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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Thermal and Thermo-Oxidative Destruction of Poly(Ethylene Terephthalate) Modified with Formulation Based on Polyfluorinated Alcohol

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Abstract—Stabilizing effect of 1,1,9-trihydroperfluorononanole-1 immobilized on a montmorillonite support on the stability of poly(ethylene terephthalate) at elevated temperatures was studied. Gas chromatography, IR Fourier spectroscopy, and mass spectrometry were used to examine gaseous products of its thermal and thermo-oxidative destruction. It was found that the initial formation rate of aldehydes and carbon dioxide decreases in the course of thermostating of the fluorine-containing composite polyester material. The method of thermogravimetry demonstrated that modified poly(ethylene terephthalate) has a higher thermal stability.

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One of ways to improve the properties of poly(ethylene terephthalate) (PET) is by obtaining polymeric composites with the use of poly- and perfluorinated compounds [1]. A promising method for introduction of small amounts (10^{-3}–10^{-4} wt %) of poly- and perfluorinated compounds is by using highly dispersed supports (nanosize layered aluminosilicates, calcium carbonate).

It was shown in [2, 3] that industrially manufactured polyfluorinated alcohols $H(CF_2CF_2)_nCH_2OH$ (n = 1–5) sorbed on a montmorillonite support affect the structure and properties of amorphous and amorphous-crystalline heterochain polymers. Combined, the unique nature of polyfluoroalkyl groups and the effect of the shape anisotropy of nanofiller particles provided an increase in the mechanical properties, hydrolytic stability, light and wear resistance of the resulting fluorine-containing composites.

The goal of our study was to obtain a composite material based on poly(ethylene terephthalate) and 1,1,9-trihydroperfluorononanol immobilized on montmorillonite and to examine its thermal and thermo-oxidative stability.

EXPERIMENTAL

As the polymeric matrix served preliminarily ground PET powder with particle size not exceeding 50 μm [Polief OAO, Republic of Bashkortostan, TU (Technical Specification) 2226-008-39989731–2009], content of carboxy groups of 28 mmol kg^{-1}, and characteristic viscosity of 0.79 dL g^{-1}.

The composite of 1,1,9-trihydroperfluorononanole-1 and montmorillonite was a powder in the form of a mixture of three main fractions (50–100 nm, 10 wt %; <1 μm, 80 wt %; <10 μm, 10 wt %), produced by the procedure described in [4]. The content of the polyfluorinated alcohol in the clay was 40.0 wt %.

The composite materials were prepared by mixing PET in a melt with 0.5 wt % organoclay in a double-screw Brabender extruder at a temperature of 260 ± 2°C.

The mixing occurred at a constant screw rotation speed of 150 rpm in the course of 10 min. Polymeric films were prepared by compaction of the melt, followed by quenching in water with melting ice.

An X-ray diffraction analysis of the samples was made on Bruker D8 Advance diffractometer in the transmission configuration with CuK_α radiation, and N-filter. The experimental superprotonic were processed with Diffrac. Eva and Topas software.

An elemental analysis of the polymer surface was made with a VG ESCALAB MK II X-ray fluorescence spectrometer (magnesium anode with characteristic radiation energy MgK_α = 1253.5 eV).

Thermogravimetric (TG) and differential thermogravimetric (DTG) curves were recorded with synchronous thermal analyzers [Netzsch TG 209 F1 Libra (air as medium) and Netzsch STA 449 F3 (argon as medium)] combined with an IR Fourier spectrometer (Bruker).The mass of the samples under study was 34–36 mg. On being placed in the system of thermobalances, the samples were kept at a temperature of 30°C for 10 min with an STC (sample temperature control) system and then heated at a linear rate of 10 deg min^{-1} and kept at a given temperature for 2 h. The thermogravimetric system was connected in situ via a transit line with the IR Fourier spectrometer. The temperature of the line was 250°C, and that of the gas cell of the IR spectrometer, 200°C. IR spectra were recorded at a spectral resolution of 4 cm^{-1} within the range 4400–650 cm^{-1} at a scanning rate of 16 spectra. As protective gas served high-purity (99.999%) argon delivered into the system through an SGT filter (Moisture trap), and air was used as a blowing-through oxidizing gas. The gas flow rates were 45 (protective) and 30 mL min^{-1} (blowing through).

A quantitative analysis of the gaseous products formed in decomposition of polymers in the air medium was made on a TGA-IST16-GCh/MS thermal analyzer (Mettler Toledo) combined with the gas chromatograph–mass spectrometer system.

RESULTS AND DISCUSSION

The thermal and thermo-oxidative stability of PET is closely associated with the structure of its macromolecule (presence of reactive groups, chain defectiveness, intermolecular interactions) and its structural-morphological characteristics (degree of crystallinity, specific features of the local order in amorphous regions), which are largely determined by the methods and conditions of sample fabrication [6–8]. For example, mostly the amorphous structure is formed when polyester films and threads are molded from a polymer melt under fast cooling conditions.

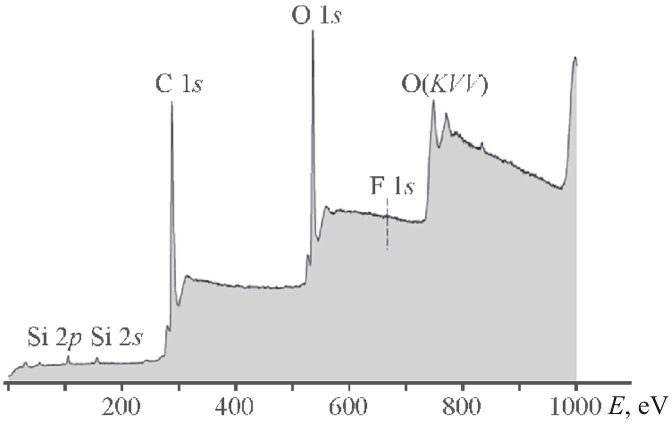

Fig. 1. Panoramic photoelectron spectrum of fluorine-containing composite PET. (*E*) Binding energy.

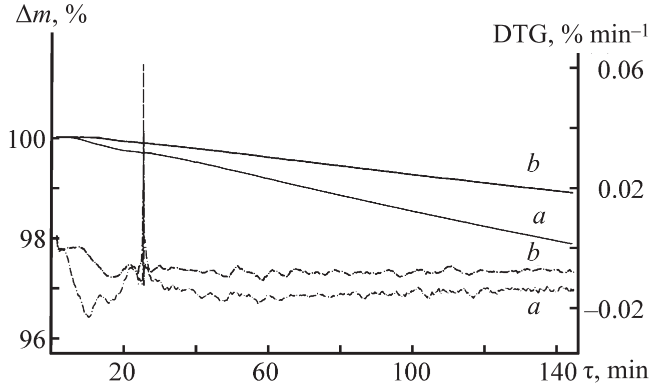

Fig. 2. TG and DTG curves of (*a*) starting and (*b*) fluorine-containing composite PET. Thermostating at 285°C in air. (Δ*m*) Loss of mass and (τ) destruction duration.

A diffraction analysis at small scattering angles demonstrated the disappearance of the basal reflection (d_{001} = 1.25 nm) corresponding to the distance between silicate plates. This indicates that the layered structure of organoclay is disintegrated and an exfoliated polymeric composite is formed. It should be noted that PET films containing a polyfluorinated alcohol immobilized on montmorillonite are also X-ray-amorphous, which is primarily due to their deposition conditions. The center of gravity of the amorphous halo is observed at 2θ = 18° (starting PET) and 2θ = 18.8° (fluorine-containing composite PET).

The chemical composition of the surface of a polymeric film filled with a fluorine-containing organo-

Table 1. Quantitative analysis of gaseous products formed in destruction of polymeric samples in air (thermostating at 285°C for 2 h)

PET sample	Onset temperature of intense decomposition, °C	Initial formation rate, mol % min^{-1}	
		aldehydes[a]	carbon dioxide
Starting	362	1.40	0.20
Fluorine-containing composite	371	1.00	0.13

[a] Acetaldehyde, formaldehyde.

clay was studied by X-ray photoelectron spectroscopy (Fig. 1) Carbon, oxygen, silicon, and fluorine were found in a very thin surface layer with depth not exceeding 3 nm. The insignificant amount of fluorine gave no way of estimating its content. Decomposition of the F1s spectrum isolated from the panoramic spectrum revealed the presence of three lines at 681.3, 687.2, and 695.1 eV, which differ in intensity and belong to fluorine in its various high-energy states (organomineral complexes with montmorillonite, proton-donor and proton-acceptor interactions of the polyfluorinated alcohol with polyester macromolecules).

The joint use of mass spectrometry and gas chromatography revealed that the main products formed in the thermo-oxidative destruction of PET are (presented for M$^+$) acetaldehyde (m/z = 45, I_{rel} = 77%) and formaldehyde m/z = 31, I_{rel} = 6%), carbon dioxide (m/z = 44, I_{rel} = 17%), carbon monoxide (m/z = 28, I_{rel} = 9%), and water (m/z = 19, I_{rel} = 5%) (Table 1). It can be seen that the introduction of a fluorine-containing organoclay has a thermally stabilizing effect and makes lower the release rate of volatile products.

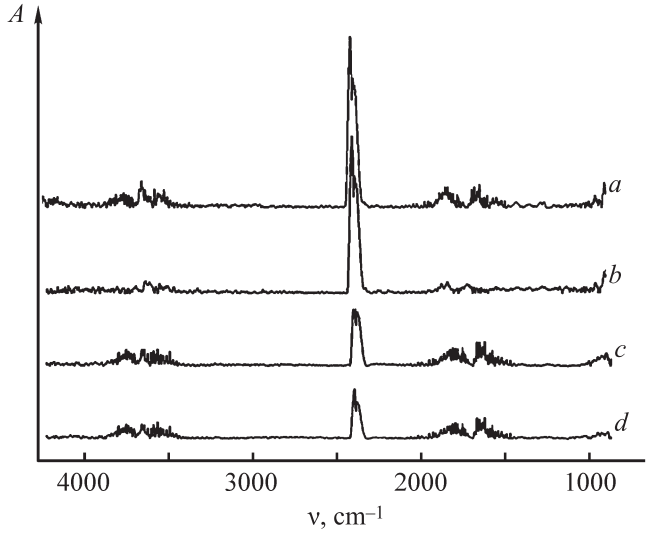

Fig. 3. IR Fourier spectra of gaseous products formed in destruction of (*a, b*) starting and (*c, d*) fluorine-containing composite PET in air at 285°C. (*A*) Absorption and (ν) wave number; the same for Fig. 4. Thermostating duration (min): (*b, d*) 35 and (*a, c*) 60.

A thermal analysis of the polymer in the air medium demonstrated that a 0.31% loss of mass is characteristic of the sample of the starting PET below the keeping temperature (Fig. 2, Table 2). The DTG curve has two peaks, the first of which (130°C) is due to the desorption of water from the polyester surface, and the second (192°C), to the onset of the thermo-oxidative destruction process. It should be noted that, as a temperature of 285°C is reached, a partial oxidation of the samples is already observed, which is confirmed by IR Fourier spectroscopy (Fig. 3). The following absorption bands are identified in the spectra: water [broad band ν(O–H) at 3500–4000 cm^{-1}, carbon dioxide (2318–2350 cm^{-1}),

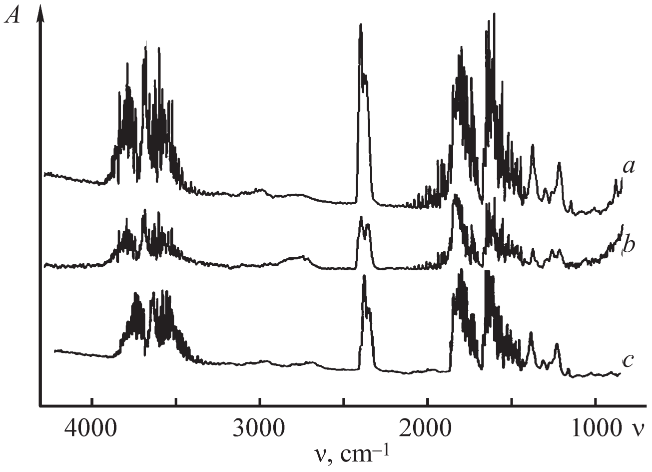

Fig. 4. IR Fourier spectra of gaseous products formed in destruction of (*a, b*) starting and (*c, d*) fluorine-containing composite PET in argon at 360°C. Thermostating duration (min): (*b*) 35 and (*a, c*) 102.

Table 2. Main qualitative characteristics of the destruction of polymeric samples in air (thermostating at 285°C for 2 h)

PET sample	Loss of mass Δm_1 up to isotherm temperature, %	Loss of mass Δm_2 upon keeping for 2 h, %	Total loss of mass Δm_{tot}	Presence of a peak in the first derivative DTG1 of TG signal, °C	Presence of a peak in the first derivative DTG2 of TG signal, °C
Starting	0.31	1.84	2.15	130.90	191.90
Fluorine-containing composite	0.11	1.00	1.11	–	198.00

and aldehydes [ν(C=O) at 1754–1760 cm^{-1}, ν(C–H at 2698–2819 cm^{-1}].

A substantially smaller loss of mass (0.11%) is characteristic of the fluorine-containing composite PET below the keeping temperature, which is due to the hydrophobizing nature of 1,1,9-trihydroperfluorononanole-1 immobilized on montmorillonite, used in the study. It can be seen from the IR Fourier spectra that the modified polyester has a higher stability at elevated temperature and its thermo-oxidative destruction is slower than that of the starting PET.

The compositions of the gaseous products of destruction in nitrogen of both the starting and the fluorine containing composite PET are similar. The products are represented by aldehydes, carbon monoxide (2015–2174 cm^{-1}), carbon dioxide, and water, the relative intensities of which become weaker in the IR Fourier spectra of the modified polyester (Fig. 4).

The main reasons for the thermal stabilization of PET under the action of the fluorine-containing organoclay being introduced is the integrated influence exerted by its organofluorine and mineral components. On the one hand, this provides that a diffusion barrier for volatile decomposition products is formed due to the exfoliation of montmorillonite particles in the polymeric matrix and ensures more effective heat dissipation. On the other hand, this enables generation of electrophilic $^{\bullet}(CF_2CF_2)_4 \cdot CH_2OH$ radicals reacting with macroscopic radials formed in the thermal decomposition of polymer chains, with radical processes thereby terminated.

Other possible reasons for the increased thermal stability of the resulting polyester composite samples is the inhibition of radical reactions by the paramagnetic iron present in a considerable amount in montmorillonite being used (3.03 wt % according to X-ray fluorescence data) [9] and the Lewis acidity of montmorillonite, associated with isomorphous substitution processes in its crystal structure, which enable intake of single electrons from donor-molecules, with the organic radicals thereby bound [9–11].

CONCLUSIONS

(1) Fluorine-containing polymeric formulations based on poly(ethylene terephthalate) and montmorillonite modified with 1,1,9-trihydroperfluorononanole-1 were obtained. The formulations have a higher stability (compared with the starting polymer) under conditions of thermal and thermo-oxidative destruction.

(2) It was found that the exfoliation of particles of fluorine-containing organoclay occurs in the polyester matrix, with an exfoliated composite formed.

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