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A Novel Crystalline Structure – Poly(tetrafluoroethylene) Spherulitic Crystal and its Crystallization Kinetics

Xiao qun Wang, Jie cai Han and Shan yi Du

(Center for Composite Materials, Harbin Institute of Technology, Harbin 150001, China)
E-mail: wxq@mtlab.hit.edu.cn
Wangxq@public.hr.hl.cn

Abstract

Spherulitic crystals of Poly(tetrafluoroethylene) (PTFE), for the first time, are observed in a kind of PTFE composite, and are verified by polarized optic microscopy (POM). Differential scanning calorimetry (DSC) is used to study the isothermal crystallization kinetics of PTFE matrix at different temperatures. The result shows that Avrami parameter is near 3, which may be elucidated that PTFE crystallizes three-dimensionally from preexisting nuclei. The result is in accordance with scanning electric microscopy (SEM) and POM observation of the crystalline morphology of PTFE. Compared with the rate of one-dimension crystallization, the rate of three-dimension crystallization is lower. So the three-dimension crystallization is easier to control than the one-dimension crystallization of PTFE.

Key words: Polytetrafluoroethylene(PTFE), spherulitic crystal, POM, Isotheraml crystallization kineitcs

INTRODUCTION

Poly(tetrafluoroethylene) (PTFE) resins are noted for their exceptional chemical inertness , broad range of thermal stability from cryogenic to very high temperatures, the lowest surface-free energy of any solid, the lowest friction constant and superior dielectric properties over the broadest range of frequencies for known plastics. So PTFE resins have been widely used in many industry fields. Because of its chemical inertness and poor process properties, design and control of PTFE micro-morphology, especially crystal state and crystallinity, has become an important approach through which properties, especially mechanical properties of PTFE and PTFE composites are improved[1].

However, the research on the crystallization of PTFE has been limited in the one-dimension crystallization and PTFE spherulitic crystal has not been observed[2]. Bunn et al.[3] reported striated band-like structures on fractured surfaces of PTFE. Symons observed dendrites and star-like crystals in the solution-grown crystals[4] and he also observed both the plate-like single crystals of clear hexagonal habit and the striated broad needles[5]. Rahl et al.[6]observed emulsion-grade PTFE and found ribbon-like and rod-like crystallites; they postulated that these crystallites consist of single crystals of

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extended chain packing. Ozawa[2] observed the nonisothermal crystallization of several PTFE materials with DSC. The results showed that Avrami exponents is all near 1, which were in accordance with the PTFE crystalline morphology[2]. Later, G.Kostov [7] studied the non-isothermal crystallization and crystalline morphology of PTFE polymerization-filled with CaCO3, the results showed that Avrami's constant is near 1, the activation energy of crystallization changed in a range of 14.7-28.7KJ/kg.deg with the degree of filling, and one-dimension growth of the crystals was found to occur. PTFE filled with molybdenum disulphide, graphite lead oxide, and basalt was studied by A.Dobreva[8] and the results showed that basalt particles did not influence the degree of crystallinity of PTFE resins and exhibited poor nucleation activity.

Under scanning electric microscopy (SEM), The present authors[9] observed PTFE spherulitic crystals in PTFE composites for the first time. In this paper, Polarized optic microscopy is used to verified the existing of the spherulitic crystals in the PTFE composites. Further, the crystallization kinetics of PTFE matrix is studied. The results show that Avrami exponent is near 3, which is in accordance with the crystalline morphology observed under POM.

MATERIALS AND EXPERIMENTAL

Materials and composites preparation

PTFE resin and glass fiber were bought from Shanghai Sanaifu (3F) New Materials Corp. and Shanxi Glass Fiber manufacturer in China, respectively. The properties of the materials and the method of PTFE composites samples preparation had been discussed in detail by X. Wang and coworkers[9].

Microscopy analysis and the verifying to PTFE spherulitic crystal

The samples were fractured in liquid nitrogen and then coated with gold . The morphology was studied by SEM using a Hitachi S-570.

For further morphology observation, the same samples were sectioned to less than 0.3mm thick using a microtome. POM (Nikon MICROPHOT-FXA) was used to observe the crystalline morphology.

PTFE Isothermal crystallization

The kinetics of the isothermal crystallization process was followed using a Perkin-Elmer DSC-7 analyzer. The experiments were carried out under nitrogen, and the calibration was performed with indium and zinc. PTFE composite samples were heated to 653K (heating rate 20K/min), held at the molten state for 3 min to erase the former thermal history, and then rapidly cooled at the maximum cooling rate (200K/min) to the crystallization temperatures, T_c (589.5K, 590.5K, 591.0K, 591.5K and 592.0K), T_c was then held constant until crystallization was completed.

RESULTS AND DISCUSSION

crystallinity morphology

SEM was used to observe the fractured surface of PTFE composites. Fiber-like crytals were observed on the fractured surface of pure PTFE matrix composites[Fig.1(a)]. This results were in accordance with the results of isothermal and non-isothermal crystallization kinetics of the pure PTFE composites[10], and were also in accordance with the above-mentioned reports about one-dimensional growth of PTFE crystals. While PTFE matrix was filled with a kind of inorganic particles, the SEM photos showed that crystalline morphology of PTFE matrix was similar to spherulites [Fig.1(b)]. In order to verify the spherulites, POM was used to observe the slices of the PTFE composites and POM photos obtained showed there were existing the PTFE matrix spherulites in the composites [Fig.2(a)]. In the Fig.2 (a), the size of one spherulite was different from that of another. It could be illustrated that the inorganic particles, which acted as nuclei, were distributed unevenly. While the particle was dense, the growth of spherulitic crystals was hindered. This leaded to the number of spherulite was bigger and the size was smaller than that of spherulite growing in a place where the nuclei was thin. From Fig.2(b), we could easily compare the size of spherulite with the size of short-cut fibers in the composites.

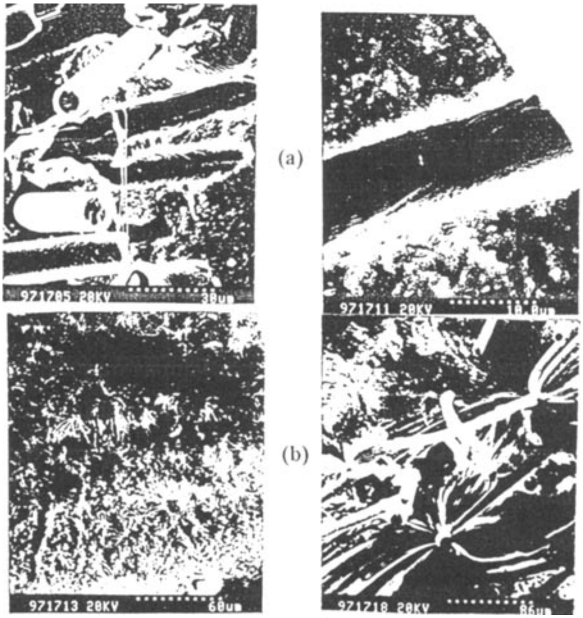


Fig.1 SEM images of cross-section of PTFE composites

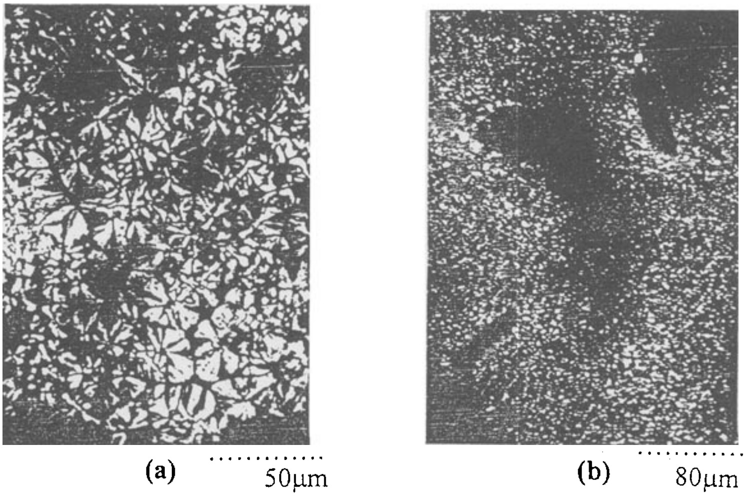


Fig.2 POM micrographs of PTFE composites

Isothermal crystallization kinetics of PTFE matrix

The well-known Avrami equation[11] has been widely used to analyze isothermal crystallization, it was assumed that the relative degree of crystallinity X_t which had been transformed by time, t, was

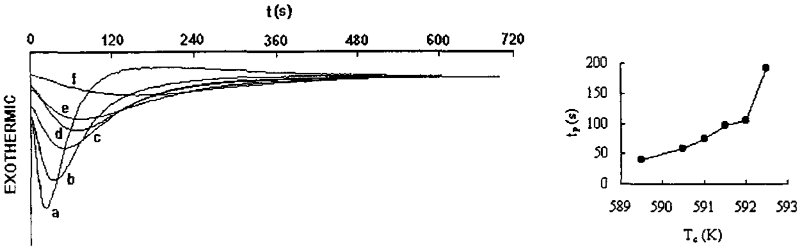
$$X_t = \frac{X_{c(t)}}{X_{c(\infty)}} = \frac{\int_0^t (dH_c/dt)dt}{\int_0^\infty (dH_c/dt)dt} = 1 - \exp(-kt^n) \qquad (1)$$

Where $X_{c(t)}$ and $X_{c(\infty)}$ are the degree of crystallinity at time t and at the end of crystallization, respectively; dHc/dt is the rate of crystallization heat evolution at time t; k is a rate constant; n is the Avrami exponent, an integer between one and four depending on the geometry of the growing entities and the nature of the primary nucleation.

In order to conveniently deal with the problem, Eq.(1) was usually rewritten as the following form:

$$\ln[-\ln(1 - X_t)] = \ln k + n \ln t \qquad (2)$$

The results of isothermal DSC experiments were presented in Fig.3. Compared with the one-dimensional crystallization of PTFE[10](Fig.4), the DSC thermograms of isothermal three-dimensional crystallization at different T_c were more integrated and the peak time for maximum crystallization (t_{max}) was longer than that of one-dimensional crystallization. So, for PTFE resins, the rate of three-dimensional crystallization was slower than that of one-dimensional crystallization and the three-dimensional crystallization process was easier to control than one-dimension. It could be seen that the peak time for maximum crystallization (t_{max}) increased with increasing the crystallization temperature [Fig.3 (b)].This indicated that with the increase of the crystallization temperature, the crystallization rate decreased.



(A) (B)

Fig.3 (A) DSC thermograms of isothermal crystallization at different Tc: (a) 589.5K; (b) 590.5K; (c) 591K; (d) 591.5K; (e) 592K; (f) 592.5K. (B) t_p as a function of T_c.

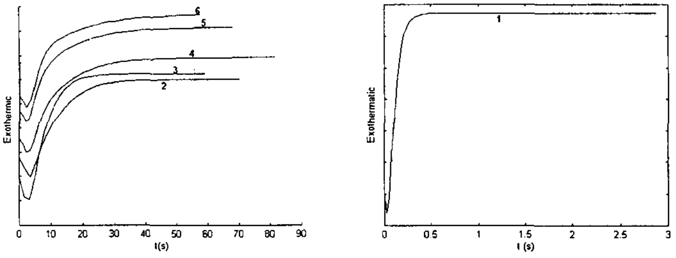


Fig.4 DSC thermograms of PTFE one-dimension isothermal crystallization at different Tc: (1) 569K (2) 577K (3) 585K (4) 586K (5) 587K (6) 588K [9]

Some typical isotherms of the relative amount of crystallinity for the crystallization from the melt state of PTFE are illustrated in Fig.5. The relative amount of crystallinity that develops at a definite time t decreases with increasing of the crystallization temperatures.

The avrami parameters n and k could be estimated (Tab.1) from the slopes and the intercepts respectively in the plots of $\ln[-\ln(1-X_t)]$ versus ln(t) as shown in Fig.6. In Fig.6, each curve showed an initial linear portion, subsequently tending to level off. This deviation was considered to be due to the effect of the secondary crystallization which was caused by the spherulite impingement in the later stage of crystallization. The linear portions were almost parallel to each other, shifting to longer time with increasing of T_c. From Tab.1, the average values of Avrami exponent are near 3. It can be concluded from the fact that the crystals of PTFE growed three-dimensional from the preexisting nuclei. In addition, the values of the crystallization rate parameters, k, are apt to decrease with increasing of the crystallization temperature due to a gradual decrease in degree of supercooling.

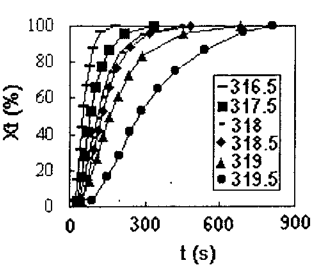


Fig.5 Development of relative crystallinity with time for isothermal crystallization

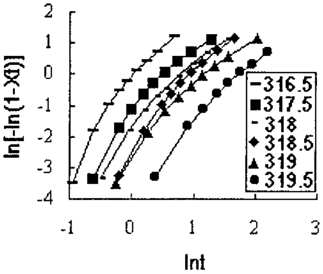


Fig.6 Avrami plots of isothermal crystallization of PTFE at different Tc.

Tab.1 The data of three-dimensional isothermal crystallization of PTFE matrix

T_c(K)	$\Delta H_m{}^a$(J/g)	$X_c{}^b$(%)	N	K (s^{-1})
589.5	32.078	36.04	2.75	0.7644
590.5	33.911	38.10	2.98	0.2775
591.0	35.120	39.46	2.65	0.8326
591.5	31.738	35.66	2.84	0.0827
592.0	31.579	35.48	2.49	0.0667
592.5	28.143	31.62	2.42	0.0171

[a] heat of fusion after isothermal crystallization of PTFE matrix at given T_c.

[b] X_c degree of crystallinity determined as $Xc=\Delta H_c/\Delta H_c{}^{*}\bullet 100\%$, $\Delta H_c{}^{*}=69J/g$[10]

This mechanism of three-dimensional growth was in accordance with the POM micrographs of PTFE composites. But the three-dimensional growth was different from the above-mentioned reports about band-like crystals[3], dendrites and star-shaped crystals[4], needle-liker crystals [5] and ribbon-like and rod-like crystals[6]. And the three-dimensional growth was also different from the results obtained by Qzawa[2] through non-isothermal crystallization of pure PTFE resins, and different from the results of G.Kostov [7] and A.Dobreva[8]. The three-dimensional growth of PTFE matrix crystals may be caused by the inorganic particles added in the PTFE suspension.

CONCLUSION

PTFE spherulitic crystals in PTFE matrix composites, for the first time, were observed. So was verified by POM micrographs of the PTFE composites. The results of isothermal crystallization of PTFE showed that PTFE crystals grow three-dimensionally, which was in accordance with the conclusion that there exist spherulites in the PTFE composites. The rate of three-dimensional crystallization of PTFE was lower than that of one-dimensional crystallization, and the three-dimension crystallization was easier to control than the one-dimension crystallization of PTFE. The discovery on PTFE Spherulitic crystal changes the fact that PTFE crystals only grow one-dimensionally, and at the same time, diversifies the crystal state of PTFE. This new discovery can be used to develop the design and control of PTFE micro-morphology, and will lead to a new promising research direction on PTFE materials.

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