Mechanical Relaxation Process at 208 K for Highly Irradiated Polytetrafluoroethylene

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Synopsis

The internal friction of highly irradiated samples of polytetrafluoroethylene(PTFE) was measured over the temperature range below the room temperature transition; the results indicated the appearance at 208 K of a mechanical relaxation between the γ and the β processes.

The relaxation at 208 K was sensitive to effects of thermal treatments; when the relaxation weakened in intensity, the α and the β processes were emphasized. The apparent activation energy estimated was consistent with that of the relaxation which had appeared at the same temperature for as-polymerized PTFE. The 208 K relaxation seems to be attributed to local mode motion in the intermediate phase, in which molecules arranged in parallel but with random chain separation.

INTRODUCTION

Polytetrafluoroethylene(PTFE) has multiple relaxations, designated by α, β, and γ in decreasing temperature order,[1,2] together with crystalline transitions at room temperature and the melting point. The γ process may be regarded as local mode motion of amorphous regions.[3] The crystalline transition at 292 K is due to hindered rotation around chain axes and that at 303 K to translational movement along chain axes; these are accompanied by structure transformations from triclinic to hexagonal through quasihexagonal.[4] In addition, internal friction measurements for PTFE particles as-polymerized pointed out the existence of a relaxation appearing at 208 K between the β and γ dispersions;[5,6] no appearance of the relaxation was detected after the virgin material was sintered at temperatures above the melting point. It appears that at least two sorts of crystalline states exist in the particles which have a high degree of crystallinity (above 85%)[5,7] and a high molecular weight; the double endothermic peaks for each of the three crystalline transitions obtained by means of differential thermal analysis give evidence for this.[8,9]

When the sintered materials of PTFE were exposed to γ-rays, the major radiation damage is scission of the backbone chains.[10,11] The decrease in temperature of the crystalline transitions becomes significant at large radiation doses.[12-14] Furthermore, crystallization of the samples irradiated with radiation doses near 10^8 roentgen(R) generated morphological banded structures on the fracture surfaces;[15,16] the length of the bands was comparable with the chain length of the sample.[16] The band width of folded chain lamellae of ordinary PTFE[17-19] is rather long, approximately 200 nm, but has never reached full chain length so far.

Effects of thermal treatments on the 208 K process for the samples with doses above 10^7 R were studied by means of an improved torsional pendulum. Highly irradiated PTFE was crystallized from the molten state in order to grow fully extended chain crystals.

EXPERIMENTALS

Materials

Commercial sheets of PTFE were used as original, unirradiated samples. Irradiation with γ-rays of ^{60}Co source was carried out in air at room temperature. Irradiated samples were the same as those used previously.[11,16] The radiation doses were 5.7×10^7, 7.5×10^7, 1×10^8, 3.2×10^8, and 5.5×10^8 R. Thermal treatments for two samples with doses of 5.7×10^7 and 1.8×10^8 R were carried out by quenching and by cooling from the melt at two different rates of 0.2 and 2 K/min. All other samples were cooled at 2 K/min from the molten state. The composite specimen impregnated into glass multifilaments was used because of the low viscosity in the molten state. A blank test of glass braids (130 × 0.3 mm) was made; no anomalous changes were observed over the measuring temperature range. The measurement was carried out at heating rates of 1–2 K/min in an atmosphere of flowing dry nitrogen over the temperature range from 90 K to 330 K. The measuring frequency was nominally 0.5 Hz. A relative shear modulus was obtained by normalizing with respect to a shear modulus at a low temperature.

Micrographs of fracture surfaces were obtained with an electron microscope (JEOL-7A); a two-stage replica technique was used after platinum-carbon evaporation. Differential thermal analysis (DTA) was carried out to confirm the melting point of the samples subjected to lower radiation. The DTA apparatus used was described elsewhere.[20]

Automated Torsional Braid Analysis(TBA)

The apparatus of TBA was made on the basis of a prototype by Gillham.[21,22] The detailed description of the apparatus has been given elsewhere.[23] An automated assembly was constructed by use of a 16-bit computer (HP-9826) and interface cards for analog-digital(A/D) and D/A converters, buffer memory, and pulse train cards. All operations were controlled from the computer in terms of softwares programmed in HP BASIC language.

An approximately linear range of light transmission versus angular displacement between two polarizers was kept by moving one lower polarizer automatically with a pulsemotor before the measurement. A stimulus of step-function type was applied through a solenoid connected to a D/A converter in order to trigger the damping oscillation.

The temperatures of the sample were read before and after input of a measuring damped wave. The average temperature was used as the sample temperature. The digitized data of a damped wave and the sample temperature were stored in a buffer memory and data processed by the computer were stored on a floppy disc as a data file.

The sampling number per damped wave was fixed to be 1024. The sampling time was of the order of ten milliseconds. The number of maximum and

TABLE I
Loss Peak Temperatures of Mechanical Dispersions for
Two Highly Irradiated PTFE Samples

Radiation dose/R	Average molecular weight[a]	Loss peak temperature/K[b]				
		γ			T_r	T_m
Unirradiated[c]	~ 10^7	166	not	292	300	600
		(0.65)		(0.4)	(0.4)	(0.15)
5.7×10^7	3.2×10^4	170	208	291	301	599
		(0.75)	(0.7)	(0.6)	(0.5)	(0.1)
1.8×10^8	1.2×10^4	163	200	288	299	591
		(0.8)	(0.7)	(0.5)	(0.45)	(0.1)

[a]Approximate values evaluated from the relation between average molecular weight and radiation dose in Ref. 16.
[b]Values in parentheses are measuring frequencies/Hz.
[c]Loss peaks obtained by TBA method for the dispersion sample melt crystallized.

minimum peaks for a damped wave was from 10 to 20. Data processing was carried out in terms of a peak-finding method.[22] The average periodic time was calculated from the time elapse between the maximum and minimum points obtained. The decay constant was estimated by plotting the amplitudes at these points versus time; the least-squares method was used to estimate its slope. The results of data processing for each run were displayed and printed out with standard deviations. Finally, storage and loss moduli and logarithmic decrement (or loss tangent) were plotted versus temperature using a plotter. Some experimental data presented in this investigation were obtained prior to the automation of the TBA system.

RESULTS

Polytetrafluoroethylene(PTFE) samples, subjected to radiation doses above 10^7 R, were measured over the temperature range from 90 to 330 K by means of a TBA method. In addition, the loss peak temperature of melting was obtained as a function of radiation dose, up to 5.5×10^8 R. Table I gives temperatures of mechanical dispersions for two highly irradiated samples with approximate values of average molecular weight.

Figure 1 shows the temperature dependence of logarithmic decrement of the samples irradiated with doses of 5.7×10^7 R; these samples were thermally treated at three different cooling rates from the melt. The γ and β processes and the room temperature transition were confirmed for all the samples. Another mechanical dispersion was found between these relaxation processes, as will be explained later.

The γ relaxation of the quenched sample showed a typical loss peak, of which the temperature was about 170 K at 0.74 Hz; the logarithmic decrement for two uniformly cooled samples showed almost the same shoulder peak. The loss intensity near 260 K for the β process was larger in the quenched sample than in two samples slowly cooled. The location of the temperature for the crystalline transition was somewhat lower for the
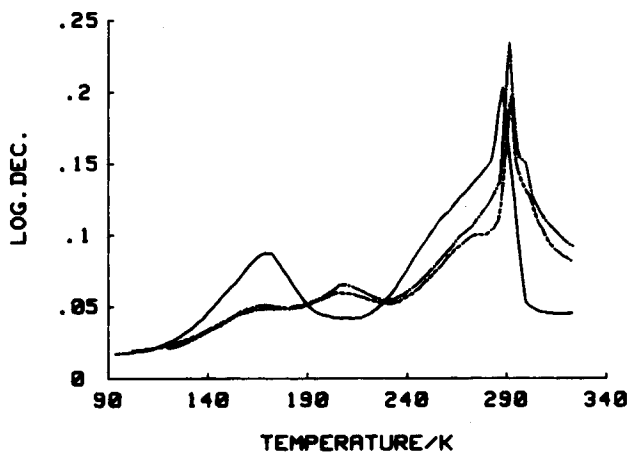
Fig. 1.   Temperature dependence of logarithmic decrement for PTFE samples melt crystallized after irradiation of 5.7×10^7 R at three different cooling rates: straight lines, quenched; two-dotted, 0.2 K/min; one-dotted, 2 K/min.

quenched sample; the other well-crystallized samples showed the same transition temperature.

A mechanical relaxation was found near 208 K at a measuring frequency of 0.7 Hz between the γ and β processes for two slowly cooled samples; the existence of the relaxation was not detected for the quenched sample. The peak of logarithmic decrement was more distinct for the sample cooled at a medium rate than for the sample cooled more slowly. It appears that an intermediate condition of crystallization brought about the larger loss in the relaxation. The tendency of change in loss intensity at 208 K was analogous to that at temperatures just below and above the crystalline transition.

Figure 2 shows the temperature dependence of the relative shear modulus of the corresponding three samples. The modulus of the slowly cooled samples gradually decreased up to room temperature, at which a discontinuous de-
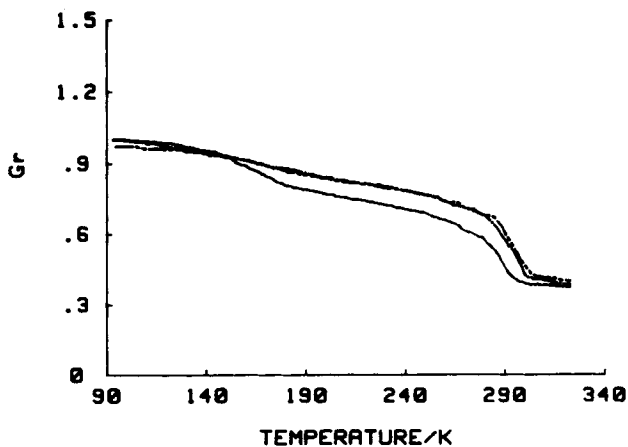

Fig. 2.   Temperature dependence of relative shear modulus for PTFE samples corresponding to respective lines in Fig. 1.
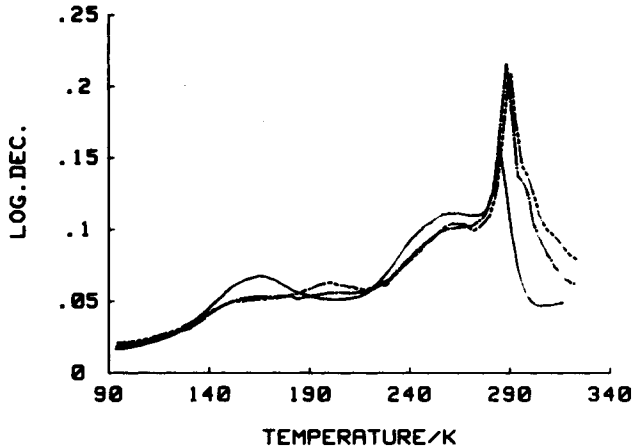
Fig. 3. Temperature dependence of logarithmic decrement for PTFE samples melt crystallized after irradiation of 1.8×10^8 R at three different cooling rates: straight lines, quenched; two-dotted, 0.2 K/min; one-dotted, 2 K/min.

crease occurred. The quenched sample showed an additional decrease, in agreement with the γ process. No appreciable changes in shear modulus at 208 K were observed in this measurement.

Figure 3 shows the temperature dependence of logarithmic decrement of the samples irradiated with doses of 1.8×10^8 R. The three kinds of heat treatments were carried out as well. The overall behavior of logarithmic decrement for two slowly cooled samples paralleled each other up to room temperature, except for the slight differences existing near 200 K and at room temperature. Mechanical loss peaks of the quenched sample were observed in the γ and β processes; the corresponding decrease in shear modulus was also seen, as Figure 4 shows. A shallow loss was found near 200 K in a measuring frequency of 0.7 Hz for the samples cooled at 0.2 K/min; the loss intensity increased as the cooling rate was decreased. Changes in loss at 200 K reflected
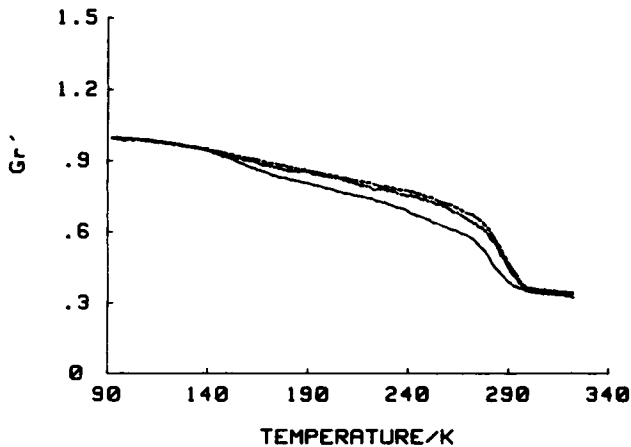
Fig. 4. Temperature dependence of relative shear modulus for PTFE samples corresponding to respective lines in Fig. 3.
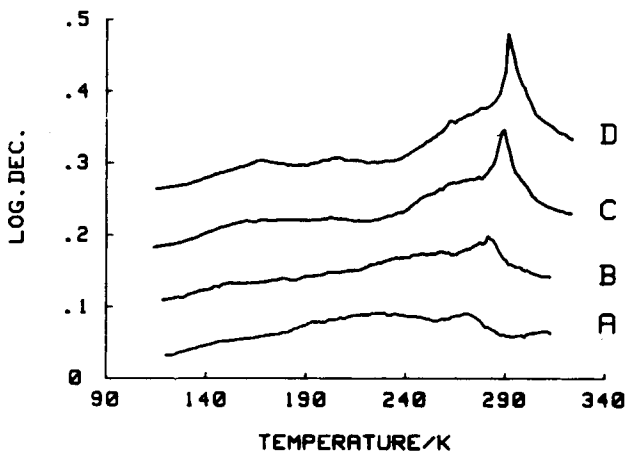
Fig. 5. Logarithmic decrement against temperature for PTFE samples highly irradiated with different radiation doses: A, 5.5×10^8 R; B, 3.2×10^8 R; C, 1×10^8 R; D, 7.5×10^7 R. All samples were cooled from the melt at a 2 K/min. Curves of samples B, C, and D are shifted upward for clarification.

those at temperatures above 303 K. Similar behavior was seen for the samples irradiated with doses of 5.7×10^7 R, as described above.

Figure 4 shows the temperature dependence of the relative shear modulus of the samples with radiation doses of 1.8×10^8 R. The shear modulus decreased monotonically as the temperature was increased, then decreased rapidly in the vicinity of the room temperature transition of all the samples; a slight decrease was observed in the region of the γ relaxation of the quenched sample. The temperature location of the decrease corresponding to the room temperature transition was slightly lower for the quenched sample.

Figure 5 shows the temperature dependence of logarithmic decrement for the samples irradiated with doses from 7.5×10^7 to 5.5×10^8 R. The thermal treatment of all the samples was made by cooling at an intermediate rate of 2
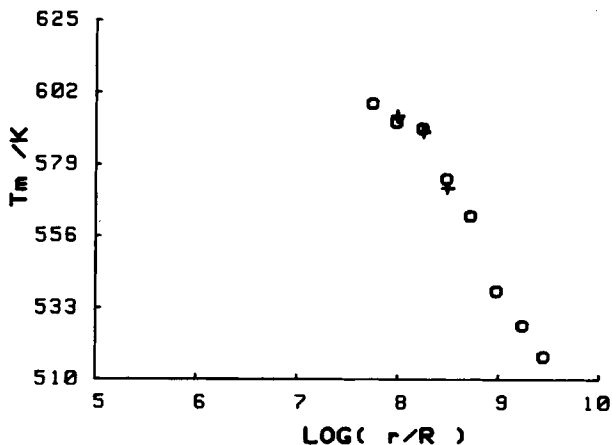

Fig. 6. Loss peak temperatures of melting for highly irradiated PTFE as a function of radiation dose. Cross denotes the melting point from DTA.

K/min from the melt. The γ relaxation showed a small loss shoulder, independent of radiation dose. The loss intensity of the crystalline dispersion became smaller as the doses increased. The so-called 208-K relaxation existed for these samples; its loss region gradually overlapped the β relaxation. The temperature location of each mechanical dispersion tends to decrease with increasing radiation dose.

Figure 6 shows radiation dose dependence of the loss peak temperature in the melting region for several highly irradiated samples. The apparent melting temperature, which was about 600 K for unirradiated material, became lower at radiation doses above 10^8 R. The decreasing temperature appears to be proportional to the logarithm of the radiation doses. In addition, the melting temperatures determined from DTA for lower irradiated samples were consistent with values obtained from mechanical loss.

DISCUSSION

Since the overall damage of r-irradiation to PTFE is scission of backbone chains,[10,11] the radiation effect facilitates crystallization from the melt; for the highly irradiated samples, crystalline portions formed by melt crystallization can be constructed from almost fully extended chains.[15,16] A typical micrograph of fracture surfaces of the sample crystallized after irradiation of 1×10^8 R showed that end-surfaces of fully extended chain crystals were exposed among morphologically banded structures.[16] In radiation dose regions above 10^8 R, the growth of such crystalline structure is feasible, instead of the growth of folded chain crystals which are a typical crystal state for PTFE with long chain length.[19] Furthermore, the feasibility of transformation of crystal morphology at about 10^8 R can be supported from the results that the melting points begin to decrease and that chain scission leads to an average molecular weight of the order of 10^4.

When the samples were irradiated with doses of 1.8×10^8 R, the relaxation appearing at 200 K resulted in the largest loss intensity for the slowest crystallization among the three sorts of thermal treatments. The quenched sample showed no loss peak at 200 K but only the shallow loss peak in the γ process which arises from the amorphous regions. In view of the γ process, the amorphous content of two slowly cooled samples seems to be saturated and its decrease is not able to predict by slower coolings because of existence of chain ends. It appears that chain ends caused by high irradiation disturb complete crystalline arrangements. Further crystallization gives rise to the higher loss at 200 K, although the amorphous loss peak remains constant. In addition, the temperature location of the 200 K relaxation suggested that the relaxation originated from a region of more ordered structure \rather than from the amorphous phase.

The samples with doses of 5.7×10^7 R have low molecular weights, but formation of fully extended chain crystals is relatively hard for crystallization of short times; this sample has the largest molecular weight among the samples used here. The rapid cooling for the sample showed a large amorphous loss peak and the loss intensity was changed by cooling rates. In addition, the incomplete segregation of crystals seems to contribute to the γ and the 208 K loss peaks. Behavior of the 208 K relaxation is sensitive to thermal treat-

ments; some moderate crystallization brought about the highest loss peak. It appears that the related region readily transforms to more random structure on rapid cooling and to crystalline phase on more slow cooling. The frequency dependence of the relaxation temperature was obtained by altering moments of inertia of the measuring system, although some uncertainty exists owing to the small shift of the broad loss peak. The apparent activation energy estimated was about 20 kcal/mol.

The 208 K relaxation has been distinctly observed for as-polymerized PTFE;[5,6] this specimen has high molecular weight and high degree of crystallinity. The as-polymerized PTFE particles consist of folded flexible plates in which chains are nearly arrayed;[24] conformational disorders are involved in the high-crystallinity particles.[5,25] Mechanical loss occurs over the short temperature range form 208 K to room temperature. The loss peak at 208 K decreased in intensity as the annealing temperature was increased, while alternatively the γ and β processes were emphasized. The apparent activation energy estimated was about 15–20 Kcal/mol.[6] These results suggest that the relaxation phenomenon at 208 K for as-polymerized PTFE is analogous to that for highly irradiated samples.

The relaxation at 208 K for the irradiated samples seems to result from the regions related to an intermediate structure in which chains were arranged in parallel to each other, with a distribution of interchain distances;[3] in other words, it may be equivalent to a disordered crystalline state involving conformational defects and mobile species. In view of the viscoelastic results and the structure, it seems that motions in the intermediate regions have interacted with amorphous parts and crystalline cores. The 208 K relaxation for highly irradiated samples seems to be ascribed to local mode motion in the intermediate regions. Such intermediate states are generated on formation of fully extended chain crystals; in residual regions except for crystals, more ordered states are favorable rather than random amorphous states owing to shorter chains and the chain stiffness.

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