

# Deformation Behavior of Polytetrafluoroethylene Films Under Tensile Stress at Various Temperatures

KEN YAMAGUCHI, MASAYUKI TAKACHI, and SUSUMU HIRAKAWA

Department of Applied Physics, Faculty of Science, Fukuoka University, Jonan-ku, Fukuoka 814-80, Japan

## SYNOPSIS

Deformation behavior of polytetrafluoroethylene (PTFE) films was investigated by thermomechanical analysis (TMA) under various tensile stresses ( $\sigma$ ) up to 1.15 MPa in the temperature range from room temperature to 360°C. In the heating process above  $\sigma \approx 0.25$  MPa, a contraction of the PTFE film occurs in the melting temperature region. In the cooling process above  $\sigma \approx 0.05$  MPa, an elongation occurs in the crystallization temperature region, and above  $\sigma \approx 0.5$  MPa, it reaches 20–30% of the original length of the film. The PTFE films in the melt state above  $\sigma \approx 0.5$  MPa contract with increasing temperature up to 360°C and elongate with decreasing temperature. For the films that underwent deformation in the TMA, the crystalline orientation and the surface morphology were investigated by wide-angle X-ray diffraction and scanning electron microscopy, respectively. The degree of crystalline orientation in the deformed films increases with increasing  $\sigma$  and approaches a plateau at  $\sigma \approx 0.4$  MPa. On the surface of the deformed films, alignment of the bands and deformation of granules, which are formed by heat treatment above the melting point, are observed. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

Polytetrafluoroethylene (PTFE) has many superior properties: very high melting point, extreme resistance to solvents and corrosive agents, unusual nonadhesion, very low coefficient of friction, and so on, and is used as manufactured products in various forms: film, fiber, and bulk. In the case of use in the film form, the film is produced by rolling the powder or skiving the sintered block of PTFE, and the rolled or skived film is sometimes drawn in order to improve the end-use properties.

A study of deformation behavior of PTFE films is important for optimizing the processing conditions and for improving the mechanical and other properties. There have already been some reports on a study of molecular orientation for PTFE film deformed below its melting point. Wecker et al.,<sup>1,2</sup> having studied the orientation of the crystallites in the uniaxially deformed PTFE films by X-ray diffraction, found that the crystallites undergo plastic deformation and that the deformation at low extension is caused by slip occurring on planes along the

tangent to the helix formed by the PTFE molecule. Davidson and Gounder<sup>3</sup> investigated the crystalline and the noncrystalline phases of uniaxially elongated PTFE films by IR dichroism and broad-line NMR. Yeung and Jasse<sup>4</sup> studied the orientation of chains in crystalline and amorphous regions of uniaxially oriented PTFE films by FTIR measurements.

In PTFE, the molecular orientation by drawing can occur even above its melting point,<sup>5</sup> since PTFE has extremely high melt viscosity. In this study, the deformation behavior of PTFE films in the heating and cooling processes, especially in the melting and crystallization temperature regions and in the melt state, was investigated by thermomechanical analysis (TMA) under various tensile stresses. The result of the TMA measurement is discussed in relationship to the crystalline orientation investigated by wide-angle X-ray diffraction (WAXD) and the morphology observed by scanning electron microscopy (SEM) for the deformed films.

## EXPERIMENTAL

The polymer used in this study was granular PTFE powder (Polyflon M-12). The PTFE powder was

performed cylindrically and then sintered at 370°C for 24 h. The PTFE films were prepared by skiving the sintered block. The skived films were heat-treated at 350°C for 5 h in order to remove the residual stress. The PTFE films (0.1 mm in thickness) were cut to 2 mm in width for the measurements.

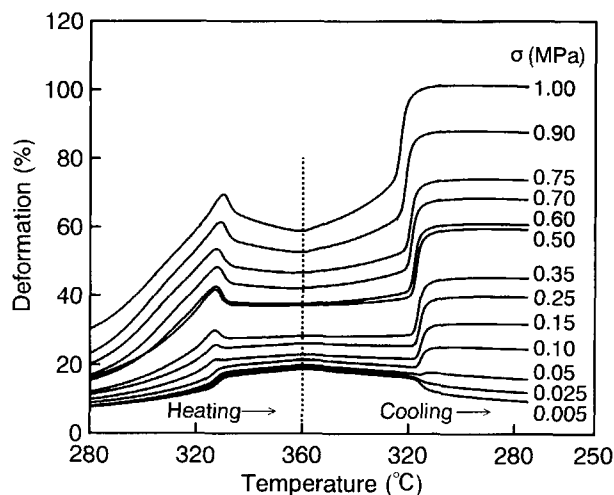
The deformation measurement of the PTFE films was carried out using a thermomechanical analyzer (Seiko Denshi TMA 120). In this measurement, both ends of the PTFE film were gripped by two chucks at an interval of 5 mm. The chucks were set between a holder and a probe through which constant tensile force was applied to the film. With the applied constant tensile force, the film was heated to 360°C at a rate of 5°C/min and then cooled down to 250°C at the same rate. The deformation curves, the thermomechanical analysis (TMA) thermograms, of the PTFE films were obtained as a function of temperature under various constant tensile forces.

The crystalline orientation in the PTFE films that underwent deformation in the TMA measurement was investigated using a WAXD apparatus equipped with a fiber specimen attachment (Rigaku Denki). The degree of the crystalline orientation was calculated from the full-width of half-maximum intensity of the Debye ring for the (110) plane. The morphology of the free surface of the deformed PTFE films was observed using a scanning electron microscope (JEOL).

## RESULTS AND DISCUSSION

### TMA

Figure 1 shows the TMA thermograms of the PTFE films obtained under various tensile stresses ( $\sigma$ ). The indicated values of  $\sigma$  are the applied forces per the cross sections of the films at the start of the TMA measurement. The vertical axis in the figure indicates the percentage of the deformation to the original length of the films. In the curve obtained under  $\sigma = 0.005$  MPa, which can be regarded as zero stress, two temperature regions in which an elongation and a contraction occur stepwise exist in the heating and cooling processes, respectively. These temperature regions correspond to those of the melting and crystallization observed in differential scanning calorimetry, respectively. In the TMA thermogram obtained under higher tensile stress, however, a contraction and an elongation that occur stepwise are observed noticeably in the melting and crystallization temperature regions, respectively.



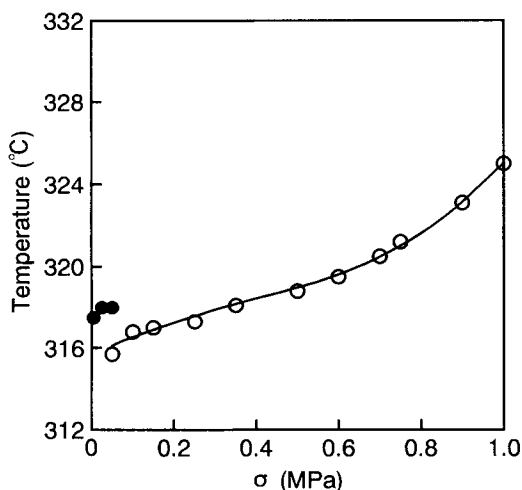
**Figure 1** TMA thermograms of PTFE films under various tensile stresses ( $\sigma$ ).

The contraction in the melting temperature region is considered as follows: In the heating process up to the melting point, the films are elongated by the tensile force and orientation of the molecular chains occurs to some degree. Since the oriented chains are disordered partially in the melting process by enhancement of the thermal motion of the chains, the contraction of the films occurs. In this stage, the contraction overcomes the elongation by the thermal expansion and the melt flow hardly occurs because of the very high melt viscosity of PTFE. The contraction in the melting process for rolled PTFE tapes has been observed by Haneda et al.<sup>6-8</sup>

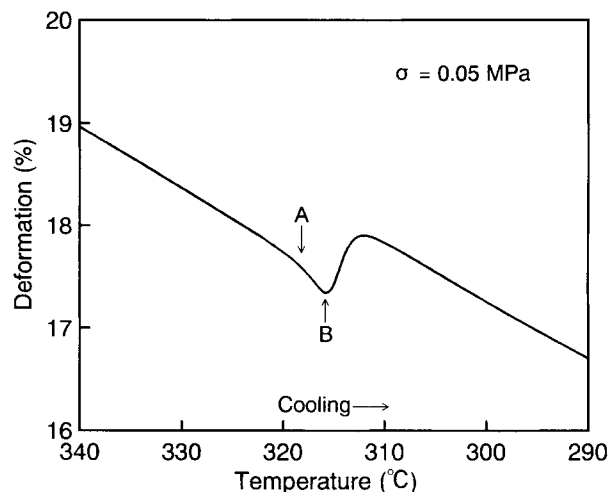
The deformation behavior in the melt state under higher tensile stress is different from that under lower tensile stress, as seen in Figure 1. The length of the films in the melt state above  $\sigma \approx 0.5$  MPa decreases with increasing temperature in the heating process up to 360°C and increases with decreasing temperature in the cooling process. This fact suggests that loosely oriented chains in the melt state are disordered by enhancement of the thermal motion in the heating process. In the cooling process, the chains that are disordered considerably in the high temperature are oriented loosely under the tensile force as the thermal motion abates. These contractions (in heating) and elongations (in cooling) in the melt state that are caused by the thermal motion of the oriented chains overcome the inherent thermal expansion (in heating) and shrinkage (in cooling) that occur in the unoriented PTFE film. Through other deformation measurements for the PTFE film, we also obtained the following two results that characterize the deformation behavior in the melt state of PTFE: (1) The PTFE film did not

deform while the temperature was held for about 10 min in the melt state under constant tensile force. (2) The film deformation in the melt state was approximately reversible when the tensile force applied to the film was changed. These results suggest that the melt flow in PTFE hardly occurs within the measuring conditions in this study, i.e., PTFE in the melt state shows a rubberlike deformation behavior. Therefore, it is considered that under higher tensile force the chains in PTFE can be oriented loosely even in the melt state.

Figure 2 shows the relationship between the tensile stress applied to the films and the starting temperature of the elongation in the crystallization temperature region appearing in the TMA thermograms of Figure 1, but the three points plotted for the lower stress, which are indicated by filled circles, show the starting temperature of the crystallization. Both the starting temperatures of the elongation and the crystallization are observed in the TMA thermogram of  $\sigma = 0.05$  MPa shown in Figure 3, which is a magnified figure of a part of Figure 1. From Figure 3, it is found that the starting temperature of the elongation (point A) is lower than that of the crystallization (point B). Above  $\sigma = 0.1$  MPa, however, the contraction at the crystallization cannot be observed. Then, it is considered that the tensile force applied to the films suppresses the contraction at the crystallization. In Figure 2, the starting temperature of the elongation increases with increasing the tensile stress. Generally, the crystallization temperature of polymers such as



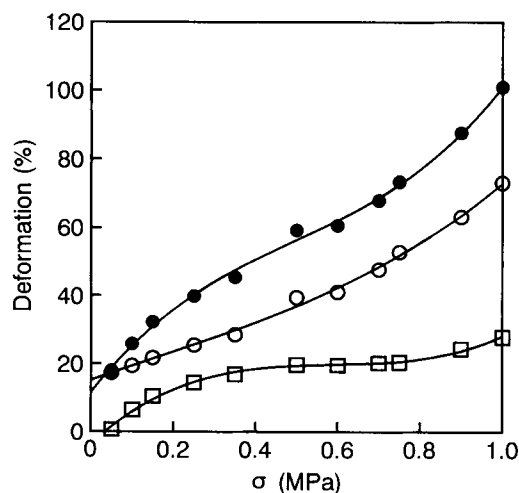
**Figure 2** Starting temperature of elongation in the crystallization temperature region as a function of tensile stress ( $\sigma$ ) applied to PTFE film, provided that the three filled circles indicate the starting temperature of the crystallization.



**Figure 3** TMA thermogram of PTFE film under  $\sigma = 0.05$  MPa. This curve is a magnified one of a part of Figure 1. The labels A and B in the figure indicate the starting points of the elongation in the crystallization temperature region and the crystallization, respectively.

rubber rises by chain orientation and/or stress applied to chains. Since the PTFE chains can be oriented loosely in the melt state under tensile force, the starting temperature of the crystallization must increase with increasing tensile stress. Therefore, it is considered that the starting temperature of the elongation in the crystallization temperature region increases as the crystallization temperature increases.

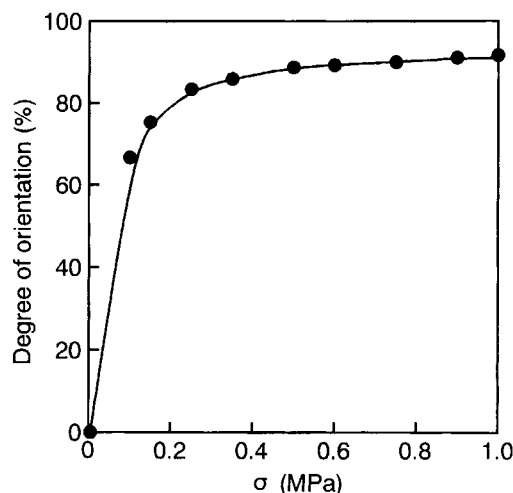
Figure 4 shows the elongation of the films in the



**Figure 4** Deformation of PTFE films as a function of applied tensile stress ( $\sigma$ ): (□) elongation in the crystallization temperature region; (○) deformation just before the crystallization; (●) deformation just after the crystallization.

crystallization temperature region and the deformations just before and after the crystallization vs. the tensile stress applied to the films. The elongation in the crystallization temperature region above  $\sigma \approx 0.5$  MPa reaches 20–30% of the original length of the film. Haneda et al.<sup>6</sup> studied the melting and recrystallization behavior of rolled PTFE tapes by TMA. They also observed an expansion in the rolling direction in the crystallization process from the melt for the rolled virgin PTFE tape and the sintered one. They explained the origin of the expansion as follows: The structure oriented by rolling reproduces in the crystallization process from the melt because the memories of its structure are maintained even in the melt; therefore, the expansion in the rolling direction occurs. However, our result cannot be compared simply with their study because of the difference in the samples and measurement methods. We consider that the elongation in the crystallization temperature region under tensile force is caused by crystalline orientation and/or by slip between crystallites, because the elongation occurs in the crystallization process as seen in Figure 3. It is considered that a number of chain entanglement points produced by the thermal motion decrease considerably in the crystallization temperature region and then slip between the chains occurs easily under the tensile force. The excessive slip under a very high tensile force forms voids, as shown later by SEM observation. It is also considered as an additional origin of the elongation that the loosely oriented chains in the melt state change into the tightly oriented ones: crystallites.

To investigate the crystalline orientation of the PTFE films that underwent deformation in the TMA measurement, WAXD measurement was carried out at room temperature. Figure 5 shows the relationship between the degree of the crystalline orientation and the tensile stress applied to the films. The degree of the crystalline orientation increases abruptly with increasing the tensile stress and approaches a plateau at  $\sigma \approx 0.4$  MPa. This result is similar to the relationship between draw ratio and crystalline orientation that has been investigated for uniaxially drawn PTFE films by Hashida et al.<sup>5</sup> They obtained the result that the orientation of the crystallites increases abruptly with increasing the draw ratio and is almost completed at the draw ratio of about 1.5 for the films drawn above the melting point. From Figure 4, it is found that the deformation of the film just after the crystallization at  $\sigma \approx 0.4$  MPa is equivalent to the draw ratio of about 1.5.



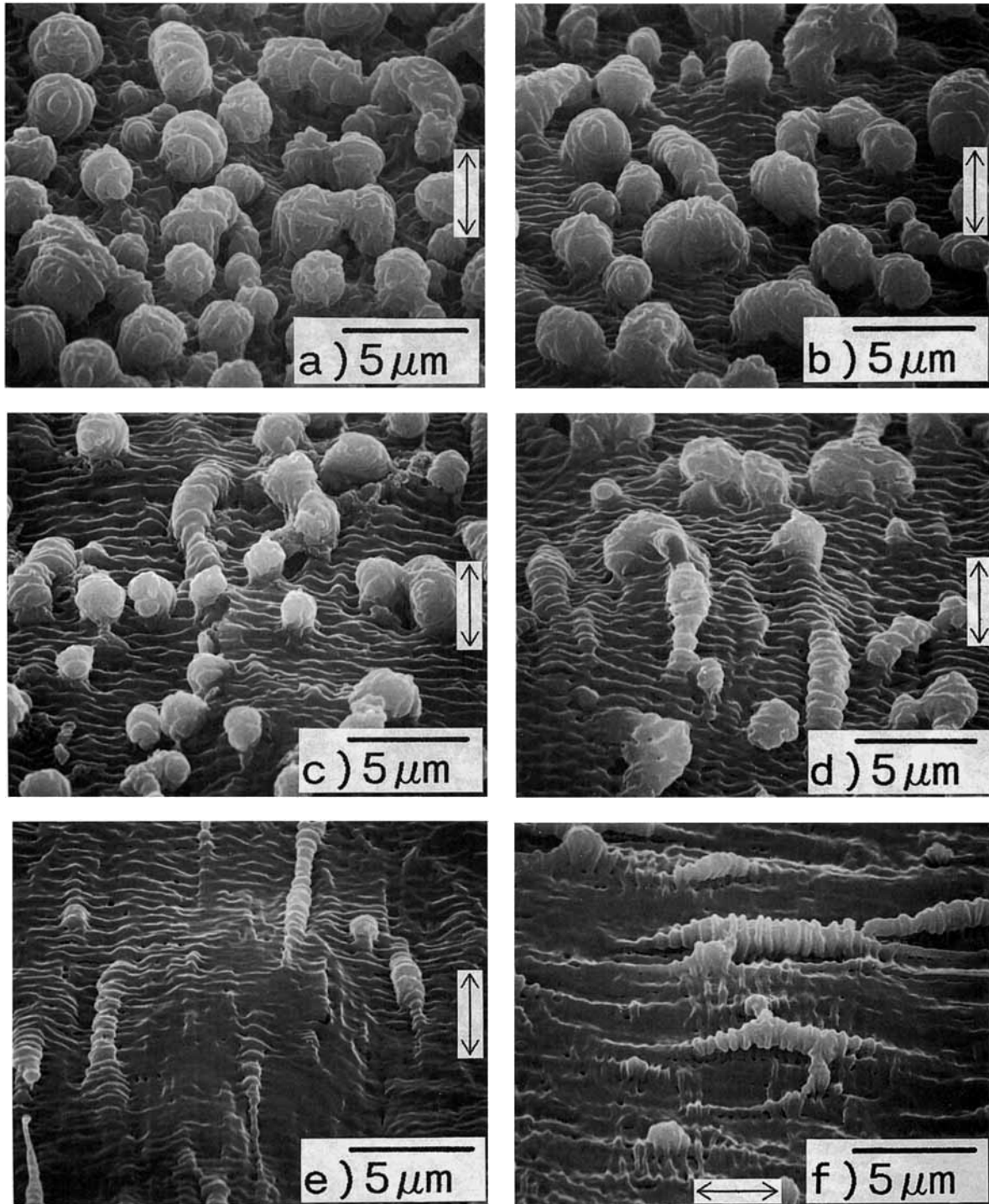
**Figure 5** Degree of crystalline orientation of PTFE films as a function of applied tensile stress ( $\sigma$ ).

Above  $\sigma \approx 0.4$  MPa, the degree of the crystalline orientation does not increase with the tensile stress very much, as shown in Figure 5, whereas the deformation of the film just after the crystallization increases progressively, as shown in Figure 4. This represents that above  $\sigma \approx 0.4$  MPa the further elongation in the crystallization temperature region contributes little to the crystalline orientation. It is considered from a morphological observation that the further elongation is caused mainly by the slip between the crystallites.

### Morphology

The morphology of the PTFE films that underwent deformation in the TMA measurement was observed by SEM. Figure 6(a)–(f) shows the free surface of the films crystallized from the melt under the various tensile stresses. Granules with a diameter of about  $2 \mu\text{m}$  and randomly oriented bands with a width of about  $0.3 \mu\text{m}$  can be seen on the surface of the film deformed under  $\sigma = 0.005$  MPa [Fig. 6(a)]. These granules and bands are formed by heat treatment above the melting point.<sup>9</sup> Above  $\sigma = 0.25$  MPa, the long axes of the bands are oriented perpendicularly to the direction of the tensile force [Fig. 6(b)–(f)]. Moreover, the stretched granules are observed above  $\sigma = 0.5$  MPa [Fig. 6(c)–(f)].

The bands seem to be sheaflike bands, as observed by Yamaguchi.<sup>10</sup> He reported that the rodlike particles<sup>11,12</sup> observed in virgin PTFE are changed to sheaflike bands by heat treatment. The sheaflike band is formed by the chain folding that takes place perpendicularly to the long axis of the band. There-



**Figure 6** Scanning electron micrograph of the free surface of PTFE films crystallized from the melt under tensile stress  $\sigma$  (MPa): (a)  $\sigma = 0.005$ ; (b)  $\sigma = 0.25$ ; (c)  $\sigma = 0.50$ ; (d)  $\sigma = 1.00$ ; (e)  $\sigma = 1.15$ ; (f)  $\sigma = 1.15$  in different view. The arrow represents the direction of the tensile force.

fore, it is considered that the long axis of the band, the axis perpendicular to the chain direction, is oriented perpendicularly to the direction of the tensile force. From considering the deformation behavior of the granules on the film surface, the granules may be sheaflike entities that gather locally and do not grow so long as do the bands. Above  $\sigma = 1.0$  MPa, highly stretched granules and a few voids are observed [Fig. 6(d)–(f)]. On the surface of the film deformed under  $\sigma = 1.15$  MPa, the granules are hardly observed because they are stretched highly [Fig. 6(e) and (f)]. In the deformation process of the granules, we consider that slip between the crystallites or sheaflike entities occurs.

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