

STUDY ON FACTORS AFFECTING ROOM TEMPERATURE TRANSITION OF POLYTETRAFLUOROETHYLENE

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ABSTRACT

In the X-ray diffraction intensity distribution diagram of PTFE, three diffraction peaks exist in the range of Bragg angle $30-45^\circ$, which are very sensitive to the crystal transition at room temperature. At 15°C , the crystal is triclinic and the "small spikes" along with the main peaks appear on the diffraction scans due to the distortion of the unit cell, while at 23°C , distortion no longer exists, "small spikes" disappear completely. When the temperature is raised to 34°C , the hexagonal crystal further randomizes and the peak at Bragg angle 42° vanishes. We assigned correctly Miller index (108) to this peak and used $2\theta=30-45^\circ$ region ("sensitive region") as a criterion to characterize qualitatively the crystal transition. It has been found that some factors such as γ -irradiation, cold pressing, drawing, calendaring and copolymerization which are usually encountered in the fabrication or application of PTFE articles have profound effect on the crystal transition as evidenced by X-ray diffraction patterns and DSC thermograms. The information obtained in the present work is beneficial to the use of PTFE articles.

It is well-known that polytetrafluoroethylene (PTFE) exists in two helical conformations, which may be described as twisted ribbons in which the fully extended planar form is distorted to have a 180° twist in thirteen CF_2 units below 19°C . Above 19°C , this form is replaced by a slightly untwisted conformation with fifteen CF_2 units per half-twist. If the temperature is raised further to above 30°C , the molecules lose their preferred angular orientation, becoming randomly misaligned about their long axes. Different conformation constitute different crystalline structure. Below 19°C PTFE crystal belongs to the triclinic and above this temperature to the hexagonal crystallographic system. Above 30°C the crystal is further transformed to a somewhat randomly packed hexagonal structure. Since Bunn and Howells^[1] and Piece et al.^[2] published their work concerning the structure of PTFE, many workers have further ascertained the presence of this transition by a variety of methods in different respects^[3-5]. Microscopically, this transition reflects the abrupt changes in the interplanar spacing and the corresponding parameters of the unit cell; macroscopically, this transition is accompanied by a volume change of 1.3%. Therefore, investigation on the room temperature transition of PTFE is of significance both from practical and academic viewpoints.

In the course of studying the effect of γ -irradiation on PTFE by WAXS, we found that there was a "sensitive region" in the X-ray diffraction intensity distribution diagram ($2\theta=30-45^\circ$), where there were three diffraction peaks the intensity of which varied with the transi-

tion. Among the three peaks, the peak with the highest 2θ value has long been overlooked. Until recently, no accurate Miller index has been assigned to it in the literature. In the present work, we calculated the Miller index of this peak based on our experimental results, and used the variation of peak intensities in the "sensitive region" and DSC thermogram as criteria to characterize the effect of high temperature aging, γ -irradiation, external force and the presence of comonomer in PTFE on the room temperature transition.

EXPERIMENTAL

Samples

Virgin as-polymerized PTFE and also FEP and PFA—kindly supplied by Shanghai Institute of Fluoro-containing Organic Materials. In some cases, virgin PTFE powder of commercial origin (made in FDR) was used.

PTFE sheet and film—commercial product of the 9th Plastic Works, Tianjin. Sheet thickness, 1.0mm; film thickness, 60μ .

PTFE thread sealer tape—kindly supplied by Shanghai Institute of Fluoro-containing Organic Materials. In some cases, tapes from abroad (Daikin Co., Japan; Permacel, USA) were used.

Instrumentation and test procedure

A Rigaku Model 2028 X-ray diffractometer with Nickel foil filtered $\text{CuK}\alpha$ source was used to obtain the diffraction scans for samples at different temperatures. 2θ value was recorded in $0.1^\circ/\text{division}$ and calibrated with a standard silicon sheet.

A Perkin-Elmer Model DSC-2C differential scanning calorimeter was used to determine the transition temperature of the samples. Temperature and calorimetric calibration were done by means of high purity In as a standard. Scanning rate, $10^\circ\text{C}/\text{min}$; sensitivity, 2 or $5\text{mcal}/\text{sec}$; sample weight, $25 \pm 0.2\text{ mg}$; chart speed, $20\text{mm}/\text{min}$.

RESULTS AND DISCUSSION

1. X-ray diffraction scan of PTFE

The X-ray diffraction intensity distribution diagram of PTFE at 23°C is shown in Fig. 1. The peaks (I), (II) and (III) have already been indexed, while peak (IV) has not yet been clearly

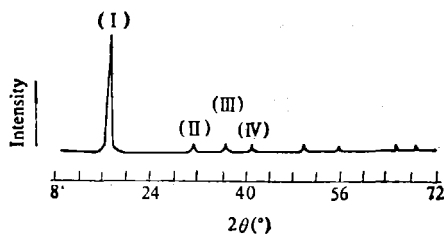


Fig. 1 X-ray diffraction intensity distribution diagram of PTFE at 23°C

assigned. As to the room temperature transition, it was found that there was a "sensitive region" in the range of $2\theta = 30-45^\circ$, where existed the peaks (II), (III) and (IV). On the other hand, peak (I) and those peaks existed in the range of $2\theta > 45^\circ$ showed no response to this transition. Besides, on the diffraction scans for both virgin powder and commercial sheet samples recorded at 15°C , there were many "small spikes" along with the main peaks (see Fig. 2). It implies that the triclinic crystallographic system is more susceptible to lattice distortion^[7] with the commercial sheet much more so. Possibly, the fabrication process of the commercial sheet prompts the lattice distortion of the crystal structure. If the temperature of both samples was raised to 23°C , the spikes in the "sensitive region" vanished completely. It follows that at this temperature, no distortion of the unit cell occurred. At 34°C , the peak (IV) of both samples disappeared. Considering the role of planes in crystal structure, it is realized that the disappearance of peak (IV) corresponds to the more pronounced deviation of PTFE molecules from the hexagonal structure. The above mentioned phenomenon is true for all PTFE samples studied.

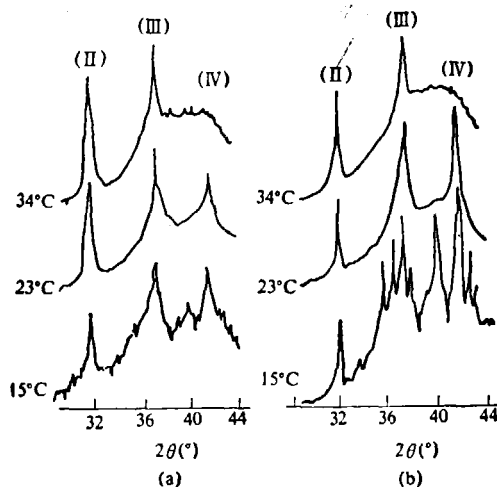


Fig. 2 "Sensitive region" in X-ray diffraction diagram of PTFE
(a) virgin powder, (b) commercial sheet.

2. Miller index of Peak (IV)

In order to facilitate the discussion of the "sensitive region", it is necessary at first to evaluate the Miller index of peak (IV). By using virgin powder, we prepared standard samples according to ASTM standards^[8]. Five parallel samples were used to measure their X-ray diffraction scans in the range of $2\theta = 30-45^\circ$ at 23°C . For a hexagonal crystallographic system, the relationship between interplanar spacing d and Miller index, h , k and l , is given by the equation^[9]

$$\frac{1}{d^2} = \frac{4}{3} \cdot \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

where the unit cell constants are $a=b=5.61\text{\AA}$, $c=19.5\text{\AA}$ ^[10]. Based on crystallographic principles, the term hk has 23 possible permutations, while for l , there are 10 possible ways to match with each permutation of hk . The interplanar spacing value d and the Miller index of each peak in the "sensitive region" are listed in Table 1. In the lower part of the table are shown the results calculated based on equation (1) by means of a microprocessor. The Miller indexes of peak (I), (II) and (III) are completely in conformity with the published values^[9]. Using the same computation program, we obtained Miller index (108) for peak (IV)*.

Table 1 Interplanar spacing and Miller indexes of peak (I)–(IV)

Order of diffraction peaks		(I)	(II)	(III)	(IV)	
Interplanar spacing (<i>d</i>)	Present work	1	4.928	2.835	2.428	2.187
		2	4.917	2.831	2.426	2.183
		3	4.885	2.824	2.419	2.177
		4	4.912	2.833	2.423	2.183
		5	4.885	2.826	2.422	2.178
	mean value	4.905	2.830	2.423	2.182	
std. dev.	±0.020	±0.005	±0.004	±0.004		
	Literature value ^[6]	4.90	2.83	2.43	2.18	
Miller index (<i>hkl</i>)	Present work	(100)	(110)	(200)	(108)	
	Literature value ^[6]	(100)	(110)	(200)		

3. Factors affecting room temperature transition of PTFE

Although fabricated PTFE articles are of wide application, the volume change accompanying crystal transition at room temperature usually causes trouble in some applications. For example, gasket made of PTFE could lose its sealing ability if the room temperature crystal transition has not been taken into consideration. Because this transition is closely related to the reliability of the fabricated PTFE articles, the effect of some factors which are usually met in fabrication and application on the room temperature transition was studied in order to avoid the troubles occurred in some uses.

(1) High temperature aging and γ -irradiation

Commercial sheet and standard sheet samples prepared by cold pressing and sintering virgin powder according to ASTM standards were aged in a muffle furnace at 380°C for 2 to 120 hours. Fig. 3 illustrates the X-ray diffraction scans of standard sheet samples in the "sensitive region" for eight samples subjected to different time of aging. At 15°C , all samples

* One of the authors of the present work assigned $\begin{smallmatrix} (105) \\ (107) \end{smallmatrix}$ to peak (IV) several years ago^[12], but now it has been realized that (108) is more reliable.

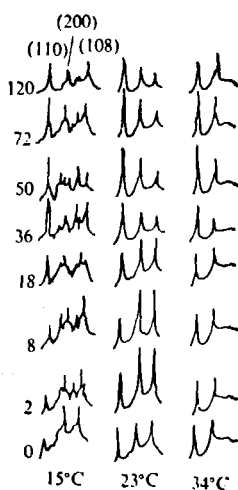


Fig. 3 "Sensitive region" X-ray diffraction diagram of standard sheet samples subjected to different time of 380°C aging (figures denote the aging time in hours)

showed "small spikes" along with the main diffraction peaks; at 23°C, all "small spikes" disappeared; at 34°C, diffraction of plane (108) vanished completely. The same holds true for the commercial sheet.

The "sensitive region" X-ray diffraction diagram of standard sheet samples subjected to different radiation dose in a 60,000 curie radiation source (dose rate 1905 röntgen/sec) are shown in Fig. 4. The results showed that at 15°C, the structures of samples subjected to a dose of larger than 140 Mrads are equivalent to that of samples at 23°C that had been subjected to a dose larger than 120 Mrads, and to the unirradiated samples at 34°C. The criteria is the disappearance of the plane (108) in the "sensitive region", i.e., the samples all exist in a randomized state of hexagonal crystal structure.

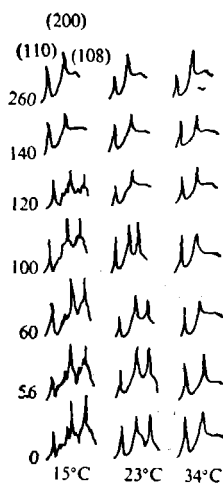


Fig. 4 "Sensitive region" X-ray diffraction diagram of standard sheet samples subjected to different radiation dose (figures denote the dose in Mrads)

On comparing Fig. 3 with Fig. 4, it was questioned whether the discrepancy between the two kinds of samples was due to the fact that the irradiated samples had been severely degraded by the action of high radiation dose. Thus the $\bar{M}_n$ of both oven-aged and γ -irradiated samples were measured by means of calorimetric method^[11] in this work. The variation of $\bar{M}_n$ with aging time and radiation dose was studied. For irradiated samples, no MW change was evident before a dose of 10^3 rads. In the range of 10^4 — 10^6 rads, $\bar{M}_n$ decreased rapidly, and levelled off to a value of ca. 10^4 even at larger dose of up to 10^6 — 10^8 rads. This result is quite in conformity to the published work of Ferse^[12]. As to the samples aged in muffle furnace at 380°C , there was a rapid decrease in $\bar{M}_n$ for time less than 20 hours, and then also levelled off to 10^4 even at a length of 120 hours of aging. Since the diffraction scans in Fig. 3 showed no pronounced difference between the aged and the original samples, more severely degraded samples were prepared by pyrolyzing the virgin powder at 500°C . Two samples were obtained: one had lost 4.6% of its original weight, and the other, 32%. The X-ray diffraction patterns in the "sensitive region" of both samples are shown in Fig. 5. The diffraction patterns of the former was exactly the same as that of the original sample (Fig. 5 (a)), while for the latter, the peak (110) were profoundly weakened at all temperatures, and at 34°C , (200) peak also nearly disappeared along with peak (108) (Fig. 5 (b)). The above mentioned facts indicated that the diffraction patterns of severely thermo-degraded samples was quite different from that of the γ -irradiation degraded samples. The dissimilarity between them should be attributed to the difference in degradation mechanism.

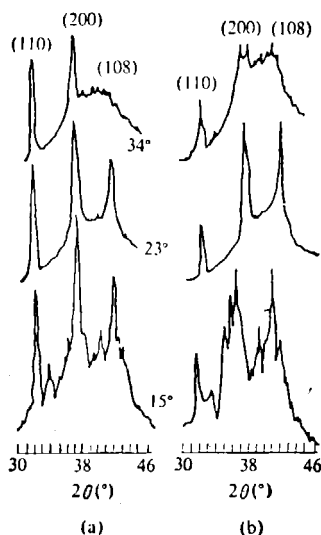


Fig. 5 "Sensitive region" X-ray diffraction scans of PTFE standard sheet samples subjected to pyrolytic action at 500°C
Wt. loss: (a) 4.6%. (b) 32%.

X-ray diffraction scans were recorded at 34° , 23° , 15° , 11° , 6° and 2.5°C respectively on samples which had been subjected to a dose of 140 Mrads. It was found that peak (108) reappeared gradually with lowering of temperature. Fig. 6 illustrates the DSC curves of

samples irradiated with different amount of radiation dose. Apparently, with the increase in radiation dose, the room temperature transition did gradually shift to lower temperatures. In contrast to the irradiated samples, the DSC thermograms of both aged and pyrolyzed samples showed no lowering of transition temperature at all.

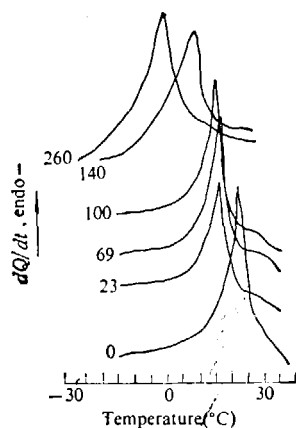


Fig. 6 DSC thermograms of PTFE irradiated with different amount of radiation dose (figures denote the dose in Mrads)

(2) External Force

In the course of PTFE fabrication, articles are inevitably subjected to external force. We found that the crystal transition was impelled when external force was applied. As can be seen from the X-ray diffraction patterns in the "sensitive region" of cold pressed virgin PTFE powder (Fig. 7) that at 15°C, while the unpressed samples showed pronounced "small spikes", when the pressure reached 350kg/cm² (specified pressure of ASTM standards in preparing standard sheet), the spikes lessened considerably. It implies that in this case, the crystal structure is nearly the same as that of the unpressed sample at 23°C. With further increase in pressure, the intensities of peak (200) and (108) decreased gradually. Eventually, the peak (108) disappeared completely when the pressure was higher than 1300kg/cm².

After quenching the cold pressed (2000kg/cm²) sample shown in Fig. 7 in liquid nitrogen, the X-ray diffraction scan was recorded immediately while the sample was still in the cryogenic condition. The peak (108) reappeared again. In conformity with this, the DSC determined transition temperature of the cold pressed PTFE crystal also shifted to lower temperature with the increase in pressure. Therefore, under the action of pressure or external force, the crystal structure of virgin as-polymerized powder could be transformed from triclinic to hexagonal and further to randomized hexagonal system.

The effect of external force on the crystal structure was further ascertained by drawing the commercial PTFE film. Fig. 8 shows the X-ray diffraction patterns of films drawn with different draw ratios. Since the commercial film had been subjected to some external force in the fabrication process, even though the draw ratio is equal to 1, the intensity of peak (108)

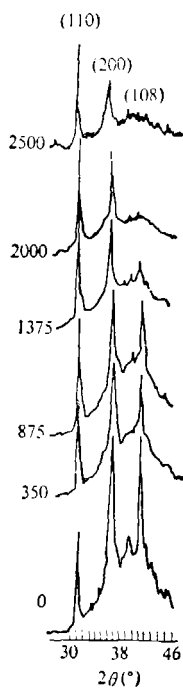


Fig. 7 "Sensitive region" X-ray diffraction scans of cold pressed virgin powder at 15°C (figures denote the pressure in kg/cm²)

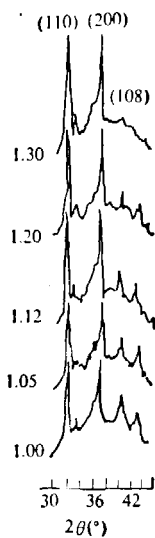


Fig. 8 "Sensitive region" X-ray diffraction scans of PTFE film after drawing (15°C) (figures denote the draw ratio)

was appreciably weakened. With the increase in draw ratio, peak (108) vanished eventually. For film drawn with draw ratio=1.30, the crystal structure at 15° is no longer triclinic or hexagonal, but transformed to a randomly packed hexagonal structure.

Recently, the newly developed PTFE thread sealant tape is an ideal sealing material used in the piping of chemical works. As the tape had been subjected to calendering action in the fabrication process, its peak (108) almost vanished even though it was at 15°C. Similarly, if a commercial PTFE film had been calendered on a two roll calender six times, peak (200) and (108) nearly completely disappeared; after eight times, even peak (110) was also weakened. Thus the severe deterioration action of calendering on PTFE crystal structure is very evident. The use of PTFE powder as a filler to modify the performance of certain engineering plastics is a common practice. If a calender is used in the mixing process, the effect of calendering on the property of the resulting blends due to change in crystal structure must be taken into account.

(3) Copolymerization

By copolymerizing tetrafluoroethylene (TFE) with a comonomer, the PTFE crystal structure can be profoundly affected even if the amount of the comonomer is relatively small. For copolymer hexafluoropropylene (HFP) and TFE (FEP), not only peak (108), but peak (100) and (200) also vanished gradually with the increase in hexafluoropropylene content (see Fig. 9). The DSC thermograms for FEP samples containing different amount of HFP shown in Fig. 10 also ascertained that PTFE crystal transition is very sensitive to the comonomer content. The X-ray diffraction scans of a copolymer of perfluoroalkoxylate and TFE (PFA) also showed the same trend.

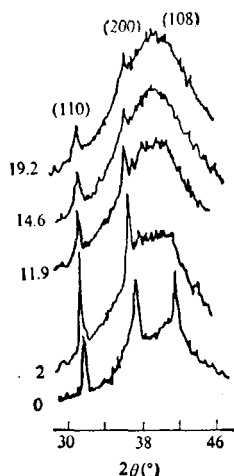


Fig. 9 Effect of HFP content on the X-ray diffraction scans of FEP in the "sensitive region" at 15°C (figures denote the content of HFP in %)

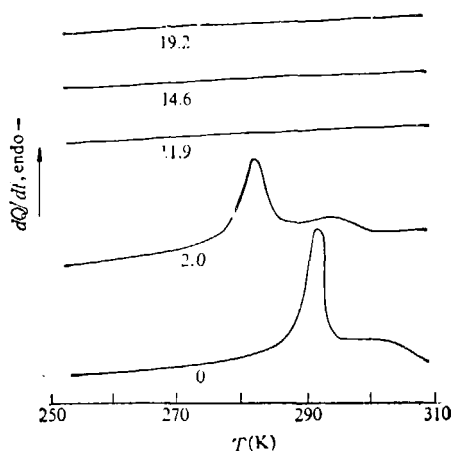


Fig. 10 Effect of HFP content on the DSC thermogram (figures denote the HFP content in %)

In summary, peaks (100), (200) and especially (108) in the X-ray diffraction scans of PTFE are very sensitive to its room temperature transition. The peak (108) vanishes with the randomization of the hexagonal crystal. The intensities of peaks (110) and (200) weaken and eventually completely vanish if the crystal is severely attacked. Factors which deteriorate crystal structure and thus shift the transition to lower temperature are γ -irradiation, external force and copolymerization. This phenomenon has not ever been reported in the literature. In the use of fabricated PTFE articles, care must be taken to the dimensional change resulted from the crystal transition which is caused by the above-mentioned factors.

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