

Low Temperature Post Radiation Polymerization of Tetrafluoroethylene in the Presence of the Graphene 3D Material

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(Received 01 July 2013; published online 03 September 2013)

It was found that irradiation by γ -rays at the liquid nitrogen temperature of a mixture of C₂F₄ with the graphene 3D material obtained by explosive exfoliation of graphite oxide gives a composite in which the concentration of polytetrafluoroethylene is 80 wt %. In the case of C₂F₄ polymerization under similar conditions in the absence of the carbon material, the PTFE yield is six times lower. The results of certification of both the parent carbon material and the composite obtained via polymerization are also reported.

Keywords: Graphite Oxide, Tetrafluoroethylene, Post Radiation Polymerization, Polymer-Graphene Composites.

PACS numbers: 82.50.Hp, 78.40.Ri

1. INTRODUCTION

The use of polytetrafluoroethylene (PTFE) is sometimes limited by its high flow under load. The standard method of elimination of these shortcomings is to introduce fillers with improved mechanical properties into polytetrafluoroethylene. One of the candidates for this role can be graphene, a material with the declared outstanding mechanical properties [1]. However, pure graphene is quite an expensive material, which is also very difficult to handle. In this regard, various graphene-like structures that are expected to retain at least partially the unique properties of graphene come to the fore [2].

In this communication, we describe our experiments on low temperature polymerization of tetrafluoroethylene (TFE, C₂F₄) in the presence of the graphene like material obtained by microwave treatment of graphite oxide films. The results of certification of both the parent carbon material and the composite obtained via polymerization are also reported.

2. EXPERIMENTAL

Graphite oxide was prepared by the Hummer's method [3]. The synthesis procedure is detailed in [4]. Typical procedure for suspension production involved mixing of GO with water and following ultra-sound treatment within 30 min. The suspension was centrifuged for 20 min to remove large solids at 4000 g; afterwards it could be stored for a long period of time without splitting.

Graphite oxide films of 200–300 μ m thickness were prepared via deposition from aqueous suspension by evaporation. The films were separated from the glass substrates mechanically.

A GO film with an area of about 1 cm² was placed in a deep fused silica vessel, which had a cotton fabric filter mounted on the mouth to capture the explosion products. Then, the vessel was placed in a microwave oven (2450 MHz, 900 W) and heated to explosion; after that, the product microwave exfoliated graphite oxide (MEGO) was mechanically collected in the form of fine powder.

The C, N, and O contents of GO and MEGO samples were determined with an Elementar Vario Cube analyzer. The specific surface area of the samples was measured on an Autosorb 1 device (Quantachrome Corp.) using the low temperature nitrogen adsorption technique.

IR spectra were measured using a Perkin Elmer Spectrum 100 Fourier transform spectrometer with a UATR attachment over the range of 4000–670 cm⁻¹.

Micrographs of the samples were obtained using a Zeiss LEO SUPRA 25 scanning electron microscope.

Low temperature polymerization of C₂F₄ was performed according to the procedure detailed in [5, 6]. The procedure comprised the following steps. A MEGO powder was placed in a glass vial (of ~2 cm³ capacity) and pumped under vacuum at a temperature of 100°C. Then, the vial was cooled to 77 K, filled with TFE via its condensation by freezing to have a MEGO: TFE ratio of ~1 : 30, and sealed. The mixture prepared in this way was slowly warmed to room temperature and allowed to stand for 60 min. Then, the vial was cooled to 77 K and irradiated at this temperature on a Gammatok 100 cobalt radiation source. The absorbed dose was 40 kGy, and the dose rate was 0.17 Gy/s. After irradiation, the sample was subjected to gentle heating (0.6 K/min), during which the TFE polymerization took place [5]. The yield of the product was determined gravimetrically after removal of the unreacted monomer in a vacuum.

3. RESULTS

Elemental analysis data and the specific surface area measurement results for GO and MEGO are given in the table. It is seen that the microwave treatment significantly reduces the oxygen and hydrogen content of the sample and dramatically increases the specific surface area.

Table 1 – Specific surface area and concentration of some elements in the samples

Sample	Concentration of elements, wt %			S _{sp} , m ² /g
	C	O	H	
GO	50.10	44.81	2.69	20
MEGO	89.95	4.19	0.73	600

The mass increment of the sample on a TFE basis also corresponds to the transition of about 12.5% of TFE molecules to the solid phase. In the case of the low temperature postradiation polymerization of TFE under the same conditions in the absence of MEGO, the polymer yield does not exceed 2%.

Figure 1 shows the IR spectra of the product formed by γ -irradiation of TFE in the presence of MEGO and the spectrum of PTFE for comparison. The positions of the main absorption bands in these spectra are close enough: 1205.0 and 1150.3 cm^{-1} for PTFE and 1205.7 and 1150.6 cm^{-1} for the test product. It can be concluded that PTFE was produced during low-temperature irradiation and subsequent heating. Moreover, the spectra suggest that the PTFE chain length in the resulting composite is large enough. In the case of a short polymer chain length, the half width of the absorption bands due to C-F stretching increases and absorption bands characteristic of the end groups appear [7].

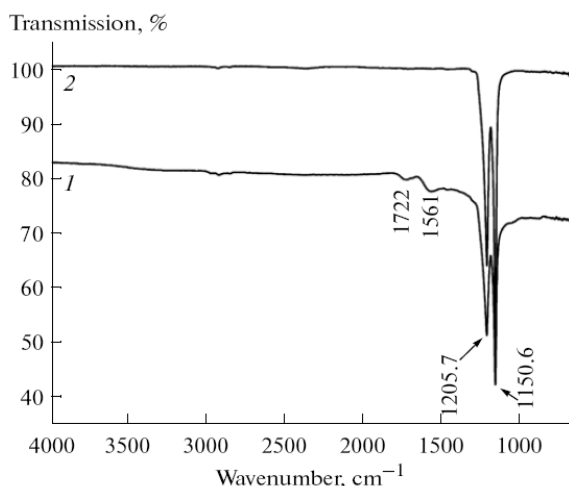


Fig. 1 – IR spectra of (1) the composite material obtained by low-temperature radiation polymerization of tetrafluoroethylene in the presence of MEGO and (2) polytetrafluoroethylene

The scanning electron microscopy images are shown in Fig. 2. Flat particles formed by the parallel planes of graphene oxide are seen in the initial GO. After explosive treatment, the planes of reduced graphene oxide bend. This prevents them from collapsing and provides a high surface area of MEGO. The photomicrographs of the product obtained by TFE γ -irradiation in the presence of MEGO show entities that resemble polytetrafluoroethylene globules in shape against the background of the morphological features of MEGO.

Thus, it was found that irradiation by γ -rays at the liquid nitrogen temperature of a mixture of C_2F_4 with the carbon material obtained by explosive exfoliation of graphite oxide gives a composite in which the proportion of PTFE is 80 wt %. In the case of C_2F_4 polymerization under similar conditions in the absence of the carbon material, the PTFE yield is six times lower. Consequently, MEGO in this case acts as an initiator of the low temperature TFE polymerization process.

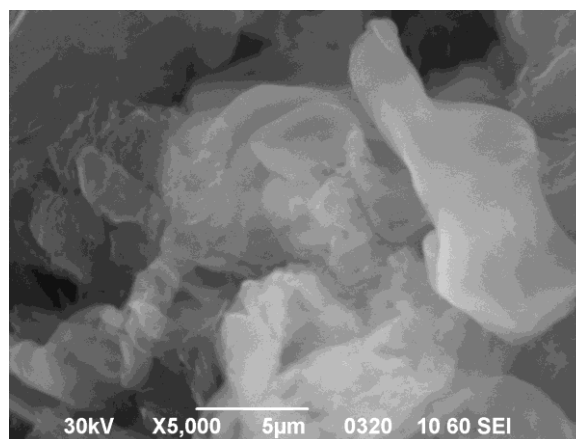
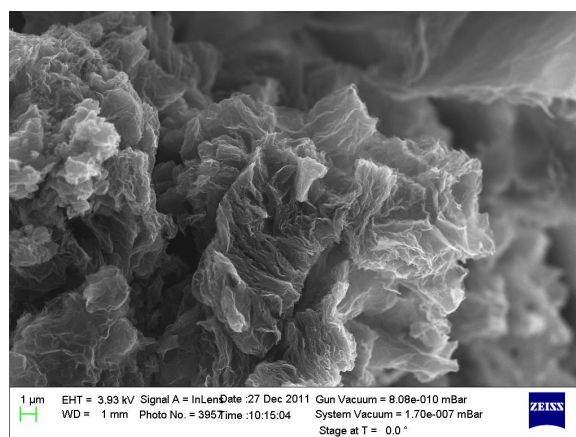
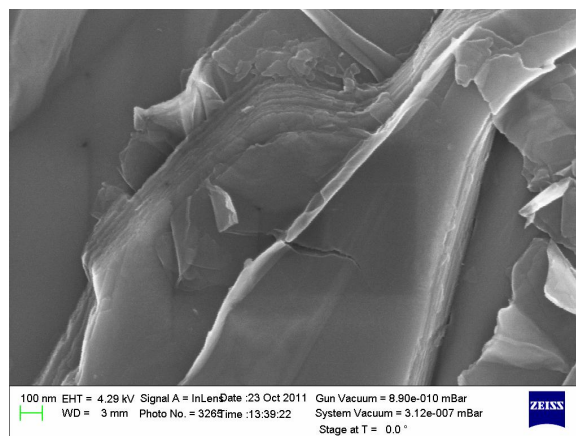


Fig. 2 – Photomicrographs of GO (top), MEGO (middle), and the composite (bottom)

The composite material resulting from this polymerization and consisting of PTFE (80%) and MEGO (20%) holds promise as a basis for manufacturing products with a low flow and an enhanced wear resistance as compared to pure Teflon.

ACKNOWLEDGEMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 13-03-00398-a).

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