

THERMAL BEHAVIOUR OF γ -IRRADIATED NYLON 610

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ABSTRACT

The thermal behaviour of γ -irradiated nylon 610 was investigated. In DSC (differential scanning calorimetry) thermograms in addition to general features characteristic of γ -irradiation cross-linked crystalline polymers, a typical cold-crystallization phenomenon was observed during the second scan for samples that had been subjected to high radiation dose. G-values for crosslinking nylon 610 were estimated from gel fraction measurement and TMA (thermomechanical analysis). From TMA curves it was estimated that the dimensional stability of properly irradiated nylon 610 articles might be raised up to ca. 300°C.

Nylon 610 is one of the important engineering plastics. In addition to a combination of high strength, elasticity, toughness and abrasion resistance in common with other polyamides, it features lower moisture absorption and thus higher dimensional stability. Since the additional hydrocarbon segments in the sebacic acid gives the polymer a lower melting point (215°C for nylon 610 vs. 265°C for nylon 66), it is of interest to upgrade its properties by transforming it into a network polymer as nylon is a γ -radiation crosslinkable crystalline polymer^[1]. In the present work, the thermal behaviour of the γ -irradiated nylon 610 was studied by using differential scanning calorimetry, thermomechanical analysis and gel fraction measurement techniques. The G-value which characterizes the γ -radiation effect on the polymer was evaluated and an estimation was made that it is possible to raise the dimensional stability of the irradiated article up to ca. 300°C.

EXPERIMENTAL

Sample: Nylon 610 used in this study was a granular commercial product of Heilongjiang Nylon Factory, Harbin. Its intrinsic viscosity $[\eta]$ in m-cresol at 25°C was 0.96 dl/g which corresponded to a $\bar{M}_n$ of 1.02×10^4 ^[2]. The granules were extracted with methanol. After vacuum drying, films of 0.15 and 0.5 mm in thickness were prepared by compression moulding at ca. 220°C for 1 to 2 mins. Thereafter, they were cooled under different conditions. Thus, the prepared specimens were all in α -crystalline form as evidenced by WAXD. Irradiation was carried out in a ⁶⁰Co γ -ray source at room temperature under vacuum (1×10^{-3} torr). After irradiation, the samples were annealed with the exclusion of air at 120°C for 4 hours.

DSC: A Perkin-Elmer differential scanning calorimeter (DSC-2C) equipped with a 3600 TADS microprocessor was used to record the thermograms (normalized to sample weight). The instrument was calibrated with a standard indium. Unless otherwise stated, the scan rate was 20K/min.

TMA: The thermomechanical experiment was performed on a Perkin-Elmer model TMS-2 thermomechanical analyzer. The effective dimension of the specimen was $0.15 \times 2 \times 5$ mm. Th-

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specimen was first heated at a rate of 10K/min to the prescribed temperature, where the specimen was in its rubbery state, and the temperature was held isothermally. Load was applied in steps of 1 gram and the corresponding elongation of the specimen was recorded.

Gel fraction determination: Gel fraction of the irradiated specimen was determined by extraction with m-cresol at room temperature for 15 days in dark.

RESULTS AND DISCUSSION

I. Thermal behaviour of γ -Irradiated Nylon 610

Fig. 1 illustrates the DSC endotherms and exotherms (normalized to sample weight) of γ -irradiated water-quenched nylon 610 specimen. The specimen is shown to have three transitions in the heating curves (a). The transition around 325K is the glass transition. A small peak at ca. 410K corresponds to the melting of imperfect crystals formed during 120°C annealing subsequent to

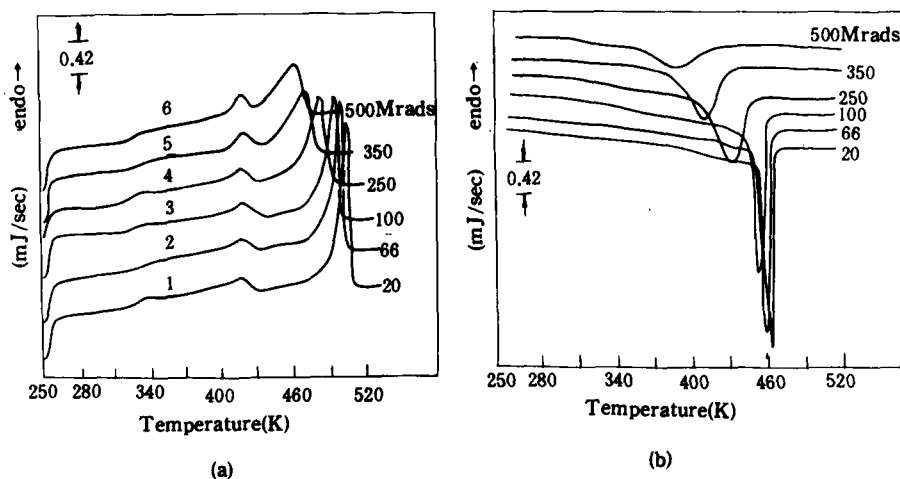


Fig. 1 DSC 1st scan endotherms (a) and exotherms (b) of nylon 610 subjected to different radiation dose

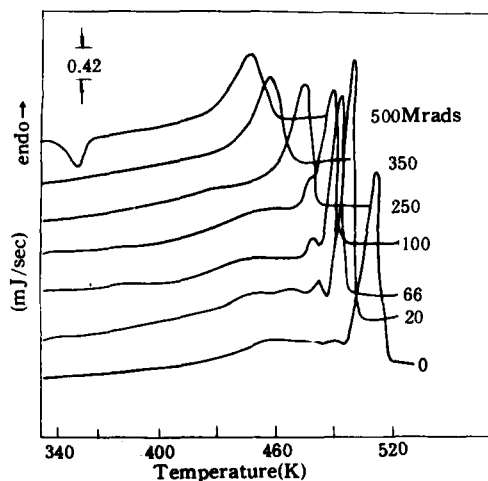


Fig. 2 Second scan endotherms of irradiated nylon 610.

irradiation. The location of the peak on the curve is independent of the radiation dose R . However, the position of the main peak is closely related to R . The higher the radiation dose, the lower the peak temperature. In the cooling curves (b), only a single crystallization peak is observed, which also shifts to lower temperature and broadens with R . The heat of fusion ΔH_m and heat of crystallization ΔH_c of the irradiated specimen also decrease with the increase in radiation dose.

A second scan was made to single out the thermal behaviour of the crosslinked and degraded molecules resulting from the γ -irradiation (Fig. 2). The curves shown in Fig. 2 are quite different from those in Fig. 1(a) in points of detail. Instead of the annealing peak at around 410K, there is a small lower melting peak beside the main peak. A supposition proposed in a previous paper^[3] has attributed this endothermic effect to the melting of imperfect crystals formed during cooling of the melted specimen after first heating. When the radiation dose was further increased, a completely different thermal event, i.e. a typical cold crystallization exotherm, manifested itself above T_g .

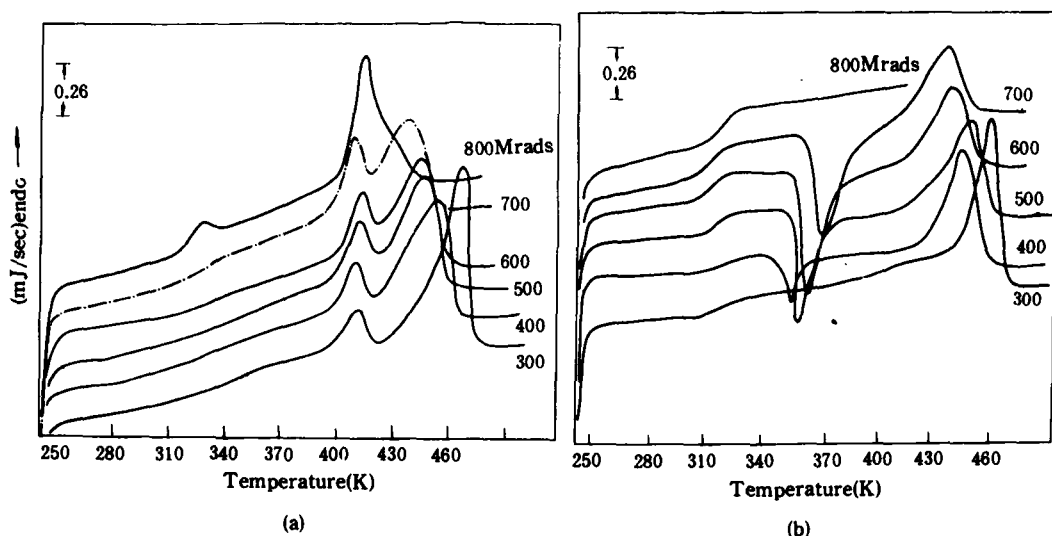


Fig. 3 DSC endotherms of 1st-scan (a) and 2nd-scan (b) for nylon 610 samples subjected to high radiation dose.

In order to elucidate the appearance of cold crystallization, additional samples were irradiated at doses around 500 Mrads. It is again found that although the first-scan endotherms (Fig. 3(a)) are similar to those of low dose irradiated samples, the second-scan DSC curves are markedly different from the first-scan curves. Except for the sample subjected to a dose of 300 Mrads where no cold crystallization peak appeared, and for the sample subjected to 800 Mrads for which neither cold crystallization peak nor melting peak showed up, samples irradiated at 400–700 Mrads all exhibited cold crystallization. Besides, on increasing radiation dose, cold crystallization peak shifted to higher temperatures while the melting peak to lower temperatures (see Fig. 3(b)).

The cold crystallization phenomenon is related to the thermal history of the sample. The higher the crystallinity of the sample before irradiation, the less obvious is the phenomenon. For samples with higher crystallinity, the cold crystallization temperature, T_c , is lower than that of the low crystallinity samples and T_m is also higher. In addition, it is also found that the programmed cooling rate during crystallization from the melt also influences the cold crystallization behaviour, i.e. the phenomenon is less obvious with the lowering of cooling rate. However, neither T_c nor T_m is affected

in this case.

No work has been published on the cold crystallization phenomenon of high dose irradiated crosslinkable crystalline polymers. We realized that only with the presence of a definite amount of crosslinked network and also of molecules partly crosslinked but not yet transformed into a complete network, the cold crystallization would manifest itself in the second-scan DSC thermogram. The inability for cold crystallization to occur above T_g during the first-scan is due to the presence of the original crystal which restricts the free motion of the above-mentioned molecules. Furthermore, the specimen crystallizes only poorly after first heating because of the presence of a considerable amount of crosslinks in the melt, and is basically non-crystalline as evidenced by the distinct glass transition in the second-scan endotherms. When it is heated above T_g , the molecules are mobile and cold crystallization sets in. Since molecular motion for a densely crosslinked sample is rather difficult than that in a lightly crosslinked one, on increasing radiation dose, T_c is increasingly higher and T_m of the thus formed less perfect crystals becomes lower and lower.

As it is well known, a high dose irradiated crosslinkable polymer is composed of sol and gel fractions. It is questioned which one, the gel or sol fraction, plays an important role in the appearance of cold crystallization. In order to solve this problem, irradiated samples were separated into gel and sol fractions by m-cresol extraction and observed separately. The second-scan DSC curves of the gel samples are shown in Fig. 4. In comparison with their respective unextracted samples, only those gel samples irradiated with doses of 400 and 500 Mrads exhibit distinct cold crystallization peaks. Gel sample of $R = 600$ shows only a trace of cold crystallization. The magnitude of the exhibited cold crystallization peak of the gel is considerably smaller than the of the corresponding unextracted sample. Besides, T_c is higher and T_m is lower than the original sample. All these facts indicate that the cold crystallization of the gel is rather difficult and the crystal thereof is very poor in its perfection.

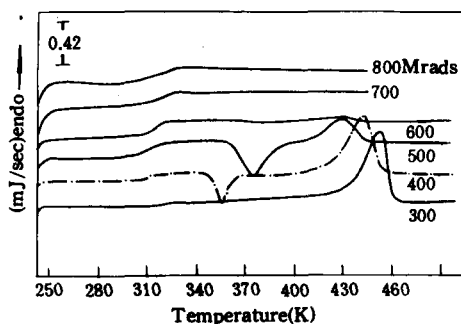


Fig. 4 2nd-scan DSC curves for gel samples extracted from high radiation dose irradiated nylon 610 samples

Therefore, it is believed that the second-scan cold crystallization of high-dose irradiated nylon 610 results from two different kinds of molecules in the glassy state before programmed heating. The one is the molecules in the gel, the chain length between crosslinks in the network is long enough to crystallize. The other is the molecules in the sol, partly crosslinked or branched but not yet transformed into a complete network and thus still soluble. However, chain length between crosslinks in a dense network is too short to participate in cold crystallization; or long enough partly crosslinked or branched molecular chains would have already crystallized during cooling from the

melt. Thereby cold crystallization would never take place in either case.

To examine the effect of γ -irradiation on nylon 610 samples in a different way, stretching in rubbery state was used to evaluate the average molecular weight of the chains between crosslinks, M_c . Fig. 5 illustrates TMA curves of the irradiated nylon 610 specimens. Since T_m is different for

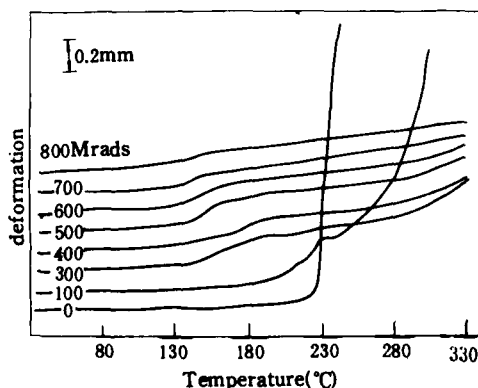


Fig. 5 TMA diagram of nylon 610 samples irradiated with different radiation dose.

samples irradiated at different R , the temperature at which rubbery plateau manifests itself is also different. Except for the sample with $R=100$ Mrads, which would flow under load due to incomplete network formation, the relationship between stress σ and stretching ratio λ for all other samples is in agreement with the classical expression of high elasticity in terms of plateau temperature $T^{[6]}$.

$$\sigma = \frac{\rho RT}{M_c} (\lambda - \lambda^{-2}) \quad (1)$$

where ρ is density and R gas constant. Listed in Table 1 are the M_c values for samples irradiated with different R .

It is obvious that below 500 Mrads M_c decreases linearly with R . However, it drops right at $R = 600$ Mrads and seems to be unchanged with further increase in R . This result is quite in conformity with the change of gel fraction values g with R , where an abrupt decrease in g with R also occurred when R is greater than 500 Mrads. Possibly, with $R > 500$ Mrads, the whole specimen is nearly a complete network. If the radiation dose is further increased, instead of linear macromolecules, crosslinked network is now the predominate place subjected to γ -irradiation. Additional crosslinking in network leads to further decrease in M_c and at the same time some part of the network chains is cleaved and become soluble. Therefore, under high radiation dose, the

Table 1 M_c values for nylon 610 samples irradiated with different radiation dose

R (Mrad)	300	400	500	600	700	800
T (K)	473	473	463	443	443	443
$M_c \times 10^{-3}$	6.1	5.9	5.7	3.1	3.6	3.0

mechanism and district subjected to γ -irradiation might be quite different from those under low radiation dose.

II. γ -Irradiation effect on Nylon 610

Based on the relationship between g and R as well as the dependence of M_c on R , an estimation of the effect of γ -irradiation on nylon 610 was made. The values ($S + S^\dagger$) and their corresponding $1/R$ for samples irradiated with different dosage in the range of $R < 500$ Mrads are tabulated in Table 2, where S is the sol fraction of the irradiated sample ($S = 1 - g$).

Table 2 $S + S^\dagger$ and the corresponding $1/R$ of irradiated nylon 610

$S + S^\dagger$	1.27	0.901	0.354	0.290	0.233
$1/R$ (Mrad $^{-1}$)	0.020	0.010	0.0033	0.0025	0.0020

The values in Table 2 show linearity in ($S + S^\dagger$) vs. $1/R$ plot leading to the following equation by linear regression with a correlative coefficient r of 0.982.

$$S + S^\dagger = 0.169 + 58.3(1/R) \quad (2)$$

If equation (2) is compared with the well-known Charlesby-Pinner's equation⁽⁴⁾

$$S + S^\dagger = P_0/q_0 + 1/q_0 u_1 (1/R) \quad (3)$$

the ratio of fracture to crosslinking p_0/q_0 is 0.169 and $1/q_0 u_1$ 58.3, where p_0 is the proportion of main chain units fractured per unit radiation dose, q_0 the proportion of monomer units crosslinked per unit radiation dose and u_1 the average degree of polymerization before irradiation. Since u_1 is known, q_0 is equal to 4.72×10^{-4} . According to the following expression^[5a]

$$G = 0.48 \times 10^6 q_0 / w \quad (4)$$

the G -value for crosslinking nylon 610 is calculated to be 0.80, where w is the molecular weight of the monomer unit. By putting $S + S^\dagger = 2$ into equation (2), the gelation radiation dose is evaluated to be 31.8 Mrads.

From an alternative expression of equation (4)^[5a]

$$G = 0.48 \times 10^6 M_c R \quad (5)$$

G -value can also be calculated in terms of M_c and its corresponding R . In the dose range, where $R \leq 500$ Mrads, the calculated values for $R = 300, 400$ and 500 according to equation (5) are 0.26, 0.20 and 0.17 respectively. The mean value is 0.23. This value is at best a rough estimation, because strictly speaking, M_c should be independent of the radiation dose subjected to. Possibly, it is because that, as stated by Charlesby^[5b] during the derivation of equation (5), for very high degree of crosslinking, the average length of the chains falls well below that required to justify the assumption of a Gaussian distribution in chain length. But it is more possible that the discrepancy in G -values may arise from the fact that these two different methods of measurement are sensitive to different definitions of crosslinking. In the case of TMA, only those crosslinks which sustain the applied stress, i.e. effective crosslinks, will be reflected in the stretching behaviour. Thereby the resulting

M_c value is higher and G-value is depressed. However, in the case of gel fraction measurement both effective and ineffective crosslinks in the mechanical sense are basically responsible for the gel formation, thus leading to a higher G-value.

So far we have discussed the different aspects of the effect of γ -radiation on the thermal properties of nylon 610. An inevitable question is that to what degree could the temperature be raised to keep the dimension of a properly irradiated nylon 610 article still remaining stable as compared to that of the unirradiated one. In the light of TMA curves in Fig.5, it is estimated that with $R = 300$ Mrads nylon 610 sample could be kept in rubbery state up to 300°C without flow. Therefore, the irradiated nylon 610 appears to be a potential high temperature engineering plastic.

Keywords:

γ -Irradiation; Crosslinking; Nylon 610; Cold crystallization

Acknowledgment:

The authors wish to thank Professor Z.L. Feng for her constructive comment and valuable instruction.

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