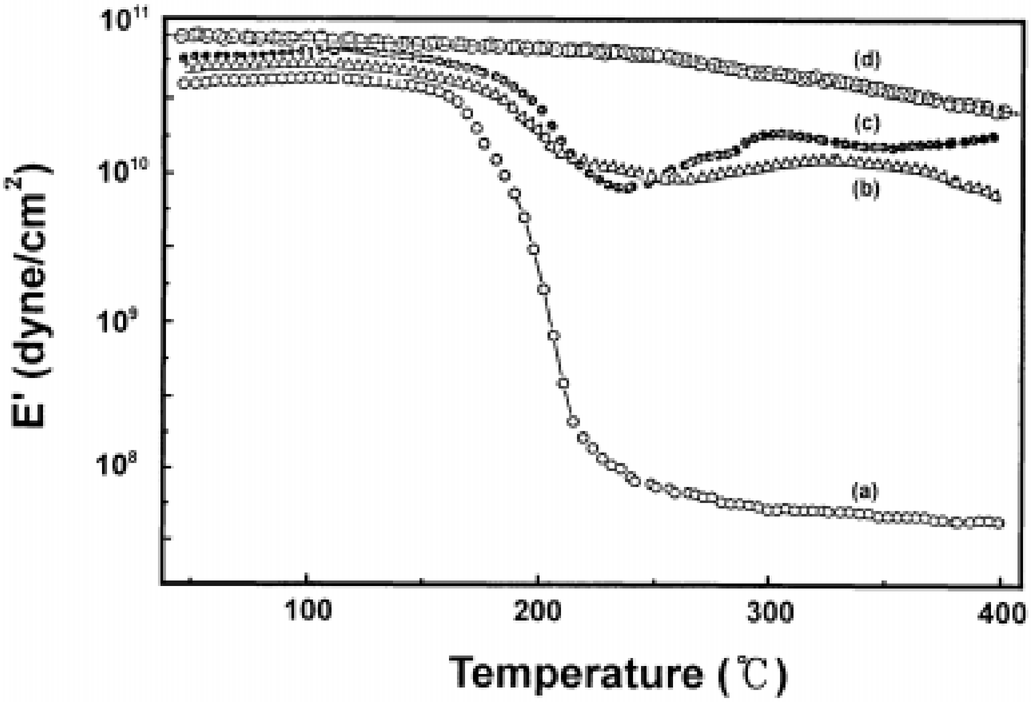


Figure 1. The storage modulus, E', of (a) P-LCl, (b) uncyclized p-PDCBTA, (c) uncyclized p-PDCBTA/P-LCl composite, and (d) cyclized p-PDCBTA/P-LCl composite films.

This observation is supported by Figure 2 that shows the FTIR spectra of the composite film heat treated at 300 °C for 1 hour. It can be clearly seen that the thermally cyclized p-PDCBTA gives absorption bands at 1,774 cm^{-1} and 1,671 cm^{-1} which are attributed to the lactone carbonyl and lactam carbonyl, respectively. However, the cyclized p-PDCBTA/P-LCl composite film gives the lactam carbonyl band at 1,664 cm^{-1} which is slightly lower wavenumber possibly due to the interaction effect between lactam carbonyl group(1,671cm^{-1}) and amide carbonyl group(1,656 cm^{-1}) of P-LCl.

It is worth mentioning that, on the heat-treatment of the composite film at 300 °C for 1 hour, the complete cyclization occurs to yield the molecular composite film having excellent mechanical performance even upto 400 °C.

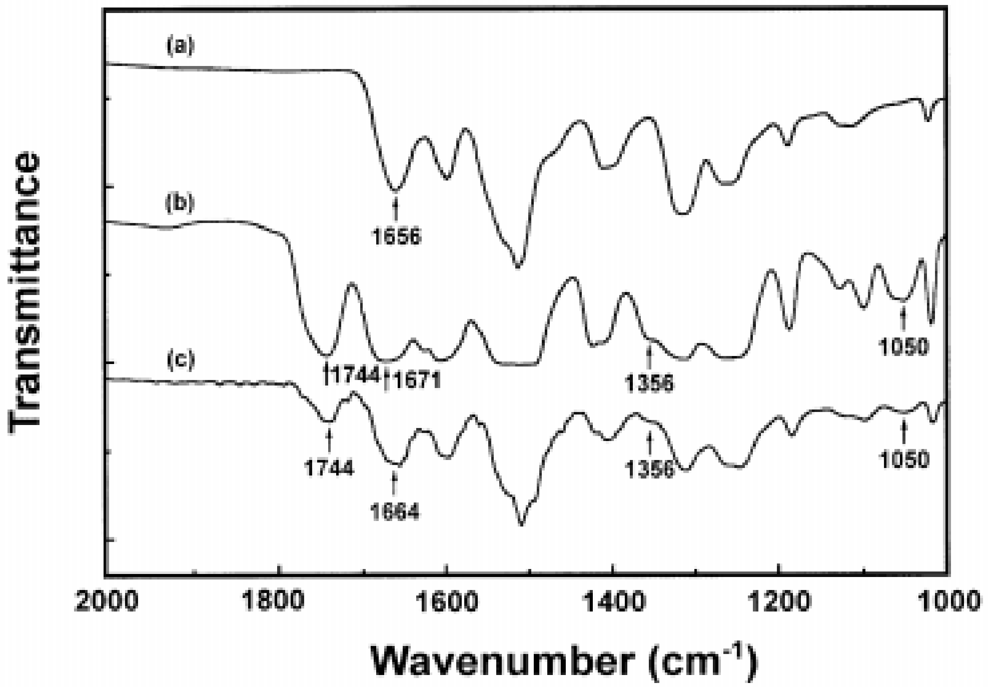


Figure 2. FT-IR spectra of (a) P-LCl, (b) p-PDCBTA cyclized at 300℃, and (c) p-PDCBTA/P-LCl composite film cyclized at 300℃.

Structure and physical properties of the molecular composite film of p-PDCBTA and P-LCl

Table 1 lists the tensile property of the cyclized p-PDCBTA/P-LCl composite film. The p-PDCBTA film heat-treated at 300 °C exhibited the tensile strength of 283 MPa and the modulus of 9.7 GPa. Similar values, i.e. the tensile stress of 270 MPa and the modulus of 9.7 GPa, were obtained from the composite film drawn by 40%. However, when the composite film was drawn by 40% and subsequently heat treated the tensile property of the film increased considerably to give the tensile strength of 450 MPa and the modulus of 24 GPa which is much higher than 16.4 GPa of cyclized p-PDCBTA. This may result from the orientation of P-LCl molecular chain along the drawing direction. Indeed, Figure 3 shows that the undrawn P-LCl film gives broad diffraction peaks at 2θ = 13.5° and 20°, indicating poor crystal structure. The undrawn molecular composite film gives the peak of shoulder type at $2\theta=23°$ arising from the uncyclized p-PDCBTA(Figure 3(b)). However, on drawing by 20%, the peak intensity increases slightly(Figure 3(c)) and by the combination of drawing by 40% and heat-treatment at 300°C, the diffraction peak intensity increases remarkably. *Although the intensity was not normalized by the specimen thickness, this considerable increase in the intensity with the increase of drawing ratio indicates that the peaks at* $2\theta=23°$ *and 20° are developing due to the combined effect of both thermal crystallization and orientation of p-PDCBTA and P-LCl, respectively.*

The thermal stability of the molecular composite film was examined by thermogravimetric method. As shown in Figure 4, the degradation onset temperature of the composite film is observed at 524 °C, being the same with cyclized p-PDCBTA, and the char yield is about 65%.

In conclusion, this study presents that thermally stable, high strength, high modulus film can be prepared via the formation of molecular composite of p-PDCBTA and chlorinated liquid crystalline polymer, and the subsequent heat treatment.

Table 1. Tensile properties of undrawn and drawn p-PDCBTA and p-PDCBTA/P-LCl composite films cyclized at 300℃ for 1.5 hour

	p-PDCBTA		p-PDCBTA/P-LCl	
	λ =1	λ =1.4	λ =1	λ =1.4
Tensile stress (MPa)	283	421	270	450
Elongation (%)	11	5	8	2
Young's modulus (GPa)	9.7	16.4	9.1	24.0

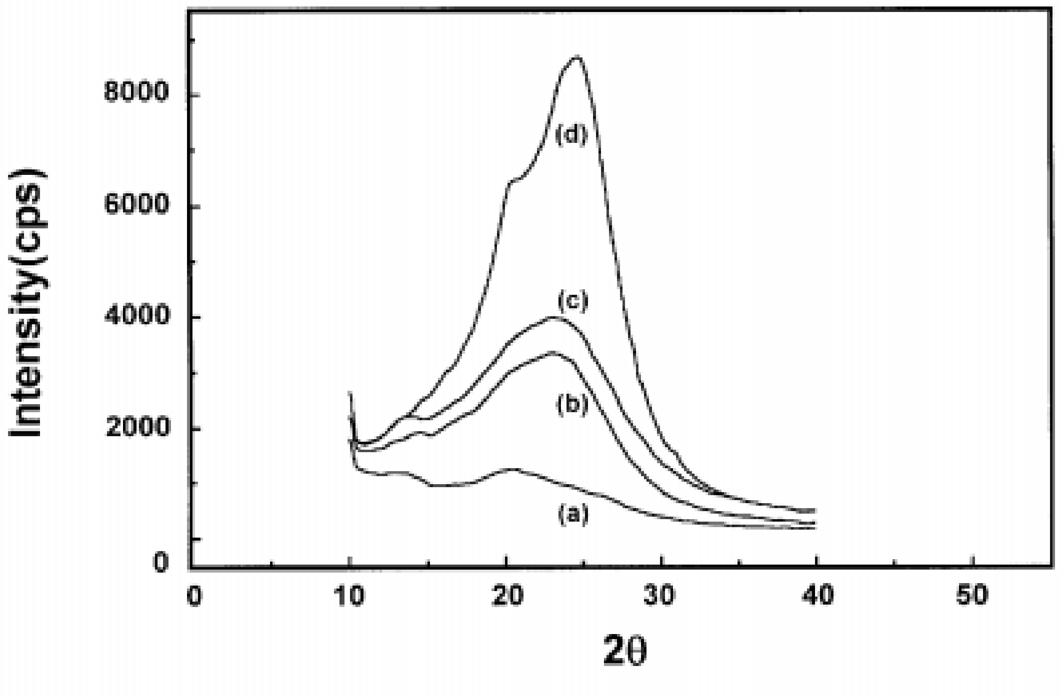


Figure 3. Wide Angle X-ray diffraction patterns: (a) P-LCl, (b) uncyclized p-PDCBTA/P-LCl(λ =1), (c) uncyclized p-PDCBTA/P-LCl(λ =1.2), and (d) cyclized p-PDCBTA/P-LCl(λ =1.4) composite films.

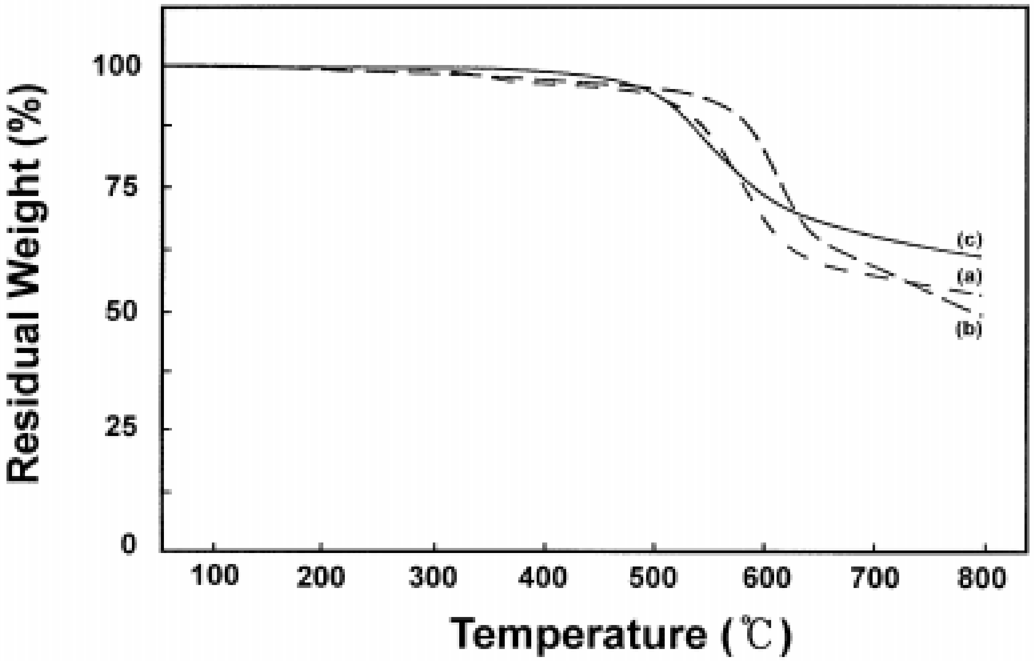


Figure 4. TGA thermograms of (a) cyclized p-PDCBTA, (b) P-LCl, and (c) cyclized p-PDCBTA/P-LCl composite film.

Acknowledgements: This paper is dedicated to the late Prof. W.S. Ha of Department of Fiber and Polymer Science, Seoul National University.

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