

POLYCAPROLACTAM MODIFIED BY POLYBENZIMIDAZOLE *

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ABSTRACT

Three polycaprolactam samples modified by 0.05 — 0.50% polybenzimidazole (PBI) by weight were prepared. Their structure and mechanical properties were characterized by means of FT-IR, SEM, DTA, density tensile, impact and viscoelastic method. PBI delayed the superimposed polymerization-crystallization process of the activated anionic polymerization of caprolactam. The monomer casting (MC) nylons modified by PBI had lower crystallinities, lower T_g and more nearly perfect spherulites than MC-nylon itself, and showed a typical toughening effect.

INTRODUCTION

The concept of molecular composite^[1-8] represents one of the most exciting fields in composite materials and polymer science. This new concept is based on a composite material made of rigid rod and flexible coil polymer molecules in which the rigid rod polymer is dispersed on the molecular level in a flexible coil matrix. There are three routes to molecular composites. The first is the coagulation of isotropic ternary solutions of rod-like polymer and coil matrix polymer^[1-5]. The second is the block polymer composed of a rigid rod segment acting as reinforcement and a flexible segment as matrix^[6, 7, 9]. The third is in situ polymerization process^[8]. Composites formed from aromatic heterocyclic polymers have been described by Helminiak and co-workers^[1-3], while Takayanagi has reported composites of more conventional polymers reinforced with aramid polymers^[4-6].

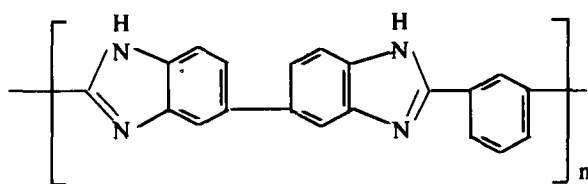
Nevertheless, the aromatic heterocyclic polymers such as PBI, PPQ, etc., which were used as the coil matrix in molecular composites, are much stiffer than the conventional polymers such as nylon-6. Hence, the rigid rod molecules were merely limited to several polymers, mainly poly(p-phenylene-benzobisthiazole) (PBT), poly(p-phenylene-benzobisoxazole) (PBO), and poly(p-phenyleneterephthalamide) (PPTA). Thus, an extensive application of the concept of molecular composite is required.

The present investigation was undertaken in an attempt to modify monomer casting nylon (MC nylon, polycaprolactam) with aromatic heterocyclic polymers such as polybenzimidazole (PBI) and polyphenylquinoxaline (PPQ) which were used as the flexible matrix in molecular composite^[1, 10]. The in situ polymerization process was used, in which the monomer containing an aromatic heterocyclic polymer was polymerized. Of primary interest are the significant effects of small amounts of PBI upon the polymerization of caprolactam, structure and properties of MC nylon. Because of its participation in the polymerization process, PBI produced a toughening effect.

Received December 28, 1987

* Project supported by the National Natural Science Foundation of China.

This is the repeat unit of PBI :



PBI

EXPERIMENTAL

1. Preparation of MC nylon

The method reported in the literature was improved in our laboratory. To a 250 ml, three-necked, round-bottomed flask, fitted with thermometer and argon flush, 160 g. of caprolactam was added. At reduced pressure under argon, the monomer melted and continued to boil for 20 min. Then, vacuum was turned off and 114 mg of NaOH was added to the monomer, and then the reaction mixture continued to boil for 30 min. under vacuum. The mixture was heated gradually to 150 °C and then under normal pressure, N-acetyl caprolactam was added. After well stirring, the mixture was poured into a mold kept at 165 °C for 25 min., and then MC nylon and the mold were removed from the heater. The white and tough MC nylon was separated from the mold after thorough cooling.

2. Preparation of modified MC nylons

PBI or other aromatic heterocyclic polymers were mixed with caprolactam at different ratios. The procedure to prepare the modified MC nylon is the same as that described above.

3. Characterization of structure of MC nylon and modified MC nylons

FTIR spectra of samples were obtained through KBr pressed disc method on IFS-113V (Germany).

The densities of the nylons were measured by specific gravity bottle method. Crystallinities were calculated from the densities :

$$X_c = \frac{\rho_c (\rho - \rho_a)}{\rho (\rho_c - \rho_a)} \times 100 (\%)$$

where X_c is crystallinity, ρ , ρ_c , ρ_a are the densities of sample, crystalline nylon-6 and non-crystalline nylon-6, respectively. $\rho_c = 1.230 \text{ g/cm}^3$, $\rho_a = 1.084 \text{ g/cm}^3$.

The nylons were chemically etched without damaging the surface. After gold-plating the specimen was observed by means of Hitachi S-530 SEM.

The melting temperature (T_m) and the crystallization temperature (T_c) were measured by Mettler 2000 DTA instrument. The testing temperature was first programmed rising to 260 °C, and maintained at that temperature for 10 min., then programmed dropping to measure T_c . Both rising and dropping rates were 10 °C per minute.

The size of samples used to measure their visco-elastic properties is

$40.0 \times 4.0 \times 1.0 \text{ mm}^3$. After drying under reduced pressure, the samples were tested by N-VES (Japan) at the frequency of 3.3 Hz.

4. Characterization of mechanical properties of non-modified and modified nylons

The nylon rods were processed to various samples with different sizes to meet the needs of various instruments. Each kind of nylon for each instrument has at least 3 specimens. Before testing, all samples were treated in the atmosphere of 70% relative humidity at 25°C for 80 hours.

The tensile samples were dumb-bell in shape in which the mid-section was 12 mm long, 2 mm wide, and 2 mm thick. The tensile testing was done on Instron 1122 at 28°C . The tensile rate was 20 mm per minute.

The Charpy impact specimen was $55.0 \times 6.0 \times 4.0 \text{ mm}^3$ with a slot of $6.0 \times 2.0 \times 1.3$ (thick) mm^3 in the middle. The impact strength was obtained on Lowis Schopper 10/40 kg-cm at 27°C .

RESULTS AND DISCUSSION

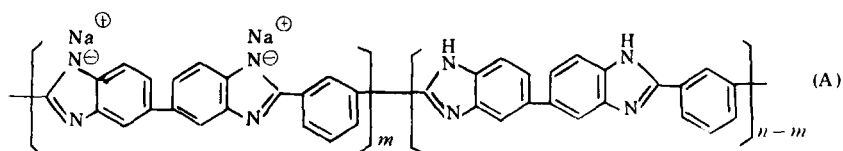
The anionic polymerization of caprolactam to form MC nylon was originally described by Joyce and Ritter in 1941^[11] and has been studied by many researchers. The modifications of MC nylon were reported^[12, 13], in which inorganic powders^[12] and carbon-fiber^[13] were added to the monomer to improve the modulus and wear properties of MC nylon, but the relationship between structure and properties of these modified polycaprolactam had not been discussed.

In the case of polymerization, the miscibility between caprolactam and additives is vital in determining the structure and properties of modified articles. If the additives and caprolactam are incompatible with each other, the additives will not be well-distributed in the ultimate modified MC nylons.

In the present investigation, ten different aromatic heterocyclic polymers were used as additives. Because of the limited solubilities of additives in caprolactam and the density difference between additive and caprolactam, these polymers except PBI and PPQ (containing ether linkage) did not dissolve in the monomer, and precipitated during the polymerization of caprolactam, although the contents of aromatic polymers were very low, even only 0.05% by weight. Thus, our further work was concentrated on the MC nylons modified by PBI or PPQ, in which the heterocyclic polymer was well-distributed. In this paper, MC nylon modified by PBI will be discussed.

1. Preparation of polycaprolactams modified by PBI

MC nylon and three modified ones with different contents of PBI were prepared. As shown in Table 1, addition of PBI changed the colour of MC nylon. The higher the contents of PBI, the deeper the colour. As the contents of PBI increase, the polymerization time of the monomer turns longer. When the content of PBI was



raised to 0.50% by weight, the mixture could not solidify in the mold. This was caused by the reactive hydrogen of imidazole ring in PBI which reacted with NaOH, thus produced a more stable polymeric anion (A)^[14, 15]. This means that the effective concentration of NaOH was reduced. According to the polymerization kinetics^[16, 17], the polymerization rate decreases with the decrease of the concentration of catalyst NaOH. So the polymerization was delayed.

Table 1 Preparation of MC nylon and modified ones by PBI

Sample	PBI contents by weight (%)	Polymerization time (min)	Color
No.1	0	9.5	white
No.2	0.05	14.5	light yellow
No.3	0.20	24.5	yellow
* No.4	0.50	21.5	brown
No.5	0.50	not solidifying	

*The amount of NaOH used in this synthesis was doubled.

FT-IR spectra showed that the main absorption bands of MC nylon were also present in the spectra of modified MC nylons. This proved that the main chain of modified samples remained polycaprolactam.

It was measured that the water absorption of all four samples except No.3 was almost at the same level, while the water absorption of No.3 was twice more than that of others, and so was its soluble weight in water. This means that the low molecular weight ratio of sample No.3 is higher than that of others.

2. Structure characterization

Modified nylons remained polycaprolactam, a kind of crystalline polymer. Their crystal morphological structure was observed by means of SEM, after their surface was chemically etched and therefore the amorphous part was removed. All the samples have spherulites (Fig. 1). Addition of PBI did not produce a new phase. But PBI made the spherulites of polycaprolactam in modified samples larger and more nearly perfect. The crystals of MC nylon appear in "bundle shape" and the boundaries between crystals are not clear, as shown in Fig. 1, these are characteristics of early spherulites^[18, 19]. But the spherulites of all the modified samples are really sphere-shaped and have clear boundaries. The perfection degree of spherulites in these samples is decreased in the following order :

$$\text{No. 3} > \text{No. 4} > \text{No. 2} > \text{No. 1}$$

It is interesting that this order agrees with that of polymerization time.

As Table 2 shows, as the densities of modified MC nylons are smaller than that of MC nylon, so are their crystallinities. The order of crystallinity increase is opposite to that of perfection degree of spherulites, i. e.,

$$\text{No. 1} > \text{No. 2} > \text{No. 4} > \text{No. 3}$$

Addition of PBI decreased the T_g of modified nylons. The decrease order of T_g is

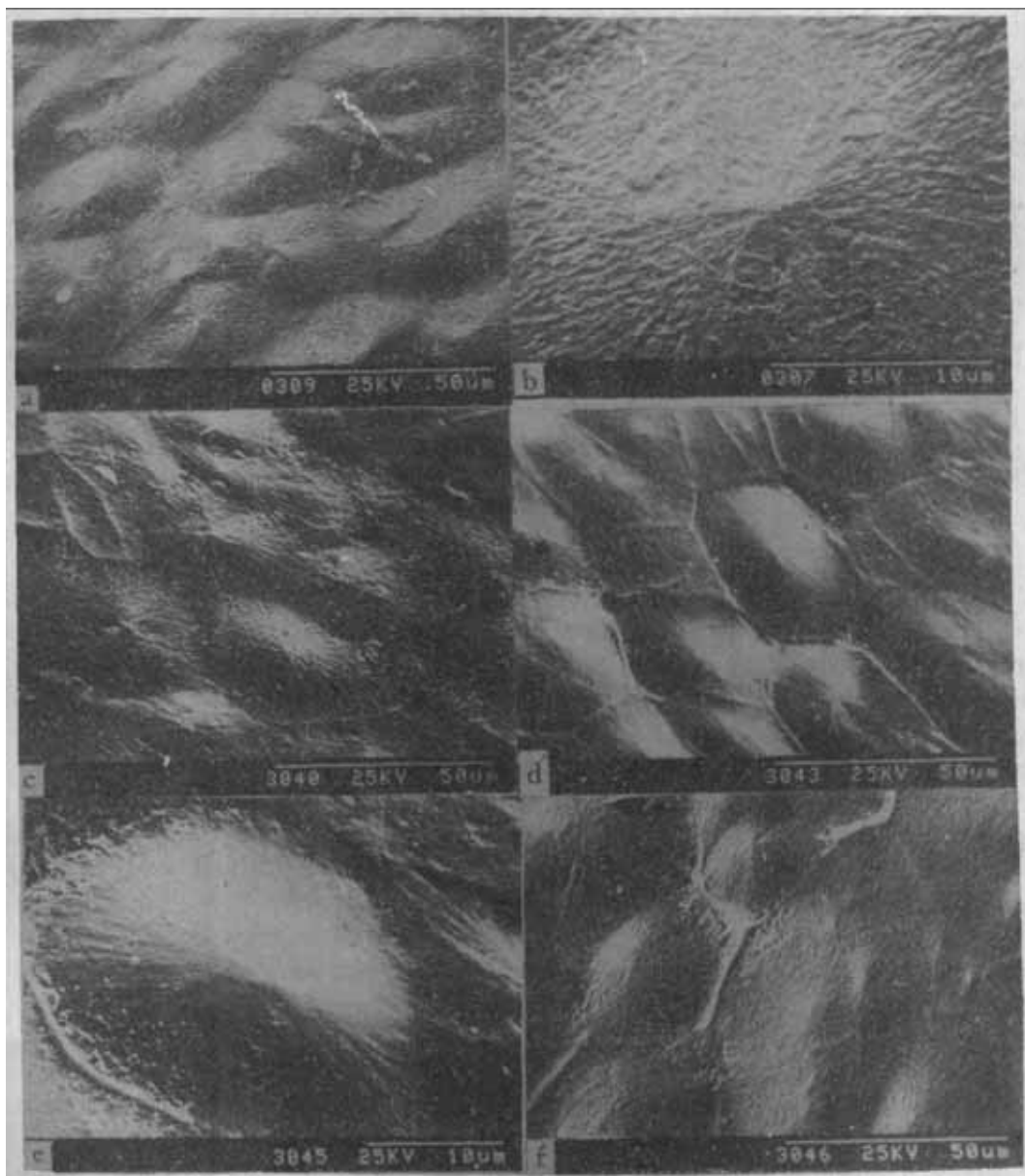


Fig.1 SEM micrographs of MC nylons modified by PBI. Their PBI contents (by weight) are 0% (a,b); 0.05% (c); 0.20% (d,e); 0.50% (f)..

just the same as that of crystallinity (Table 3). If a sample has lower crystallinity and larger spherulites, the volume between its spherulites will be larger. Therefore, chain segments of its non-crystalline part move more easily, thus its T_g turns lower. Sample No.3 was most marked in this respect, because its more low molecular weight part acted as a plasticizing agent.

PBI has little effect on the melting temperature (T_m) and crystallization temperature (T_c) of modified nylons (Table 3).

Table 2 Densities and crystallinities of the samples

Sample	Density (g/cm ³)	Crystallinity (%)
No.1	1.1543	51.3
No.2	1.1529	50.3
No.3	1.1471	46.3
No.4	1.1500	48.3

Table 3 T_m , T_c and T_g of samples

Sample	T_m (°C)	T_c (°C)	T_g (°C)
No.1	224.4	174.0	39.0
No.2	224.2	175.2	35.0
No.3	225.8	175.4	10.0
No.4	224.2	173.0	32.0

3. Mechanical properties characterization

The stress-strain curves (Fig. 2 and Table 4) show that MC nylon and modified ones are all strong- and -tough type plastics. They all have very high ultimate elongation because of "cold drawing". For a crystalline polymer, the cold drawing happens when its T_g at tensile testing is lower than the tensile temperature. Actually, all the samples had the much lower T_g 's at tensile testing than those discussed above, because they absorbed moisture during pretreating. It is very amusing that second-yield appeared in all samples except No.3, perhaps because No.3 had the lowest T_g .

The introduction of PBI led to a decrease in tensile strength and yield strength, and an increase in ultimate tensile elongation and yield strain, i. e., "toughening effect". This effect was caused by the lower crystallinities of modified samples together with their larger and more nearly perfect spherulites. Their tensile strength and yield strength are reduced in the following order:

$$\text{No.1} > \text{No.2} > \text{No.4} > \text{No.3}$$

This order is the same as that of crystallinities, and is opposite to that of perfection degree of spherulites.

This toughening effect also appeared in the impact testing. After pretreating in 70% relative humidity at 26 °C for 80 hours, none of the samples broken when impacted at room temperature. This is because the absorbed water acts as a plasticizing agent. After all the samples were dried under reduced pressure, No. 3 and No. 4 still have high impact strength (Table 5).

From the visco-elastic curves (Fig. 3), PBI improves the low temperature modulus of modified samples, and decreases the high temperature modulus. Their storage modulus at room temperature is decreased in the following order (Table 6):

$$\text{No.1} > \text{No.2} > \text{No.4} > \text{No.3}$$

Once again this order agrees with those described above.

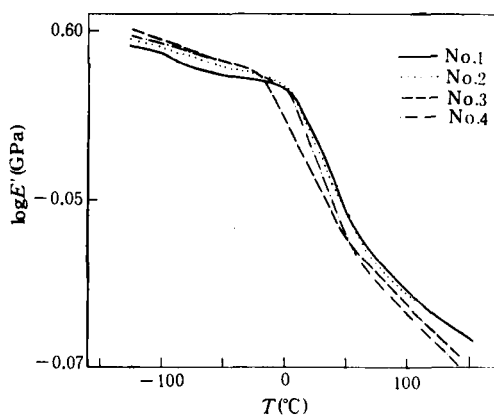
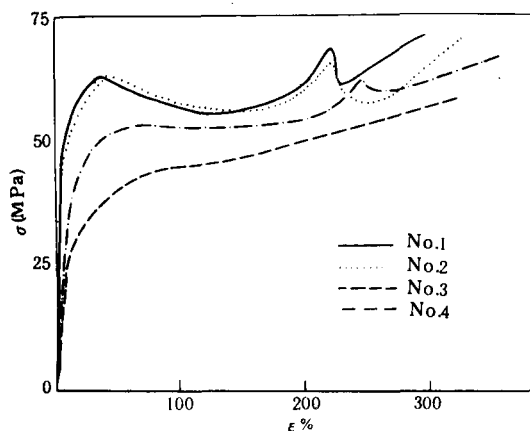


Fig.2 The tensile properties of modified MC nylons Fig.3 The dynamic mechanical properties of MC nylons

Table 4 The tensile properties of modified MC nylons

Sample	Tensile strength MPa	Ultimate elongation (%)	First – yielding		Second – yielding	
			σ MPa	ε (%)	σ MPa	ε (%)
No.1	69.5	294	61.6	39	67.7	221
No.2	69.2	337	61.3	47	65.3	222
No.3	57.6	332	no yield		no yield	
No.4	64.2	354	50.8	76	59.6	251

Table 5 The Charpy impact strength of modified samples

Sample	J/m (2.84mm)	KJ/m ²
No.1	50.3	17.7
No.2	49.3	17.1
No.3	149.2	51.3
No.4	116.4	41.4

Table 6 The storage modulus of samples at different temperatures, GPa

Sample	-100 °C	-50 °C	0 °C	25 °C	50 °C	100 °C
No.1	3.26	2.65	2.38	1.49	0.80	0.39
No.2	3.40	2.82	2.31	1.40	0.80	0.38
No.3	3.50	2.99	1.78	1.04	0.63	0.36
No.4	3.54	2.94	2.27	1.30	0.65	0.32

Keywords :

Polycaprolactam; Polybenzimidazole; Modified MC nylon; Spherulite.

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