

06.4

The phenomenon of movement of organic matter (polypropylene) in a temperature field

© B.K. Zuev, A.E. Zaitseva

V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia

E-mail: mihneva.1999@yandex.ru

Received April 15, 2024

Revised May 22, 2024

Accepted June 3, 2024

In the process of studying the oxidative thermal degradation of polypropylene by the method of oxythermography, the phenomenon of movement of matter in a gradient temperature field was discovered. When the sample was introduced into a high-temperature reactor, being in a gradient temperature field, the sample passed into a liquid state, and then in the form of a drop remains on the surface of the quartz tube of the boat holder, where the sample was placed. The drop in space remained in place, and the boat holder to which the drop was attached moved. A drop relative to a quartz tube moves from an area with a high temperature to an area with a lower temperature..

Keywords: thermal methods of substance research, oxythermography, substance in a temperature gradient field, movement of the substance, polypropylene.

DOI: 10.61011/TPL.2024.09.59166.19952

Classical methods of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) [1] are traditionally used to study the process of thermal destruction of organic substances heated in air. These methods rely on programmed heating (in most cases, linear) of a sample.

In recent years, oxythermography has also been used actively for analysis of matter [2]. The method of thermal oxidation spectroscopy (oxythermography) is based on programmed heating and high-temperature oxidation of organic substances in a flow of a binary mixture (inert gas–oxygen) or air and quantification of molecular oxygen spent on high-temperature oxidation. Gases other than oxygen (carbon dioxide or water vapor) may also be detected. This method may provide data on the organic matter content in the bulk [3,4] and in films on the surface of water, the surface of human skin [5], or a chemically grafted layer on silica [6] and on the distribution of highly volatile and non-volatile organic components [7]. The possibility of oxythermographic monitoring of circulating water aboard spacecraft in long-term and interplanetary space flights is being examined [8].

An oxythermography-based method for examining the oxidative thermal destruction of organic substances was proposed in [9]. The phenomenon of movement of matter in a gradient temperature field, which is reminiscent of the phenomenon of helium superfluidity discovered by Kapitsa, was observed in oxythermography studies of oxidative thermal destruction of polypropylene (PP). In spite of the influence of gravity, the examined substance shifted from its initial position.

The experimental setup presented in [10] was used in this study.

This setup was initially designed to examine the process of thermal destruction of PP samples with stepwise intro-

duction of a boat into the reactor [11]. Experiments with linear sample heating, which is customary in TGA and DSC, were subsequently carried out.

The aim of the present study was to investigate the feasibility of oxythermographic examination of oxidative thermal destruction of polymer samples with different filler (TiO₂) content. Samples of original polypropylene or a composite material filled with TiO₂ (1–5 mass%) had the shape of disks with a diameter of 3 mm and a thickness of 50 μm. The sample mass was 0.27 mg. A sample was positioned at the bottom of a boat, and the boat was introduced into the reactor in accordance with a given program. Programmed heating of the sample was performed by transferring the boat into different temperature zones of the reactor. A decrease in the oxygen concentration and an increase in the carbon dioxide concentration in the gas leaving the reactor characterize the process of oxidative thermal destruction of the sample. An algorithm of boat motion in the reactor providing linear heating within the 50–400°C range at a rate of ~ 10°C/min was developed. The end point of the linear heating section is 400°C. The sample was held at this temperature for 15 min and then transferred rapidly to the region with a temperature of 700°C for 3-min-long annealing of the condensation products. Analysis of the gas environment with a linear (chosen) sample heating gradient provides an opportunity to determine the initial polymer heat resistance. The temporal variation of oxygen and carbon dioxide concentrations in the air flow leaving the reactor measured in the process of heating of original polypropylene and PP with 1, 2, and 5 mass% TiO₂ added to it is presented in Fig. 1. The variation of oxygen and carbon dioxide concentrations with surface temperature of the boat at its introduction into the reactor was presented in [10].

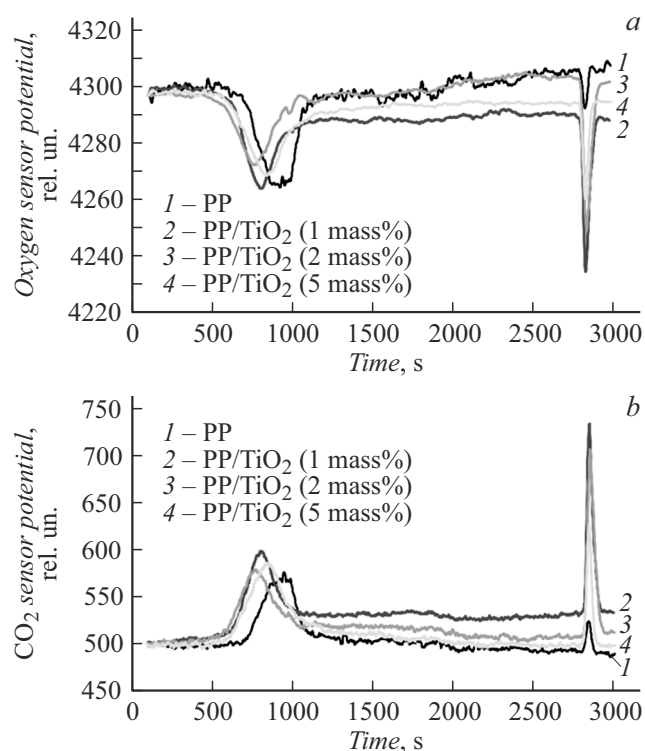
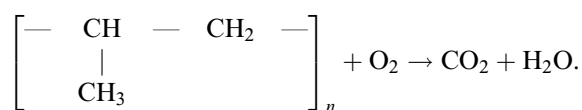


Figure 1. Variation of the concentration of oxygen (a) and carbon dioxide (b) in the air flow leaving the reactor for pure PP and the samples with 1, 2, and 5 mass% TiO₂.

Figure 1 demonstrates that the oxidative thermal destruction of polypropylene is accompanied by oxygen absorption and simultaneous emission of carbon dioxide. The obtained dependencies complement each other and characterize the process of oxidation of organic matter.

The reaction of oxidation of hydrogen-containing methyl, methylene, and methine fragments by atmospheric oxygen probably corresponds to the first peaks of oxygen consumption and carbon dioxide emission in Fig. 1:



As for the second peaks of oxygen consumption and carbon dioxide emission, it was initially suggested that they characterize the oxidation of condensed products in the form of carbon black (soot) left on the boat surface after rapid heating when the boat is transferred quickly into the high-temperature region of the reactor. The maximum reactor temperature was 700°C.

Literature data [12] on thermal destruction of polypropylene in air by the TGA method indicated that the primary reduction in sample mass (by more than 90%) occurs at temperatures below 400°C. The reduction in mass during oxidation of the sample in air corresponds in oxythermography to a reduction in the oxygen concentration and an increase in the carbon dioxide concentration in the air

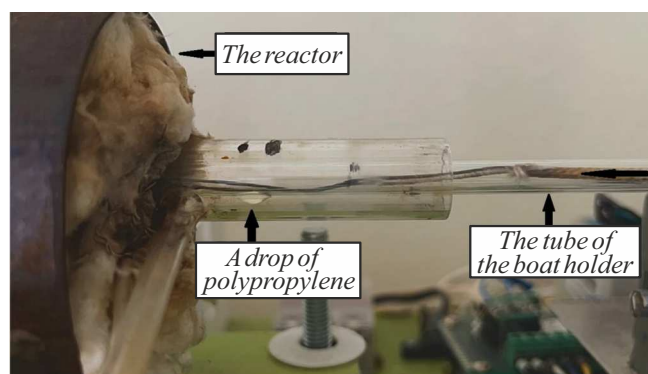


Figure 2. Photographic image of a PP drop on the boat holder in the form of a quartz tube. The drop remains in the region marked by black lines drawn on the outer face of the quartz tube of the reactor. The boat holder (quartz tube) moves into the reactor furnace. The PP drop is in a gradient temperature field and remains almost stationary.

flow leaving the reactor. The experimental curves (Fig. 1) contradict the TGA data. The second peaks in Fig. 1 should be significantly smaller or vanish altogether.

Several features of the experimental setup should be noted here. A region with a temperature gradient forms near the entrance to the high-temperature reactor furnace. When a sample is introduced into the reactor, it passes through this region. The quartz tube of the high-temperature reactor is transparent, and the sample on the boat surface can be seen moving into the reactor.

Monitoring the introduction of the boat into the reactor, we found that a drop of polypropylene moved along the surface of the boat holder. The following effect was observed: when introduced into the high-temperature part of the reactor, a solid sample of polypropylene entered a gradient temperature field. It then passed into a liquid state and was transformed into a drop on the surface of the boat holder to which the drop was attached moved. This was observed in the case of slow introduction of the boat into the reactor at a rate of about 0.8 mm/min for polypropylene samples with a mass of 20 mg. Apparently, samples with a mass of 0.27 mg are also subject to this phenomenon, but it is very hard to distinguish a drop on the holder tube surface. Figure 2 shows a photographic image of a drop of polypropylene hanging on the boat holder at the entrance to the high-temperature section of the reactor. The mass of original polypropylene was 20 mg. A video recording of a suspended drop of polypropylene moving along the surface of the boat holder tube is available online [13]. The temperature at which this phenomenon was observed was close to 140°C.

In our view, a viable explanation of this observation rests on the following assumptions: a drop has certain spatial dimensions and is in a gradient temperature field, and the temperature of the surface to which the drop is attached varies. There is a certain temperature gradient

across the surface to which the drop is attached. The drop moves from a region with a higher temperature to a lower-temperature region. The mechanism of movement is affected by the temperature dependence of adhesion (sticking) of the polypropylene drop to the quartz tube surface and the temperature dependence of surface tension of liquid polypropylene.

The rate of movement of the drop across the surface of the quartz boat holder is limited. This provides an explanation for the emergence of two peaks in Fig. 1. When polypropylene is heated, it melts, and thermal destruction of the material is initiated. This is evidenced by the first peaks in Fig. 1. The sample in the form of a drop remains in this case on the surface of the quartz tube of the boat holder in a certain gradient temperature field. The motion rate of the boat and, consequently, the boat holder is low (approximately 0.8 mm/min).

When the boat with the holder is introduced quickly into the reactor at a rate of about 70 mm/min, the polypropylene drop has no time to move relative to the surface of the boat holder. As a result, the PP drop enters the reactor region with a temperature sufficiently high for rapid oxidation of polypropylene and gets oxidized. Oxygen from the air flow is consumed in this process (the second negative peak of oxygen absorption and the positive peak of carbon dioxide emission in Fig. 1).

Funding

This study was financed from budget funds of the Vernadsky Institute of Geochemistry and Analytical Chemistry of the Russian Academy of Sciences. No additional grants for conducting or supervising this research were received.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] V.E. Sitnikova, A.A. Ponomareva, M.V. Uspenskaya, *Metody termicheskogo analiza* (Univ. ITMO, SPb., 2021) (in Russian).
- [2] B.K. Zuev, *Sposob oksitermografii*, RF Patent No. 2411509 (published on February 10, 2011) (in Russian).
- [3] I.V. Rogovaya, B.K. Zuev, T.V. Titova, S.V. Morzhukhina, A.E. Saraeva, V.G. Filonenko, J. Anal. Chem., **71** (10), 1022 (2016). DOI: 10.1134/S1061934816100117.
- [4] B.K. Zuev, V.G. Filonenko, D.S. Nesterovich, P.D. Polikarpova, J. Anal. Chem., **73** (10), 973 (2018). DOI: 10.1134/S106193481810013.
- [5] B.K. Zuev, P.D. Polikarpova, V.G. Filonenko, A.S. Korotkov, A.E. Saraeva, J. Anal. Chem., **74** (4), 410 (2019). DOI: 10.1134/S1061934819030134.
- [6] E.O. Aleksandrova, R.V. Novichkov, A.Yu. Olenin, B.K. Zuev, Russ. J. Phys. Chem. A, **91** (3), 555 (2017). DOI: 10.1134/S0036024417030013.
- [7] B.K. Zuev, I.V. Rogovaya, R.V. Larkovich, J. Anal. Chem., **75** (9), 1147 (2020). DOI: 10.1134/S106193482009018X.
- [8] G.Yu. Grigoriev, A.S. Lagutin, Sh.Sh. Nabiev, B.K. Zuev, V.A. Filonenko, A.V. Legin, D.O. Kirsanov, Acta Astron., **163**, 126 (2019). DOI: 10.1016/j.actaastro.2019.03.071
- [9] B.K. Zuev, *Sposob issledovaniya organicheskikh veshchestv, preimushchestvenno kharakteristik okislitel'noi termodestruktsii organicheskikh polimerov*, RF Patent No. 2794417 (published on April 17, 2023) (in Russian).
- [10] A.E. Mikhneva, B.K. Zuev, in *Tezisy dokladov VIII Vserossiiskoi (zaachnoi) molodezhnoi konferentsii „Dostizheniya molodykh uchenykh: khimicheskie nauki“*, Ed. by R.M. Akhmetkhanov (Ufa, 2023), pp. 354–356 (in Russian).
- [11] B.K. Zuev, V.G. Filonenko, A.S. Korotkov, S.V. Morzhukhina, E.A. Denisova, A.E. Mikhneva, M.Yu. Yablokov, I.O. Kuchkina, in *Vserossiiskaya konferentsiya s mezhdunarodnym uchastiem „Fizicheskaya i analiticheskaya khimiya prirodnnykh i tekhnogennykh sistem“*, Ed. by P.P. Gladyshev (Dubna, 2021), pp. 67–73 (in Russian).
- [12] S.M. Lomakin, I.L. Dubnikova, S.M. Berezina, G.E. Zaikov, Polym. Sci., Ser. A, **48** (1), 72 (2006).
- [13] *Oksitermografiya, yavlenie peremeshcheniya organicheskogo veshchestva (polipropilena) v temperaturnom pole* [Electronic source]. <https://rutube.ru/video/c12ee7fcf45dc168f5c728c09924ea0c/> (date of access 21.05.2024).

Translated by D.Safin