Annealing Effects on the Viscoelastic Anomaly Between the β and γ Processes for As-Polymerized Polytetrafluoroethylene

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Synopsis

The viscoelastic anomaly found at 208 K for as-polymerized polytetrafluoroethylene (PTFE) is investigated on the basis of thermal treatment dependence of mechanical spectra. The loss intensity and relaxation strength of the anomaly tend to decrease at annealing temperatures much lower than the melting point. The structural region relevant to the anomaly can be rearranged in more ordered states on annealing; accordingly, the loss peak of the crystalline dispersion is intesified, although that of the amorphous γ-relaxation remains nearly unchanged. The anomaly originates from the intermediate or paracrystalline regions, many of which are included in the virgin samples; segmental motions like local mode relaxation are considered.

INTRODUCTION

Polytetrafluoroethylene (PTFE) has relaxation processes called α, β, and γ, in the temperature range below the melting point, together with two solid–solid transitions at room temperature.[1-4] In addition to these processes, a viscoelastic anomaly has been found around 208 K at frequencies of ca. 0.5 Hz for PTFE samples as-polymerized.[5] The loss modulus of the anomaly was more predominant than other relaxation processes; the storage modulus showed an abrupt decrease from the onset temperature of the anomaly up to room temperature, passing through a stepwise change just above 208 K.[5]

The morphology of the as-polymerized PTFE consists of an assembly of particles; in each of these, molecules are arranged in parallel to each other.[6,7] Such an arrangement of long chains is reflected in the high degree of crystallinity, but it partially involves a conformation which deviates from the crystalline alignment.[8]

The viscoelastic anomaly has been observed for the PTFE samples which were irradiated with γ-rays.[9,10] The anomaly for the irradiated sample with a radiation dose of 5.7×10^7 roentgen (R) appeared at the same temperature as that for the as-polymerized PTFE. The anomaly-loss intensity varied with the condition of melt crystallization[10]; the larger loss was observed when the sample was cooled at a medium rate from the melt. Furthermore, the effects of γ-irradiation on the anomaly showed that the location of the peak temperature gradually decreases as the radiation dose was increased.

When the samples with high radiation doses were melt-crystallized, extended chain crystals could form because of the short chains which were generated by scission of backbone chains due to radiation damage.[11-14] A set of such crystals should achieve a high crystallinity, but actually tends to contain irregularities of molecular alignment due to the existence of defects like chain ends and side radicals.

We investigated the effect of thermal treatment on the viscoelastic anomaly for the as-polymerized samples. The results give aid in understanding the relationship between relaxation and structure for PTFE materials. In addition, the results obtained are compared with relaxations and transitions which have been already studied for ordinary PTFE samples. Viscoelastic measurements are carried out at a low frequency for high resolution of multiple dispersions.

EXPERIMENTAL

The PTFE material used is a 60 wt % aqueous dispersion of particles as-polymerized (D-1), supplied by Daikin Industries. The material was impregnated into glass braids consisting of multifilaments. The composite sample was immersed in propanol and then in distilled water to eliminate surface active agents. Drying was carried out by keeping the sample for 56 h in a dry chamber at ambient temperatures. A variety of thermal treatments were done in an atmosphere of flowing dry nitrogen in the measuring furnace. The treatment time, after drying, was 10 h at a treatment temperature of 423 K, and 3 h at 523, 591, and 606 K. After the isothermal treatment was completed, cooling at a rate of 2 K/min was done, except for the natural cooling for the sample of 423 K.

The storage and loss moduli were measured over the temperature range from 100 to 450 K by using an improved torsional pendulum, of which the prototype was developed by Gillham.[15,16] The measurement was run at a 1–2 K/min in flowing dry nitrogen. The storage modulus at any temperature was normalized by a value of the modulus at 100 K: It is called the relative storage modulus. The measuring system was connected with a computer (HP9826) through an HP–IB interface bus. The details of the measuring system have been given elsewhere.[10]

RESULTS

Figure 1 shows the relative storage modulus (G_r') and logarithmic decrement (LOG.DEC.) of the virgin sample as a function of temperature, for comparison with the results of the samples thermally treated at different temperatures. The viscoelastic loss spectrum is characterized by appearance of a large anomaly loss at 208 K. In addition, at least two losses exist between the anomaly loss and the crystalline dispersion, i.e., in the β process; two distinct loss peaks were seen at 238 and 268 K; the respective processes are called β_1 and β_2 here. The α process, which has been observed near 400 K for the ordinary PTFE,[1] was very slight. The γ process appeared around 165 K as a very shallow peak. The modulus G_r' showed an abrupt decrease at temperatures just below 208 K, and a stepwise decrease occurred at 223 K; then it
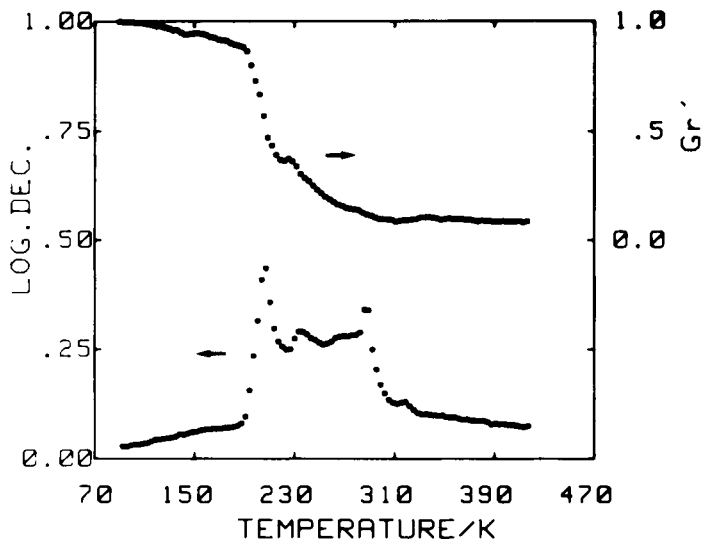
Fig. 1. Modulus G'_r and logarithmic decrement (LOG.DEC.) against temperature for the as-polymerized PTFE. Left and right sides in the ordinates correspond to LOG.DEC. and G'_r, respectively; a similar representation is used for Figures 2–5.

continued to decrease up to room temperature, as the temperature was increased. A very small decrease in G'_r was seen in the γ process.

Figure 2 shows G'_r and logarithmic decrement of the samples thermally treated at 423 K for 10 h as a function of temperature. The viscoelastic behavior almost paralleled that of the virgin sample. However, there exist some appreciable changes in the loss spectrum: a slight decrease in the anomaly loss and a slight increase in the crystalline dispersion occurred. In
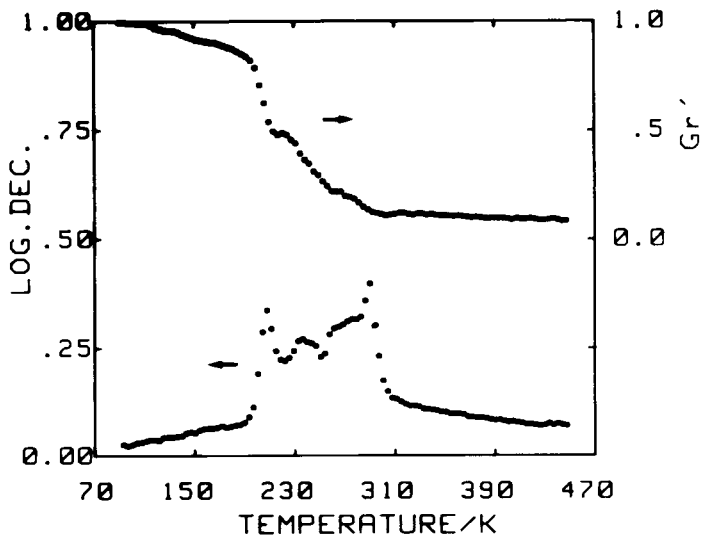

Fig. 2. Modulus G'_r and logarithmic decrement (LOG.DEC.) against temperature for the PTFE sample thermally treated at 423 K.
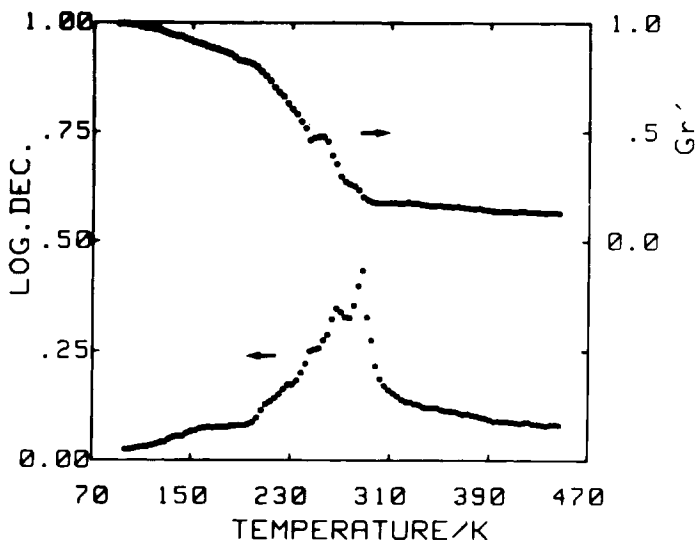
Fig. 3. Modulus G_r' and logarithmic decrement (LOG.DEC.) against temperature for the PTFE sample thermally treated at 523 K.

addition, the loss intensity of the β_2 process somewhat increased compared to that of the β_1 process. The γ process remained almost unchanged. The modulus G_r' decreased in a fashion similar to that of the virgin sample; the stepwise change at 223 K on the decreasing path occurred at a higher location of G_r'.

Figure 3 shows G_r' and the logarithmic decrement of the samples thermally treated at 523 K for 3 h. The loss spectrum indicated a significant decrease in the anomaly loss which changed to a shoulder peak. The crystalline dispersion
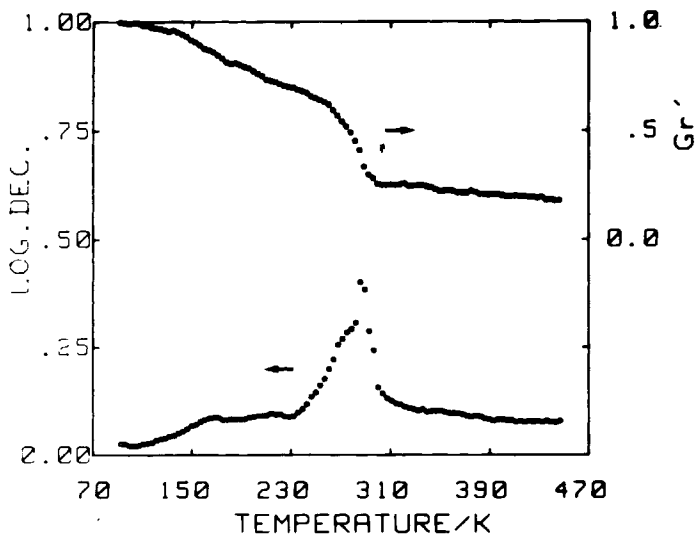

Fig. 4. Modulus G_r' and logarithmic decrement (LOG.DEC.) against temperature for the PTFE sample thermally treated at 591 K.
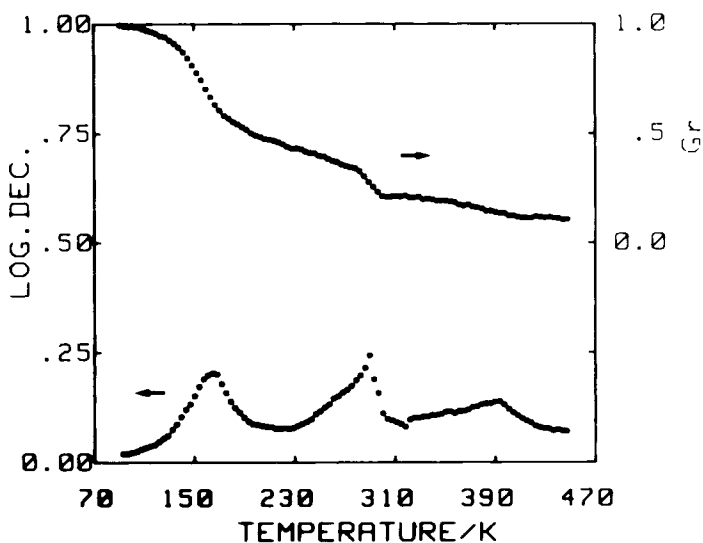
Fig. 5. Modulus G_r' and logarithmic decrement (LOG.DEC.) against temperature for the PTFE is thermally treated at 606 K.

was intensified. The γ process remains unchanged and the β_2 relaxation became larger than the β_1 relaxation. The modulus G_r' showed a gradual decrease at temperatures just below the γ process; although a break at 223 K was still observed, the value continued to decrease up to the end temperature of the crystalline dispersion.

Figure 4 shows G_r' and the logarithmic decrement of the samples thermally treated at 591 K for 3 h. Small loss peaks were observed at 165 and 208 K, corresponding to the γ process and the anomaly, respectively. The β_2 process showed a large shoulder around 270 K, where it appears that the β_1 relaxation was somewhat overlapped. The crystalline dispersions were the most distinct loss peaks. The modulus first gradually decreased at the onset temperature of the γ relaxation and next a steep decrease occurred at temperatures below the crystalline dispersions.

Figure 5 shows G_r' and the logarithmic decrement of the samples thermally treated at 606 K for 3 h. The mechanical spectrum were analogous with that of ordinary PTFE over the whole temperature range; the α, β, and γ relaxations were observed as three large peaks. The α process, which has never been clearly observed for these samples, appeared at about 395 K. Further-

TABLE I
Loss Peak Temperatures (K) for As-Polymerized PTFE Samples Treated at Different Temperatures T_a[a]

T_a (K)	γ	?	β_1	β_2	β_c		α
As-polymerized	165	208	238	268	290	300	—
523	165	Shoulder		267	289	300	—
606	165	—	Shoulder		291	301	395

[a] Measuring frequency is around 0.5 Hz. Symbol (−) denotes that it is not observable.

more, the modulus showed the stepwise decrease: There exists a large decrease in the γ region and a slight decrease in both the β and the α regions.

Table I lists values of loss-peak temperatures obtained for some treated samples. Data measured to more detail in the narrow temperature range in the vicinity of each dispersion were used for estimation. When the estimate was difficult owing to a shoulder peak including more than two losses, we used the descriptive word "shoulder." In the crystalline transition (β_c) region for the samples treated below 591 K, one of two loss peaks was somewhat broad and the other was small and shoulderlike; but these were distinctive enough for estimation. Values obtained for each dispersion were similar for other treated samples, although some ambiguity is included because of the broadness of the loss peaks.

DISCUSSION

The viscoelastic anomaly was distinctively observed at 208 K for the as-polymerized PTFE, in addition to well-known relaxations and transitions. In order to consider the annealing effect of the anomaly, we need to bear in mind the following facts: the γ process around 165 K results from the amorphous region and the crystalline dispersion at room temperature from the crystalline region.[1-4] As a qualitative mechanism of the γ relaxation, we suggest torsional motions of segments in the amorphous chains.[17] The crystalline dispersions are due to torsional oscillations around chain axis and displacements along chain axes in the crystalline chains[17]; the process is accompanied by a structure transition from monoclinic through quasihexagonal to hexagonal forms.[18, 19]

Differential thermal analysis (DTA) measurements showed that the virgin sample had a double peak for the 292 K crystalline transition, but this peak was observed to be a single peak for melt-crystallized samples. In addition, the crystalline transition at 303 K appeared to be double as well. The existence of at least two kinds of crystals is therefore obvious. Vega and English[20] reported from nuclear magnetic resonance (NMR) measurements that the virgin PTFE is an almost complete crystal and there exist at least two crystalline parts: The same crystalline part as that existing in melt-crystallized samples and a less-ordered crystalline part. Our data for the degree of crystallinity by the density method was about 90%. The high degree of crystallinity of the virgin PTFE is reflected on the very small loss peak of the γ process. Starkweather et al.[21] reported data on mechanical behavior for virgin samples extruded at 50°C obtained by means of a dynamic mechanical analyzer. They showed that the γ relaxation that occurred at -84°C for the melt-crystallized samples was replaced by a smaller loss peak at -66°C in the virgin sample, but the measuring frequency was not indicated.

Figure 6 shows the relaxation strength of the anomaly as a function of the treatment temperature T_a. The relaxation strength was estimated from the difference between values in G'_r at the onset and end temperatures of the anomaly. The relaxation strength decreased almost linearly as the treatment temperature was increased, without any particular change near the melting point. It appears that molecules in the structural region relative to the origin of the anomaly can rearrange without large displacements due to melting.
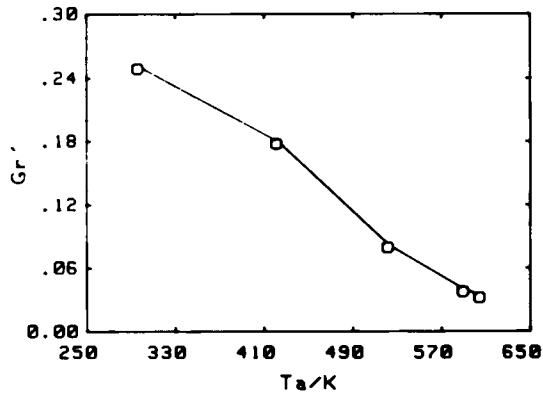
Fig. 6.   Relaxation strength of the anomaly at 208 K against the treatment temperature (T_a).

Figure 7 shows the loss intensity of the anomaly as a function of the treatment temperature, together with that of the γ and the crystalline dispersions. The intensity of the anomaly decreased with increasing the treatment temperature, and its decreasing tendency was similar to that in the relaxation strength, while the intensity of the crystalline dispersion increased up to the treatment temperature of 523 K. The amorphous γ relaxation hardly changed up to the treatment temperature of 591 K. Moreover, large changes for both the γ and the crystalline dispersions occurred at the treatment temperature of 606 K, which is near the melting point; for the anomaly, however, the intensity change at 606 K was very small. The samples treated at 606 K have already been melt-crystallized, as the mechanical spectrum in Figure 5 shows.

The results shown in Figures 6 and 7 suggest that molecules in the structural regions relevant to the anomaly can readily rearrange at annealing temperatures much lower than the melting point. As partial ordering proceeds, parts thereby additionally constrained are generated because of the difficulty of rearrangement for overall chains. When the virgin sample was sintered once, it was hard to create the structure relevant to the anomaly
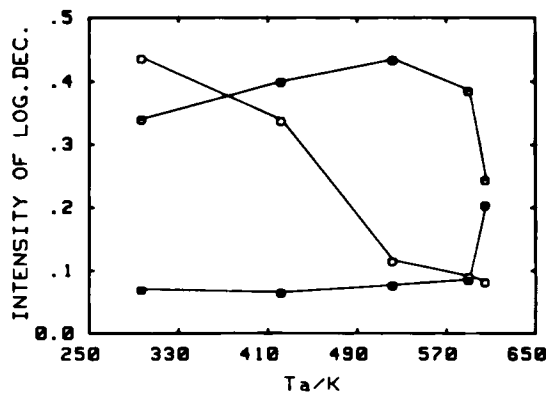

Fig. 7.   Loss intensity of the anomaly at 208 K against the treatment temperature, along with that of the γ process and the crystalline process: ($\bigcirc$) anomaly; ($\bullet$) γ; ($\ominus$) crystalline.

because of entanglement of long chains; for PTFE samples with short chains, however, such a structure can be repeatably formed by a certain crystallization from the melt.[10] It should be noted that entanglement hinders the formation of such structures on melt crystallization.

If the structural region of PTFE materials is divided into three phases: crystalline, intermediate or paracrystalline, and amorphous phases (here the two terms in the middle are used with the same meaning). Then the origin of the anomaly can be assigned to the intermediate region, in which molecules are arranged in parallel to each other but with different intermolecular distances.[17] In view of the heat-treatment effect on mechanical spectra, it seems that the virgin sample has a texture where crystalline parts are randomly distributed in a matrix of the intermediate phase or vice versa, although there exist many minor amorphous regions. Molecular conformation in the intermediate region is a metastable state, and when any hindrance was removed by annealing, its conformation can locally transform into more stable states. Since, however, it is hard to rearrange all the molecules because of the fixed crystals, strained conformers are instead incorporated in grain boundaries on ordering. We can see the feasibility of such transformations in the results that the crystalline dispersion and the β_2 process are intensified, contrary to the decreases in intensity for the anomaly and the β_1 process.

If the anomaly is assumed to be due to local mode relaxation, the theoretical relaxation strength decreases with decreasing the segment length relevant to the relaxation.[4,17] The experimental results for the relaxation strength suggest that the segment length in the intermediate region decreases as annealing proceeds.

Two large loss peaks, appearing between the anomaly and the crystalline dispersion for the virgin sample, seem to be associated with the intermediate region; the β_1 process results from more irregular, amorphous-like parts and the β_2 process from more strained parts. Annealing effects accelerate rearrangements toward more stable and regular structure, and consequently generate additional constrained parts on redistribution of conformation, because large movements of molecules are impossible. As a result, the β_2 process becomes more predominant than the β_1 process as the annealing treatment proceeds. It should be noted that the β_2 process always exists on the low temperature side of the crystalline dispersions for other ordinary PTFE samples; essentially coexistence of crystalline and noncrystalline regions is feasible only through some distorted conformation.

For the sample treated at 606 K or ordinary PTFE, in both of which the existence of the intermediate region was not so appreciable as for the virgin PTFE, the β process was observed as a large shoulder loss. In the β process, the existence of two dispersions, called the primary and grain boundary, has been reported.[4] The latter relaxation corresponds to the β_2 process described here. However, the assignment of the primary relaxation to the β_1 process is apparently inconsistent with the results of the large β_1 loss against minor amorphous content for the virgin sample. Lau et al.[22] reported that the glass transition, which is closely related to the primary relaxation, is broad because of the local chain mobility without side groups. They assigned the midpoint of the glass temperature range to 200 K. For the ordinary samples, the shoulder peak on the low temperature side of the β region tends to enlarge with an

increase in amorphous content. Furthermore, if it is recognized that some part of the intermediate region is amorphous-like, then we can assign the large β_1 peak to the primary dispersion, which is well separated from other peaks.

The α relaxation was observed when the sample was thermally treated at 606 K, i.e., partially melt-crystallized. Origin of the relaxation continues to be controversial; should it be attributed to micro-Brownian motion in the paracrystalline[4] or in the amorphous phases?[1] If the α relaxation is related to the paracrystalline phase, the α process of the virgin sample should be observable because of the major inclusion of the paracrystalline phase; however, the α process was not found. Strong interactions with crystalline parts distributed throughout the virgin sample should hinder micro-Brownian motion. On the other hand, if the α relaxation is regarded as the primary relaxation, instead of that at 240 K, nonobservation of the α process for the virgin sample is obviously due to the minor amorphous content; then the loss intensity depends on the crystallinity and the existence of entanglements and tie molecules in the amorphous region. We imply that the distinct appearance of the α process should be due to large segmental motions of noncrystalline chains which topologically entangle with each other and do not strongly interact with crystals. The motion contains movement of entangled points, but stationary flow is largely restricted by crystalline parts. On the basis of this view, we can qualitatively interpret viscoelastic behavior of the α process for a variety of PTFE samples, including the virgin sample. The α process is always observable when there exist noncrystalline regions isolated to some degrees and consisting of entangled chains.

Finally, we can treat the assignment of multiple dispersions for the virgin PTFE. The viscoelastic anomaly found at 208 K can be attributed to segmental motions in the intermediate or paracrystalline regions which include mobile conformational defects. The anomaly is sensitive to annealing effects. The β_1 process results from amorphous-like intermediate regions, and the β_2 process results from grain boundaries. The α process, which has never been appreciable for the virgin sample, is associated with large segmental motions of noncrystalline chains, which are topologically entangled with each other and which have no strong interactions with crystalline parts.

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