Radiation Physics and Chemistry 81 (2012) 256–263

Contents lists available at SciVerse ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Morphology of polytetrafluoroethylene before and after irradiation

Sergei A. Khatipov*, Sergei A. Serov, Nataliya V. Sadovskaya, Elena M. Konova

Karpov Institute of Physical Chemistry, Vorontsovo Pole street 10, Moscow 105064, Russia

ARTICLE INFO

Article history:
Received 11 August 2011
Accepted 21 October 2011
Available online 20 November 2011

Keywords:
Polytetrafluoroethylene
Morphology
Radiation modification
Scanning electron microscopy
Fibrils
Spherulites

ABSTRACT

Supramolecular structure and morphology of as-polymerized, sintered, and gamma-irradiated suspension PTFE were studied with scanning electron microscopy. Irradiation was performed both below and above melting point of crystal phase. Fibrillar supramolecular structure of as-polymerized PTFE is preserved after its sintering. In contrast to as-polymerized PTFE, in the sintered polymer some segments of fibrils form lamellae of thickness 100–300 nm and length up to several microns, with fibrils arranged perpendicularly to a lamella. Irradiation below the melting point (20 and 200 °C) does not change quantitatively PTFE morphology. In both cases and also in the case of pristine PTFE, dense and loose (porous) regions are present in its morphology. Dense regions are packages of irregular shape and consist of densely packaged fibrils. Loose regions consist of individual ribbons and fibrillar lamellae. Irradiation at 200 °C increases greatly the width of lamellae. PTFE structure rearrranges drastically under irradiation above the melting point. New morphology units, spherulites of size about 50 μm, are formed, the spherulites consisting of radially extending fibrils, and porosity decreases substantially. Formation of spherulites is ascribed to radiation-induced chain scission and decrease in molecular mass and viscosity of polymer.

1. Introduction

Recently there is a surge of interest to study PTFE irradiated with heavy ions, γ-radiation, and electron beam (Sun et al., 1994a; Oshima et al., 2007; Pugmire et al., 2009; Lunkwitz et al., 2004). Close attention to these investigations is associated with the finding that a number of the practically important PTFE properties are significantly improved when the polymer is affected by radiation at temperatures above its melting point (Sun et al., 1994b; Oshima et al., 1995, 1997a; Setogawa et al., 2002; Khatipov and Artamonov, 2009; Khatipov et al., 2009). A wide variety of modern analytical methods were used to investigate this phenomenon (Lunkwitz et al., 2004; Oshima et al., 1997b, 1997c; Lappan et al., 1999, 2000). In these works main attention was focused on molecular mechanisms and molecular structure. In addition, it is clear that macroscopic properties of the polymer depend on its supramolecular structure and morphology. Therefore, on a par with clarification of the molecular mechanisms, investigation of morphology of irradiated PTFE is of independent interest.

Morphology of as-polymerized unirradiated PTFE has been investigated for more than five decades (Bunn et al., 1958; Speerschneider and Li, 1962; Speerschneider and Li, 1963; Davidson et al., 1999; Geil et al., 2005). For the first time morphology of PTFE crystallized from melt was investigated by means of electron microscopy in ref. (Bunn et al., 1958). Existence of bands with striation structure was found. The bands were interpreted as faces of crystal lamellae. In contrast, it was concluded in refs. (Speerschneider and Li, 1962; Speerschneider and Li, 1963) that the bands consist of fibrillar crystallites packed in parralel and the striation structure is due to interfibrillar amorphous regions. On the basis of analogs with polyethylene (PE) in ref (Melillo and Wunderlich, 1972) the authors returned to the interpretation of the bands as faces of crystal lamellae and of the striations as a result of fracture. Further, this point of view has become dominant (Geil et al., 2005; Wunderlich, 1973; Androsch et al., 2005). Although, on the basis of studying supramolecular structure and particle morphology of raw PTFE it was concluded in ref. (Kostromina et al., 1990) that fibrillar structure remains after sintering.

It should be noted that, in contrast to sintered PTFE (crystallized from melt), there is a unified opinion in the literature about morphology of as-polymerized PTFE (unsintered raw PTFE). According to this opinion, as-polymerized polymer has fibrillar structure before sintering (Davidson et al., 1999; Melillo and Wunderlich, 1972; Butenuth, 1958; Kostromina et al., 1990).

In the present work a comparative study of as-polymerized PTFE, sintered PTFE, as well as PTFE irradiated at various temperatures was performed.

2. Experimental

2.1. Test objects

Particles of as-polymerized high molecular weight PTFE produced by suspension polymerization that were never milled and never heated above the polymer melting point were investigated.

* Corresponding author.
E-mail address: sakh@mail.ru (S.A. Khatipov).

0969-806X/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.radphyschem.2011.10.018

The powder was synthesized by Galogen LLC (Perm, Russia) using standard procedure (GOST 10007-80).

Block samples of sintered PTFE were manufactured by Kirovo-Chepetsk chemical plant from the polymer powder of PN grade by uniaxial molding with a further sintering (TU 6-05-810).

2.2. Irradiation

The sintered PTFE samples were irradiated at 20, 200 and 335 °C in inert gas atmosphere (argon) by ^{60}Co γ-quanta with mean energy 1.25 MeV using (КСВ-500) γ-ray apparatus located in Karpov Institute of Physical Chemistry (Moscow, Russia). The samples were placed into the radiochemical apparatus whose design makes it possible to specify required irradiation conditions.

2.3. Scanning electron microscopy

Morphology of PTFE samples was examined by scanning electron microscopy (SEM). Fractured surfaces were prepared in liquid nitrogen. A JEOL (Japan) JSM-7500F high resolution scanning electron microscope with a field-emission cathode was used to obtain images of the fracture surfaces. The images were obtained in a mode of low-energy secondary electrons because the highest resolution could be obtained in this case (the resolution was 1.5 nm at primary beam energy of 1 keV and 1 nm at 5 keV). To eliminate charging and destruction of the analyzed surface by electron beam, the following technical approaches were applied: (1) low electron beam current (3×10^{-11} A) from a cathode with cold field emission was used; (2) a special Gentle Beam mode decelerating incident electrons near the analyzed surface was used; as a result, an energy of primary electrons, on the one hand, decreases to the ultra-low values reducing the charging effects and eliminating the sample destruction, and, on the other hand, diameter of incident electron beam remains small, maintaning high resolution; (3) the fracture surface was coated with thin platinum film by magnetron deposition.

Parameters of the platinum deposition process were the following: current 30 μA, deposition time 20 s, distance from target to sample 40 cm, pressure 5 Pa. Thickness of platinum film obtained under these conditions was about 5 nm. To eliminate any artifacts associated with platinum deposition on the fracture surface, some preliminary experiments on deposition of platinum on silicon single crystals were performed under the same conditions. At the specified mode of deposition the size of platinum particles on the faces of silicon single crystal was 4–5 nm.

An increase in the sample temperature during scanning was estimated by Castaing equation (Castaing, 1960) and was below 10 °C. The regions with sizes from 0.2×0.15 to 60×45 μm^2 were investigated at magnification up to 500,000 ×.

3. Results and discussion

3.1. Morphology of as-polymerized PTFE

It is well known that the primary product of PTFE polymerization is powder with particle size ranging from tens to hundreds microns. The particles have high crystallinity about 95–98%. The synthesized powder is then milled mechanically to obtain specified distribution of particle size required for further molding and sintering.

To eliminate mechanical effects on the particle morphology, unmilled as-polymerized particles were examined. The size of these particles was in the 0.1–1 mm range.

It could be seen from Fig. 1 that the powder particles have nonuniform structure. Two kinds of regions are observed: dense and fibrous ones. The fibrous regions form the persistent continuum with a random distribution of dense inclusions, which are small regions with wide size distribution from microns to tens of microns.

Further magnification demonstrates that individual fibers have well recognizable substructure (Fig. 2). A fiber consists of several thinner fibrils. This is indicated by the presence of deep longitudinal striations and the flat fiber configuration (i.e., width of a fiber is higher than its thickness). Thereby, the fibers can be classified as ribbons consisting of fibrils oriented along a ribbon. The smallest fibril diameter, which can be recognized (detected) is ~15 nm.

Macromolecules are directed along the fibril (and the ribbon) because mean length of the polymer chains for PTFE polymerized in suspension (typical molecular weight about 5×10^6) is on the order of 5 μm, and it is unlikely that macromolecules could fold up to form such thin filament (15–20 nm). Length of fibrils is up to tens of microns and, therefore, exceeds the length of a macromolecule. Taking into account the high crystallinity (close to 100%) of as-polymerized PTFE it could be concluded that the

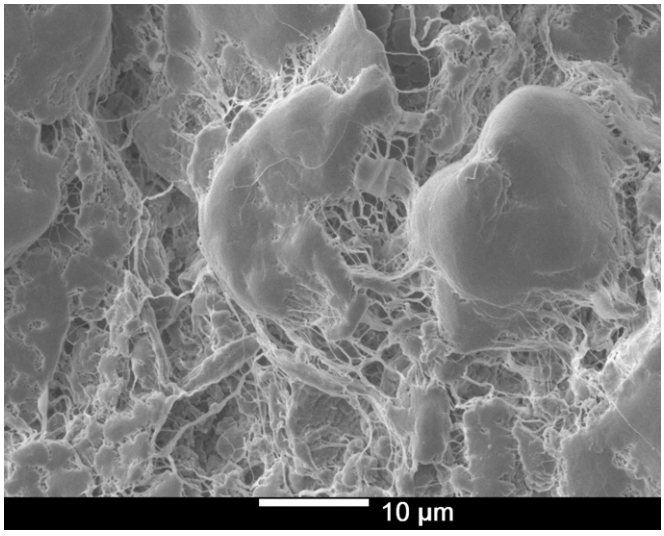

Fig. 1. A particle of as-polymerized high molecular weight PTFE produced by suspension polymerization on a substrate.

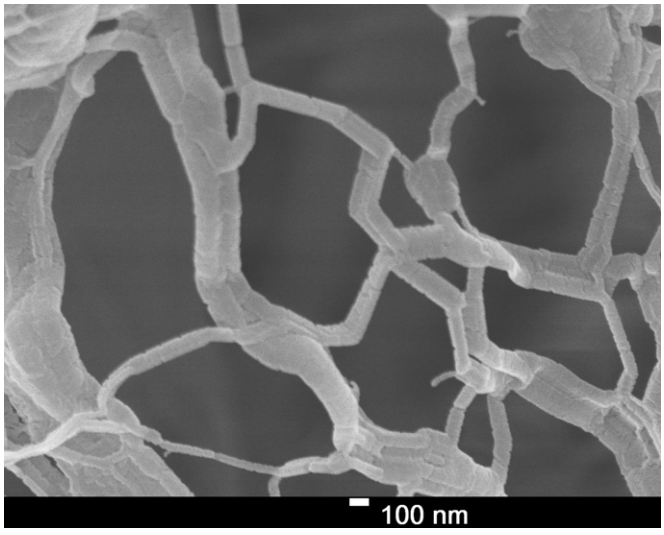

Fig. 2. Typical SEM images of fibrillar (filamentous) structures of as-polymerized high molecular weight PTFE.