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Unusually high temperature transition and microporous structure of polytetrafluoroethylene fibre prepared through film fibrillation

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ABSTRACT

The melting behaviour and structure of polytetrafluoroethylene (PTFE) fibre prepared through film fibrillation were investigated in this study. An unusually high temperature transition of PTFE fibre was observed using a differential scanning calorimeter and a hot stage polarising microscope. The network rectangular porous channel structure framed with fibrils and membranes in the PTFE fibre was obtained after an axial tear failure. It was suggested that the extruding, rolling, and drawing processes be beneficial for molecular constraints between crystals and have contributed to the presence of the unusually high temperature transition of PTFE and the formation of a rectangular porous channel structure in the PTFE fibre. The development of the microporous structure of PTFE fibre is present in diagrams in this paper.

1. Introduction

Polytetrafluoroethylene (PTFE) is a fully fluorinated polymer [1]. The rigid molecular chain with a nearly cylindrical shape of PTFE has a high melting point [2]. The equilibrium melting temperature ($T_m°$) of PTFE is 327 °C [3] and depends on the thermal history and experimental conditions [4–6]. Grebowicz et al. [7] found that drawn or sintered PTFE has a higher melting temperature at 381 °C, which was assumed to be metastable because of the strain in tie molecules between the remaining crystals within the fibre. After the PTFE sintered at 447 °C and held for 10 min, the high melting peak disappeared when it was heated in the second reheating process [7]. Khanna et al. [8] demonstrated a high temperature transition at approximately 370 ± 10 °C, which was caused by moderate shear stresses on a high molecular weight. After the PTFE was heated to 400 °C and held for 5 min, the high melting peak was reversible in the second reheating process [8]. Folda et al. [9] observed the appearance of liquid crystal, which is an anisotropic suspension of PTFE whiskers produced through emulsion polymerisation with 1% w/v of ammonium perfluorodecanoate as a surfactant. Shimizu et al. [10] also observed the birefringence phase in PTFE fibre, which exhibited an anisotropic optical property at temperatures slightly higher than their apparent melting point of 330 °C estimated according to the DSC curve; this indicated a phase transition from a solid to a liquid crystal. When heating to above 450 °C, the micrograph showed a decreasing brightness and finally a dark field, indicating a random orientation of PTFE chain molecules. The reversibility of the liquid crystal transition in the temperature range from 300 °C to 370 °C was confirmed using a crossed polarised optical microscope.

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Microporous PTFE membranes have been produced using a series of mechanical operations through extruding, rolling, stretching, and sintering [11]. PTFE particles have a distinctive form [11,12], which consists of a ribbon-like crystalline structure that is easily disassembled because of relatively weak attractive interaction forces. When receiving external stress, individual lamellae connected by distant bridges of tie chains bend and depart locally; discontinuities (i.e. pores) appear in interlamellar spaces between the tie points [13]. Additionally, the morphology and structure–properties relationship of PTFE depend on its stretching parameters, such as temperature, rate, and heat treatment [11,14–16].

The high temperature transition and porous structure of the PTFE membrane has been reported in previous studies [7–9,11,14–16], but PTFE fibre prepared through film fibrillation have not been discussed. In this study the PTFE fibre made by a slit film process, which is called film fibrillation. The PTFE powder was extruded and rolled to form a PTFE film, cut film into narrow ribbon-like sections, and then stretched with a high drawing ratio to form fibres. The melting behaviour of PTFE powder, film, and fibre was studied using a differential scanning calorimeter and a hot stage polarising microscope. The structure of the PTFE fibre was investigated after axial tear, tensile, and longitudinal fatigue failure. The development of the microporous formation of PTFE fibre after stretching was also studied.

2. Experimental

The as-received PTFE powder was obtained from Daikin Co. Ltd. (F-106 grade). Using the equation for the number-averaged molecular weight ($\overline{M_n}$) of PTFE powder, $\overline{M_n} = 3.5 \times 10^{11} \times \Delta H_c^{-5.16}$, where ΔH_c (cal/g) is the heat of crystallisation [17–19], the number-averaged molecular weight of the as-received PTFE was 9.1×10^6 g/mol. The PTFE powder was extruded and rolled at 250 °C at a drawing ratio of 10 times to form a PTFE film with a thickness of 191 μm. The film was then cut and stretched at a drawing ratio of 70 times at 400 °C to form fibres with a thickness of 27 μm. Finally, the PTFE fibres were sintered at 400 °C for 10 s. A continuous process from powder to sintered fibre was used in this study. After thermogravimetric analyses of the PTFE, the initial degradation temperatures of power, film, and fibre are 543.5, 561.4, and 550.0 °C, respectively.

The melting behaviour of the PTFE samples was studied using a Du-Pont Q10 differential scanning calorimeter (DSC) with a TA2000 thermal analysis system. The experiments were performed in a nitrogen atmosphere at 50 cm^3/min. Optical anisotropy of the samples was observed using a hot stage polarising microscope (HSPM, LABORLUX 12 POLS, Leitz), which consisted of a heater (Linkam THMS 600) equipped with an electric microscope controller (Linkam TMS91) and photographic equipment (SPOT Idea™ ID2820). The flow rate of the purge gas N_2 was 140 cm^3/min.

Tensile failure and longitudinal fatigue failure of the PTFE fibres were induced using a Tytron 250 microforce testing system machine. Sample length was set at 25.4 mm. The stretching rate of tensile failure was 0.25 mm/s. The axial tear failure of PTFE fibre was teared in fibre axis by hand. The longitudinal fatigue failure was induced at 0.1 Hz for 20 cycles at a stretching ratio of 1.2 times for PTFE fibre. The failure surface and internal structure of the PTFE fibres were observed using a HITACHI S3000 scanning electron microscope (SEM, Japan) at 10 kV. The sample was coated using an Au ion sputter (Hitachi E-1010) for 40 s.

3. Results and discussion

3.1. Melting behaviour of PTFE

Fig. 1 shows the DSC heating curves of the as-received PTFE powder from 10 °C to 420 °C at 10 °C/min. Three endothermic peaks at T_{e1p} (21 °C), T_{e2p} (31 °C), and T_{e3p} (348 °C) were found in the first heating process. PTFE has two crystal-disordering

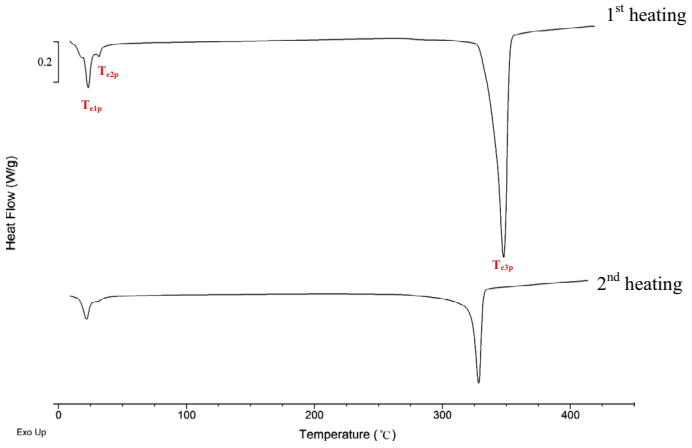

Fig. 1. DSC heating curves of as-received PTFE powder from 10 °C to 420 °C at 10 °C/min.