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# STUDIES ON THE THERMAL PROPERTIES OF CAPROLACTAM/LONG CHAIN LACTAM COPOLYMER

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## Abstract

The thermal properties of caprolactam/long chain lactam copolymer were studied with a Perkin-Elmer DSC 7. The melting point ($T_m$), heat of fusion ($\Delta H_m$), crystalline degree ($X_c$), crystallization temperature ($T_c$) and glass transition temperature ($T_g$) of the copolymers increase with decrease of the content of the log chain lactam. From the changes in the mechanical properties with corresponding changes in the thermal properties, it is clear that the copolymers are thermal plastic and elastic. In addition, it is found that the results at a heating rate of 10 deg·min$^{-1}$ are almost the same as that at 20 deg·min$^{-1}$ after thermal history is erased.

**Keywords:** caprolactam, cast Nylon, DSC, thermal properties

## Introduction

Cast Nylon (MC Nylon) is widely used as an engineering plastics for its high performance, such as high strength, good wear resistance, self-lubrication, toughness and easy processing [1].

It is convenient to add processing aids or fillers to modify Nylon. In comparison with MC Nylon, caprolactam/long chain lactam copolymers prepared below their melting point, have a lower regularity of molecular arrangement, a lower crystalline fraction and higher amorphous phase. Thus, the copolymers have different thermal and mechanical properties. In this paper, the thermal properties of caprolactam/long chain lactam copolymers are studied by thermal analysis and tested for their mechanical properties.

## Experimental

### Samples

Caprolactam/long chain lactam with various ratios were prepared by anionic copolymerization. Catalyst: NaOH, 0.41 mol/100 mol monomers; co-catalyst triphenylmethane tri-isocyanate, 0.3 mol/100 mol monomers.

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### *Analysis*

The copolymers were cut into small pieces for thermal properties measurement. The samples for mechanical measurement were cast into the standard strips. Tensile strength, elongation at break, impact strength, compressive strength at 25% strain and Vicat softening point (*VSP*) were determined according to Chinese Standards GB 1040–79, GB 1041–79, GB 1041–79 and GB 1633–88, respectively.

A Perkin-Elmer DSC 7 differential scanning calorimeter system was used to measure the thermal properties of the copolymers. Temperature and calorimetric calibration of the apparatus were made with highly pure Indium supplied by PE Company. An empty aluminium pan was used as the reference. The sample weight was about 10 mg. In order to erase the thermal history of the samples, they were heated at a rate of 10 to 30 deg·min$^{-1}$ beyond the higher end of melting peaks for 10 min and then were cooled to the room temperature at the same rate [2]. After the apparatus was stabilized, $T_m$ and $\Delta H_m$ of the copolymers were determined at a heating rate of 10 deg·min$^{-1}$, while $T_c$ was determined at a cooling rate of 10 deg·min$^{-1}$. After the samples were kept in the oven at 70±2°C for an hour, $T_g$ was determined at a heating rate of 20 deg·min$^{-1}$. All measurements were run under a nitrogen atmosphere. All data were treated by an online PC computer.

Crystalline degree of copolymers was calculated according to [3].

$$X_c = \Delta H_m / \Delta H_m^o$$

where $\Delta H_m$ is the fusion heat of the samples; $\Delta H_m^o$ is the heat of fusion for crystalline samples, for Nylon 6, $\Delta H_m^o = 188.28$ J/g [4].

## Results and discussion

### *The influence of the content of the long chain lactam on the thermal properties of the copolymers*

Figure 1 is DSC curves of caprolactam/long chain lactam copolymers. The influence of the content of long chain lactam on the thermal properties of the copolymers are shown in the Figs 2 and 3.

It was found that $T_m$, $T_g$, $T_c$, $\Delta H_m$, and $X_c$ of the copolymers all decrease linearly.

The flexibility of the primary chains of Nylon 6 is increased, whereas $T_g$ of copolymers is decreased, because the addition of long chain lactam breaks up the regularility of polymer chains and weakens the interaction between polymer chains, owing to a decrease in the number of hydrogen bonds between Nylon 6 molecules. The higher the content of long chain lactam is, the smaller $T_g$ of copolymers is, as shown in Fig. 2. $T_g$ is reduced from the original 57.25 to

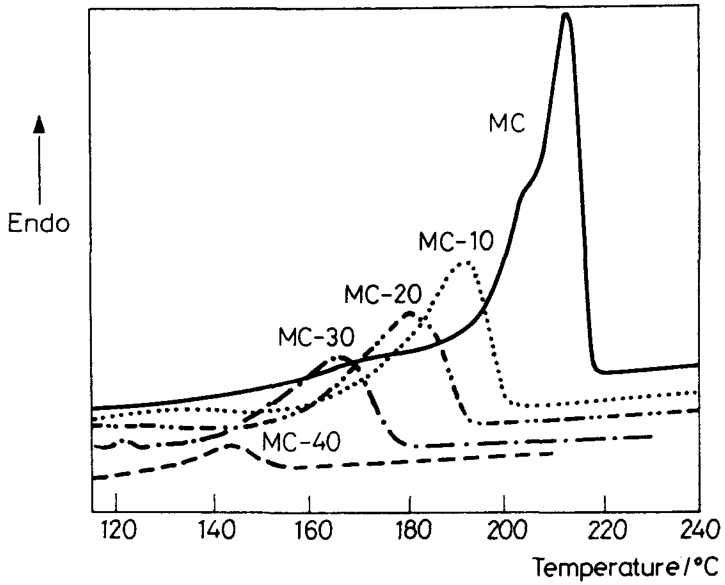

**Fig. 1** DSC curves of caprolactam/long chain lactam polymer

32.51°C with an addition of 40% long chain lactam. The long chain lactam breaks up the regularility of polymer chains, crystallizability of the copolymers is reduced and the crystalline fraction in the copolymers is reduced whereas the amorphous fraction is increased (Fig. 3). In some cases, the crystallizability is even lost entirely. The copolymer with 40% long chain lactam is almost amorphous with $X_c$=1.23%, which is about one-eighteenth of that of the original samples. The amorphous fraction packs more loosely than the crystalline fraction so as to give the copolymers elasticity. The long chain lactam acts as an inner plasticizer in the copolymer, which is substantiated by the decrease of $T_m$ and $X_c$.

## *The influence of thermal histories of the samples on the thermal properties*

Experiments on thermal histories were carried out at a heating rate of 10 deg·min$^{-1}$ and a cooling rate of 10 deg·min$^{-1}$. In order to melt the samples totally and to keep the apparatus in equilibrium, the temperature at the end of every measurement was kept constant for 10 min. Results of the three continuous measurements are summarized in Table 1. It is clear that the data for the second and the third are higher than those for the first, for the cooling history of the sample in the first measurement result from the cast process, and is different from those in the second and third measurements. Whereas, there is only

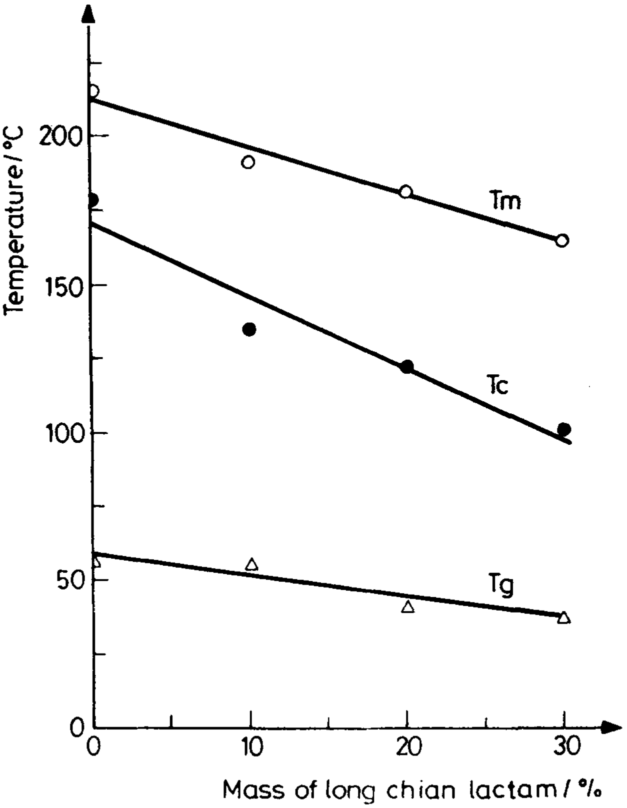

**Fig. 2** The correlation between specific temperatures and the contents of long chain lactam

a little difference between those for the second and the third, partly because the sample have the same thermal histories so that they are in the same condition of crystallization, and partly because the hydrogen bonds are formed firmly after crystallization of polyamides so that the structure of the crystal is more stable. It is concluded that the second results are fit to compare the thermal properties of the samples. However, the first heat of fusion should be used to calculate the crystalline degree of the original sample.

### *The influence of the heating rates (Φ) on the analyzed results*

$T_m$ and $\Delta H_m$ values of the sample with 10% long chain lactam with their original thermal histories erased at a variety of the heating rates are listed in Table 1. It is found that the $T_m$ values are nearly the same at $\Phi=10$ and 20 deg·min$^{-1}$, whereas at $\Phi \geq 20$ deg·min$^{-1}$, the $T_m$ value will increase with the

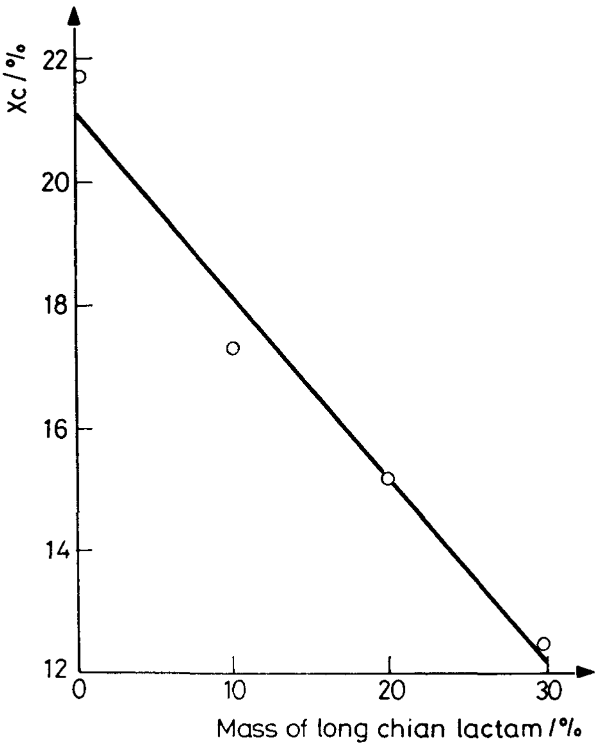

**Fig. 3** The correlation between degree of crystallinity and the contents of long chain lactam

increase of the Φ value, for the temperature gradient between oven and sample is increased with the increases of Φ value so that the system does not response as fast. However, the Φ values hardly affect the heating $\Delta H_m$ values, and the $X_c$ values derived from $\Delta H_m$ reach a constant value because the crystals are very stable. It is concluded that a heating rate of 10 or 20 deg·min$^{-1}$ is reasonable for thermal analysis.

### *Mechanical properties of the copolymers*

The mechanical properties of the copolymer are listed in Table 3.

It is found in Table 3 that the tensile strengths are reduced a little, whereas the elongation at breaking and the impact strengths at room and lower temperatures are improved remarkably with the increase of the content of long chain lactam in the copolymers. With the compressive strength at 25% strain, the higher the content of long chain lactam is, the better the rubberlike elastic resilience of the copolymers is. The thermal properties of the copolymers shown in Figs 1 to 3 supports the mechanical properties of the copolymers. It is con-

**Table 1** The influence of the thermal histories of the copolymers on thermal properties

| Percentage of long chain lactam in copolymers | $T_m$ /°C | | | $\Delta H_m$/J·g$^{-1}$ | | |
|---|---|---|---|---|---|---|
| | the first | the second | the third | the first | the second | the third |
| 0 | 214.28 | 215.82 | 216.25 | 57.25 | 41.44 | 41.42 |
| 10 | 185.43 | 191.63 | 191.83 | 27.22 | 32.61 | 31.57 |
| 20 | 173.95 | 181.62 | 184.17 | 29.08 | 29.02 | 28.09 |
| 30 | 163.23 | 165.87 | 168.50 | 27.23 | 23.93 | 23.56 |
| 40 | 139.72 | 143.67 | 144.37 | 12.17 | 2.31 | 2.27 |

Table 2 The effects of the heating rate on the thermal properties of the copolymers

| $\Phi$ deg·min$^{-1}$ | 10 | 20 | 30 | 40 |
|---|---|---|---|---|
| $T_m$ /°C | 191.35 | 191.90 | 193.33 | 195.42 |
| $\Delta H_m$/J·g$^{-1}$ | 30.51 | 31.67 | 30.27 | 30.85 |
| $X_c$ /% | 16.0 | 16.6 | 15.9 | 16.2 |

cluded that the research on the properties of polymeric materials may be used to guide the design of its engineering application.

Table 3 The mechanical properties of caprolactam/long chain lactam copolymers

| Percentage of long chain lactam in copolymers | | 0 | 10 | 20 | 30 | 40 |
|---|---|---|---|---|---|---|
| Tensile strength /MPa | | 87.4 | 81.7 | 58.2 | 57.4 | 63.6 |
| Elongation at break /% | | 30.2 | 72.0 | 232 | 294 | 337 |
| Compressive strength at 25% strain /MPa | | 93.4 | 68.7 | 45.9 | 41.3 | 30.7 |
| Vicat softening point /°C | | 213 | 200 | 171 | 141.5 | 125 |
| Impact strength (gap) / kJ·M$^{-2}$ | 25°C | 8.16 | 11.1 | 22.5 | 24.3 | 25.9 |
| | –40°C | 5.11 | 7.96 | 8.65 | 7.83 | 8.82 |

## Conclusion

1. It is concluded form the DSC analysis of caprolactam/long chain lactam copolymers that the $T_g$, $T_m$, $T_c$, $\Delta H_m$ and $X_c$ values all decrease linearly with increase of the content of long chain lactam. When the content of long chain lactam is up to 40%, the copolymer is almost completely amorphous.

2. The samples crystallize under the same conditions during the second and third heating measurements so that there is the same value of $\Delta H_m$. But $\Delta H_m$ value in the first heating measurement differs from those in the second and the third, for the crystallization conditions is determined by the cast process of the samples in the first heating measurement.

3. $T_m$ value changes only a slightly when $\Phi$ value changes form 10 to 20 deg·min$^{-1}$. However, $T_m$ value is increased with the increase of $\Phi$ value when $\Phi$ value is higher than 20 deg·min$^{-1}$.

4. The changes in mechanical properties accompany the changes in thermal properties correspondingly. Thus, the research on the thermal properties of polymer material can be used to guide the design of its engineering applications.

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**Zusammenfassung** — Mittels eines Perkin-Elmer DSC 7 wurden die thermischen Eigenschaften eines Kaprolaktam/Langkettenlaktam-Kopolymers untersucht. Mit abnehmendem Gehalt an Langkettenlaktam steigen der Schmelzpunkt ($T_m$), die Schmelzwärme ($\Delta H_m$), der Kristallinitätsgrad ($X_c$), die Kristallisationstemperatur ($T_c$) und der Glasumwandlungspunkt ($T_g$) des Kopolymers. Aufgrund der Änderungen der mechanischen Eigenschaften mit den entsprechenden Änderungen der thermischen Eigenschaften ist es eindeutig, daß die Kopolymere the mische Plaste und Elaste sind. Zusätzlich fand man, daß die Ergebnisse bei einer Aufheizgeschwindigkeit von 10 grad·min$^{-1}$ fast die gleichen sind wie bei 20 grad·min$^{-1}$, nachdem die thermische Vorgeschichte gelöscht ist.