

POLYCAPROLACTAM MODIFIED BY POLYPHENYLQUINOXALINE*

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ABSTRACT

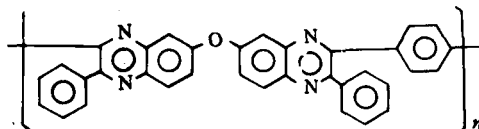
Three polycaprolactam samples modified by 0.05—0.50% polyphenylquinoxaline (PPQ) by weight were prepared. Their structure and mechanical properties were characterized by FT-IR, SEM, density, tensile impact, DTA and visco-elastic method. PPQ induced the formation of "crystal grains" distributed evenly over nylon spherulites in modified samples, which were observed for the first time, and strengthened modified samples. Modified nylons had higher crystallinities, higher T_g , more nearly perfect spherulites than MC nylon itself, and showed typical reinforcing effect on mechanical properties.

INTRODUCTION

In a previous paper^[1], the preparation, structure and mechanical properties of polycaprolactams (monomer casting nylons i. e. MC nylons) modified by PBI (polybenzimidazole) via in situ polymerization process were discussed. Because of the reactive hydrogens in PBI, a small amount of PBI had a great influence on the superimposed polymerization crystallization process in the activated anionic polymerization of caprolactam. The mechanical properties of modified MC nylons showed an increase in toughness due to lower crystallinities and larger spherulites.

This paper presents MC nylons modified by another aromatic heterocyclic polymer i. e. polyphenylquinoxaline (PPQ) with one ether-linkage in its backbone per repeat unit. The main difference between PBI and PPQ is that there are reactive hydrogens in the former, while none in the latter, which results in modifications quite different from each other. Nevertheless, the method used in the previous paper can be applied to the system of MC nylons modified by PPQ. Results showed that polycaprolactams modified by PPQ did show expected reinforcing effect. Of particular interest was their crystal morphology.

The repeat unit of PPQ is:



EXPERIMENTAL

The same as those described in the previous paper^[1].

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RESULTS AND DISCUSSION

Three modified polycaprolactam samples were prepared. Among them the highest content of PPQ was 0.50%. Beyond this, PPQ would precipitate during the polymerization process of caprolactam. As predicted, PPQ has little effect on the polymerization time of caprolactam (Table 1). This means that PPQ did not react with caprolactam. From the FT-IR spectra, all the characteristic absorption bands of MC nylon also appeared in the spectra of modified samples. So the main chain of MC nylons modified by PPQ remained polycaprolactam, i.e., nylon-6.

As shown in Table 1, the color of modified MC nylons turns deeper as the contents of PPQ increase.

Table 1 Preparation of MC nylons modified by PPQ

Sample	Contents of PPQ by weight (%)	Polymerization time (mins)	Color
No. 1	0	9.5	white
No. 5	0.05	10.0	milk yellow
No. 6	0.20	9.7	light yellow
No. 7	0.50	10.1	yellow

Table 2 Crystallinity and spherulite size of modified MC nylons

Sample	Density (g/cm^3)	Crystallinity (%)	Spherulite diameter (μm)
No. 1	1.1543	51.3	25
No. 5	1.1559	52.4	60
No. 6	1.1571	53.2	50
No. 7	1.1579	53.8	27

STRUCTURE CHARACTERIZATION

The crystallinity of modified MC nylons increases with the increase of contents of PPQ (Table 2) in the following order:

$$\text{No. 7} > \text{No. 6} > \text{No. 5} > \text{No. 1}$$

Nevertheless, as the contents of PPQ rise, the spherulites of modified samples first become larger, then become smaller.

As shown in Fig. 1, PPQ makes the spherulites of modified nylons more nearly perfect. The presence of PPQ in modified nylon is also responsible for the formation of heterogeneous structure which was absent in MC nylon and nylons modified by PBI. Far more interestingly, it is observed that "crystal grains" of $2\mu\text{m}$ in diameter are distributed evenly in nylon spherulites of the modified samples (Fig. 1). The higher the contents of PPQ, the more the crystal grains. It was obvious that these crystal grains were induced by PPQ and they were much stronger than the non-crystalline part of nylon because the latter had been removed when observed on SEM^[1]. So these crystal grains reinforced the modified nylons.

However, just like the modified system by PBI^[1], the T_m and T_c of nylons modified by PPQ measured with DTA unexpectedly vary little from one to another (Table 3). This may be caused by the high heating and cooling rate ($10^\circ\text{C}/\text{min.}$), as the DTA measurement did not completely reveal the superimposed polymerization crystallization process in the activated anionic polymerization of caprolactam^[2,3].

Actually, the effect of PPQ upon the crystalline part of modified nylons led to the differences between their non-crystalline parts. Addition of PPQ caused the T_g 's of modified nylons to shift towards higher temperature. This situation was contributed by both the higher crystallinities and the crystal grains which made segmental motion of modified MC nylons more difficult.

Table 3 T_m , T_c , and T_g of modified MC nylons

Sample	$T_m (^\circ\text{C})$	$T_c (^\circ\text{C})$	$T_g (^\circ\text{C})^*$
No. 1	224.4	174.0	39
No. 5	224.0	171.2	not tested
No. 6	224.5	174.0	48
No. 7	223.8	174.6	51

* Measured by visco-elastic method

CHARACTERIZATION OF MECHANICAL PROPERTIES

The static and dynamic mechanical properties were characterized in order to reveal the relationship between structure and properties of modified nylons.

The stress-strain curves of MC nylons modified by PPQ are quite different from that of MC nylon itself (Fig. 2). Second yielding of MC nylon does not appear in the modified systems. This may be attributed to the testing temperature which was a little lower than the T_g of modified MC nylons samples. But the yield strength of modified samples increases with increase of PPQ contents, and is higher than the first yield strength of MC nylon (Table 4). The ultimate tensile elongation of modified

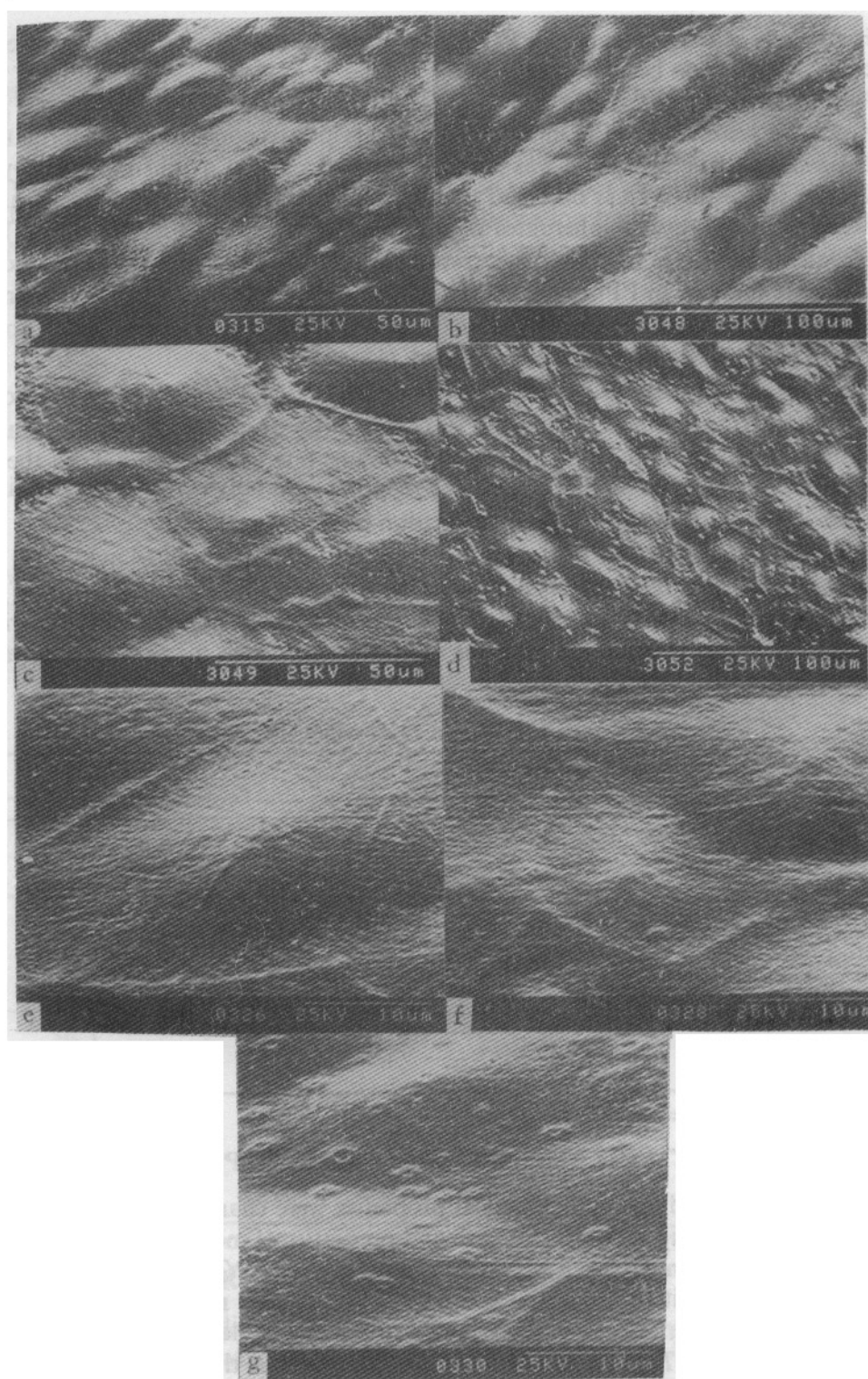


Fig. 1. SEM micrographs of MC nylons modified by PPQ. Their PPQ contents (by weight) are 0% (a); 0.05% (b,e); 0.20% (c,f) and 0.50% (d,g), respectively.

specimens is only one fourth of MC nylon 's .These curves indicate that MC nylon is strong and tough, while modified MC nylons are more stiff and brittle.This change in tensile properties is attributed to higher crystallinities together with the reinforcing effect of crystal grains in modified samples.

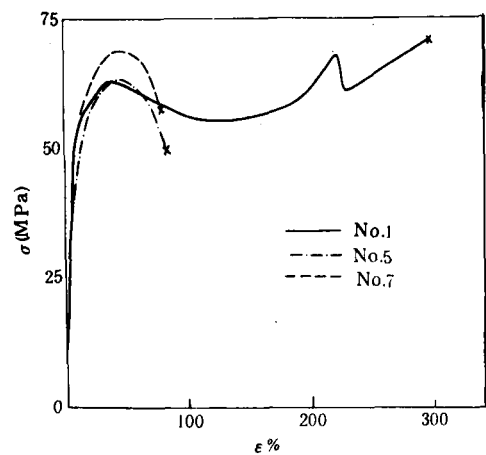


Fig. 2 The tensile properties of modified MC nylons

Table 4 The tensile properties of modified MC nylons

Sample	Tensile strength (MPa)	Ultimate elongation (%)	Yield strength (MPa)	Yield elongation (%)
No. 1	69.5	294	61.6	39
No. 5	62.0	84	62.0	46
No. 6	62.8	69	62.8	44
No. 7	67.5	78	67.5	44

This reinforcing action also appeared in the dynamic properties of MC nylons modified by PPQ (Fig. 3 and Table 5). At a given temperature, as the contents of PPQ increase , the dynamic tensile storage modulus increases. At room temperature, the tensile storage modulus of sample No. 7 (with 0. 5% PPQ by weight) is 30% higher than that of MC nylon itself.

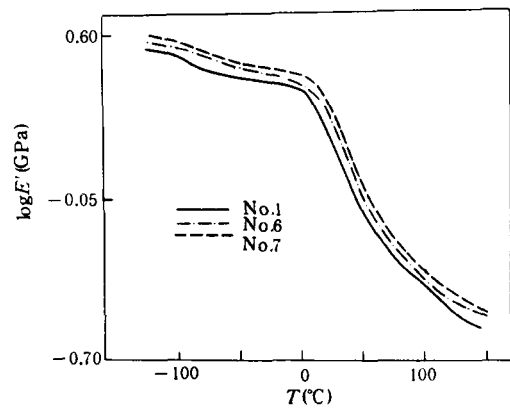


Fig. 3 The dynamic mechanical properties of MC nylons

Table 5 The dynamic tensile modulus of modified MC nylons at different temperature, GPa

Sample	-100 ℃	-50 ℃	0 ℃	25 ℃	50 ℃	100 ℃
No. 1	3.26	2.65	2.38	1.49	0.80	0.39
No. 6	3.45	2.85	2.52	1.84	0.90	0.41
No. 7	3.63	2.98	2.67	1.94	0.96	0.45

Table 6 The impact strength of modified MC nylons

Sample	KJ/m ²	J/m(2.84mm)
No. 1	17.7	50.3
No. 5	27.7	76.9
No. 6	32.8	82.7
No. 7	27.4	78.5

After drying under vacuum, the impact strength of modified nylons is about 60% higher than that of MC nylon (Table 6). The improvement of impact strength results from the larger spherulites and the strengthening effect of crystal grains.

In conclusion, MC nylons modified by a small amount of PPQ had more nearly perfect spherulites, higher crystallinities and higher T_g 's. The strength increase and toughness decrease effect appeared in mechanical properties of modified nylons. This typical reinforcing effect was contributed by their higher crystallinities and the presence of evenly distributed crystal grains. The unique strengthening effect of crystal grains which were observed for the first time, provides a new route for designing new reinforcing materials.

Keywords:

Polycaprolactam; Polyphenylquinoxaline; Modified MC nylon ; Spherulite .

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