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Study of Thermo-Oxidative Transformations of Unstabilized and Stabilized Poly(ether ether ketone)

A. S. Shabaev[a], A. A. Zhansitov[a],*, E. V. Khakyasheva[a], and S. Yu. Khashirova[a]
[a] *Kabardino-Balkarian State University, Nalchik, 360004 Russia*
**e-mail: azamat-z@mail.ru*

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Abstract—The regularities of thermo-oxidative transformations of poly(ether ether ketone) in a wide temperature range are investigated. The mechanisms of thermo-oxidation are proposed. The possibilities of stabilizing poly(ether ether ketone) against thermal and thermo-oxidative degradation are shown. The optimal values of the thermostabilizer concentration in PEEK are determined.

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INTRODUCTION

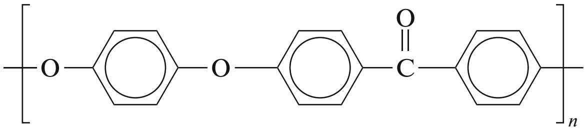
Continuing interest in poly(ether ether ketone) (**PEEK**) is due to the fact that this polymer in terms of a set of its properties meets the most modern requirements for operational behavior and it is also a promising material for the development of new polymeric composite materials [1–4].

Currently, there are very few works on the effect of prolonged exposure to high temperatures on the thermal stability of polymers of the poly(ether ketone) class, despite the fact that just comprehensive studies provide reliable information on the actual operating conditions of the polymeric material. In studies of the thermal characteristics of PEEK [5–7], the products of its thermal degradation were studied using gas chromatography/mass spectrometry. Among the gaseous products of pyrolysis, CO and CO_2 were found, and their total yield was fixed. Using mass spectrometry, various products were identified, among which benzene, phenol, hydroquinone, and other fragments were detected. It is obvious that to gain insight into the mechanism of thermal degradation of this class of polymers, it is necessary to study in more detail changes in the structural characteristics of poly(ether ether ketone) during short-term and prolonged exposure to high temperatures, including in the presence of stabilizing substances.

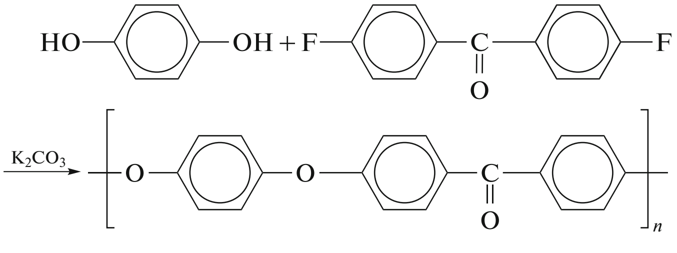
Earlier [8, 9], the laws of the thermal degradation of poly(ether ether ketones) of various structures in a wide temperature range were considered, the schemes of thermal degradation were proposed, and the effect of water on these processes was revealed. Taking into account the above data, the purpose of this work was to study the laws of thermo-oxidative transformations of PEEK and the possibility of its thermal stabilization.

EXPERIMENTAL

The object of research was poly(ether ether ketone) synthesized at the Center for Advanced Materials and Additive Technologies, Kabardino-Balkarian State University [10]:



Poly(ether ether ketone) was synthesized by the polycondensation of 1,4-dihydroxybenzene with 4,4'-difluorobenzophenone at 320°C for 5 h:



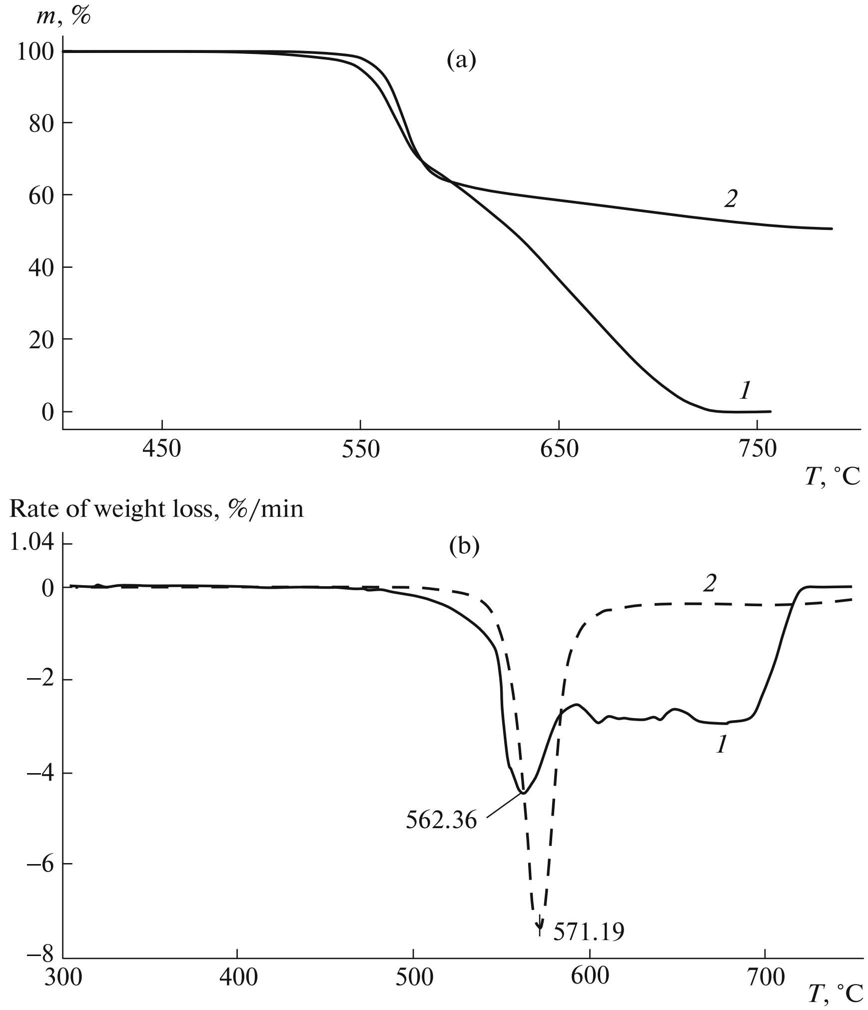


Fig. 1. (a) Thermogravimetric and (b) differential thermogravimetric curves for PEEK in (*1*) air and (*2*) nitrogen.

Diphenyl sulfone was used as a solvent. After the completion of the synthesis, diphenyl sulfone was extracted with isopropyl alcohol and acetone. The polymer was dried under vacuum at 150°C for 12 h. The viscosity of PEEK, which was measured in 0.5% H_2SO_4 solution at 25°C, was 0.4 dL/g.

Thermogravimetric studies were performed on a TGA-4000 derivatograph (PerkinElmer) at a heating rate of 5 K/min in air and nitrogen. The main gaseous products of pyrolysis were analyzed on a Tsvet-800 gas chromatograph equipped with a thermal conductivity detector as described in [11]. IR spectroscopic studies were carried out on a Spectrum Two spectrophotometer (PerkinElmer).

RESULTS AND DISCUSSION

The method of studying the thermal and thermo-oxidative degradation of polymers described in [11] made it possible to study the kinetics of oxygen absorption with simultaneous analysis of gaseous products of thermo-oxidative degradation. Preliminary experiments showed that noticeable oxygen absorption is already observed at 300°C, although according to thermogravimetric analysis (Fig. 1a), PEEK begins to lose weight at temperatures above 500°C (the loss of 2% weight in air corresponds to 530°C; in nitrogen, to 549°C).

The weight loss curve in air has two distinct stages (Fig. 1b). The first stage corresponds to the rupture reactions of the main polymer chain, the rate of which indicates the radical-chain mechanism of degradation. At this stage of degradation, both oxidation and crosslinking reactions occur simultaneously. Thus, the access of oxygen to the main polymer chain is hampered. At the second stage, at temperatures above 600°C, the diffusion processes of thermal oxidation (including coke residue) begin to prevail over simple combustion reactions. This leads to a marked decrease in the rate of weight loss observed on differential thermogravimetric curves.

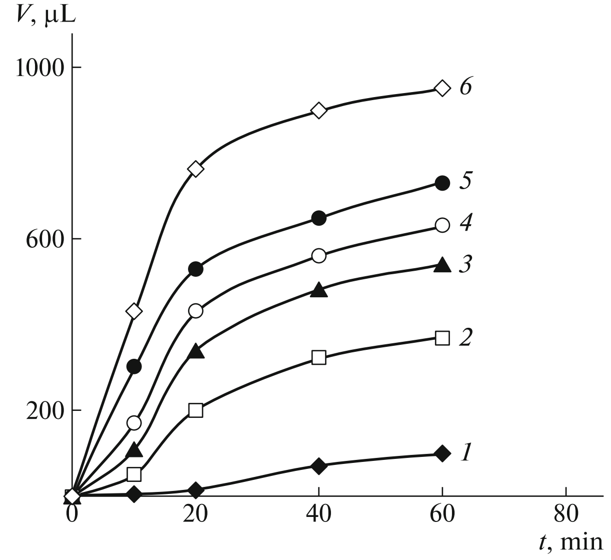


Fig. 2. Kinetic curves of oxygen absorption of PEEK at T = (*1*) 300, (*2*) 325, (*3*) 350, (*4*) 375, (*5*) 400, and (*6*) 425°C.

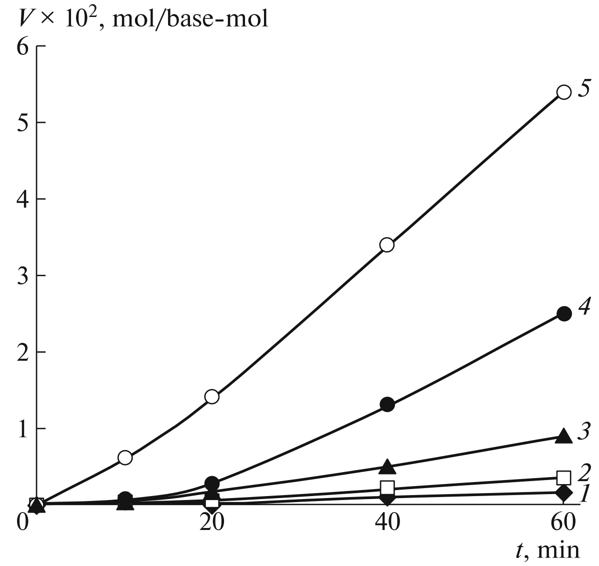
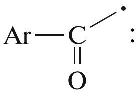


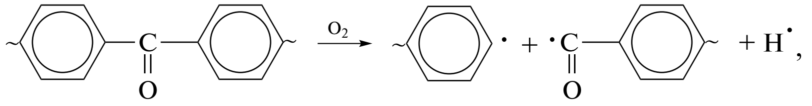
Fig. 3. Kinetic curves of hydrogen release in thermo-oxidative degradation of PEEK at T = (*1*) 325, (*2*) 350, (*3*) 375, (*4*) 400, and (*5*) 425°C.

Figure 2 shows the kinetic curves of oxygen absorption depending on the time and temperature of temperature control. It is seen that the character of oxygen absorption does not change up to 375°C. Obviously, this is due to the crosslinking ability of PEEK at these temperatures, which complicates the oxidative process. At higher temperatures (400–425°C), thermal degradation processes begin to dominate over the crosslinking processes, which inevitably affects the rate of oxygen absorption.

In the course of thermo-oxidative degradation of the polymers, gaseous products are released which mainly consist of carbon monoxide and carbon dioxide. In addition to these compounds, an insignificant amount of hydrogen (Fig. 3) and a trace amount of methane are formed.

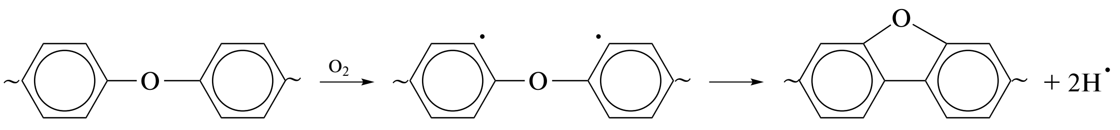
The amount of hydrogen formed at a temperature of 325–375°C approximately corresponds to its amount formed during thermal degradation. However, at a temperature of 400–425°C (thermo-oxidative degradation), the amount of released hydrogen is many times higher than that during thermopyrolysis [9]. An additional source of hydrogen released under these conditions can be the oxidation of aromatic nuclei, accompanied by the detachment of a hydrogen atom.

The interaction of oxygen with an aromatic nucleus leads to the detachment of a hydrogen atom with the formation of a carbonyl radical  $\mathrm{Ar{-}\underset{\displaystyle \overset{\|}{O}}{C}{}^{\bullet}}$:



which can be oxidized in air to carboxylic acid or transform into aldehyde accompanied by the detachment of atomic hydrogen.

The next most susceptible bond in terms of thermo-oxidative degradation is an ether bond. In this case, the recombination of neighboring radicals, accompanied by the release of atomic hydrogen, leads to the formation of parquet structures or cyclic compounds, such as dibenzofuran, which was detected in large quantities [10, 11].



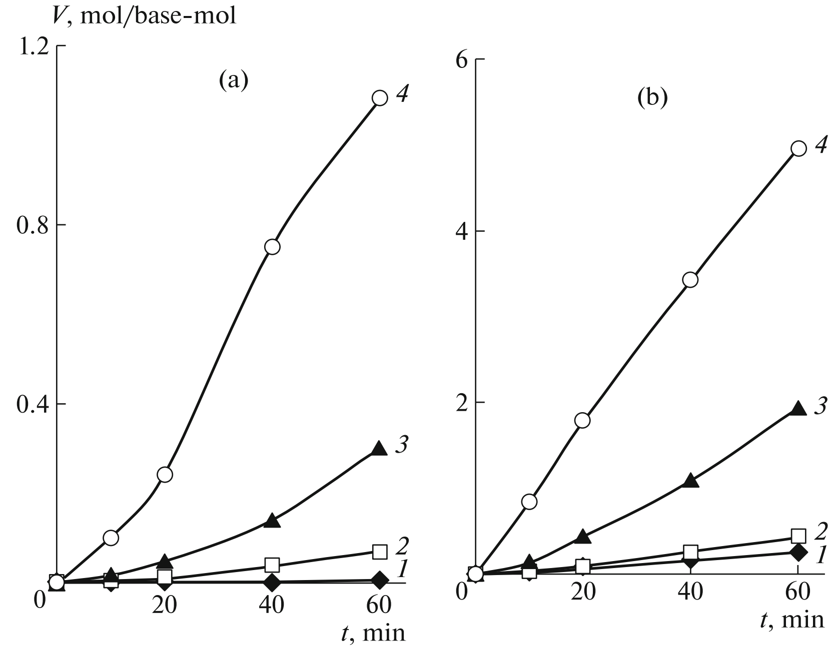
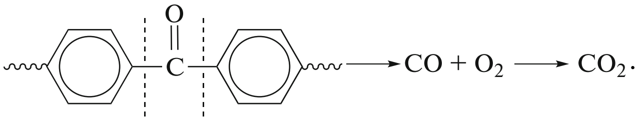


Fig. 4. Kinetic curves for the release of (a) CO and (b) CO_2 in thermo-oxidative degradation of PEEK at T = (*1*) 350, (*2*) 375, (*3*) 400, and (*4*) 425°C.

Figure 4 shows the kinetic curves of the release of CO and CO_2 in thermo-oxidative degradation. It can be seen that, at all values of the thermo-oxidation temperature, the amount of the released CO_2 is much larger than that of CO and the release of the latter can be observed beginning from a temperature of 375°C. Taking into account the structure of the polymer and the weight of the test samples, it was found that the maximum total yield of CO and CO_2 cannot exceed 1 mol/base-mol upon complete destruction of the ketone group. At temperatures of 350 and 375°C, the total yield of CO and CO_2 does not exceed 0.5 mol/base-mol, which indicates the destruction of only the ketone group accompanied by the formation of CO, which in the presence of oxygen is oxidized to CO_2:



Further temperature increase to 400–425°C is accompanied by an increase in the total amount of carbon oxides to 6 mol/base-mol (Fig. 4). An additional source of these products is the oxidation of carbon atoms that make up the benzene ring to form CO or CO_2.

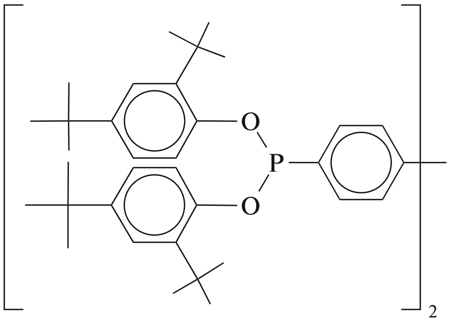
Thus, even at 325°C, the thermal oxidation of PEEK is noticeable and is accompanied by the destruction of ketone groups; further increase in temperature leads to the oxidation of fragments of the benzene ring.

Studies of PEEK samples aged for 30 min at 400°C in an inert atmosphere and in air showed noticeable changes in their IR spectra (Fig. 5). It is known [12] that the most pronounced spectral feature of the IR spectra of polymers during their degradation is the appearance of absorption bands specific to the C=O carbonyl group in the range of 1540–1870 cm^{-1}. Moreover, the exact wave number depends on the chemical structure of the polymer chain. In the case of PEEK, the maximum intensity of the peak due to the carbonyl group is at 1740 cm^{-1}.

The high thermal stability of PEEK and many other polymers is associated with the presence of aromatic groups in the molecular structure. The PEEK monomer unit includes three phenyl rings. As is seen in Fig. 5, during heat treatment, the number of aliphatic groups increases (bands with maxima at 2854 and 2925 cm^{-1}). This indicates that ring opening reactions take place during heat treatment; in air, these reactions are more pronounced (Fig. 5c). This is one of the probable reasons for the decrease in thermal stability under longer exposure to high temperatures.

In order to increase the stability of poly(ether ether ketone) during processing, the possibilities of its stabilization were studied.

Thus, the objects of research were the samples of PEEK, PEEK + 0.3% of the stabilizer, and PEEK + 0.5% of the stabilizer. As a stabilizer we used diphosphonite antioxidant Hostanox:



Thermal degradation studies were carried out at a temperature of 500°C (the start of intense weight loss according to TGA for PEEK); the time of pyrolysis was up to 80 min. The kinetic curves of CO and CO_2 formation during thermal degradation for all three samples show (Fig. 6) that, at the time of pyrolysis up to 20 min, the amount and rate of release of these gases are almost the same for the samples with and without the stabilizer.

Subsequently, with an increase in the time of pyrolysis, starting from 30 min of exposure, the rate of formation of CO and CO_2 for unstabilized samples increased several times. The character of the release of CO and CO_2 for the stabilized samples also remains unchanged. The observed relationship of stabilizer activity with the time of thermal exposure can be interpreted from several positions.

The degradation of the polymers begins from the homolytic rupture of the main polymer chain accompanied by the formation of active radicals.

For the unstabilized samples, the generated radicals are involved in the further degradation of the polymer; transition from the homolytic degradation to the radical-chain one occurs, the rate of which is much higher.

In the stabilized samples, the introduced stabilizer neutralizes the radicals generated during the homolytic degradation of the polymers, preventing transition to the radical-chain mechanism; as a result, the rate of degradation of such polymers does not increase significantly.

The yield of CO decreases in proportion to the increase in the stabilizer content. At the same time, an increase in the percentage of the stabilizer to 0.5% increases the yield of CO_2 (Fig. 6).

A similar ambiguous picture is observed on the kinetic curves illustrating the formation of H_2 during thermal degradation (Fig. 7). If the introduction of 0.3% stabilizer improves the thermal properties of the polymer, further increase in its content (to 0.5%) increases the yield of hydrogen.

Samples with a stabilizer content of 0.3 and 0.5% were also investigated in order to identify the efficiency of the stabilizer in the oxidative environment. For this purpose, the pyrolytic cell with the sample was filled with oxygen [11], after which pyrolysis was carried out at a temperature of 400°C.

In contrast to thermal degradation during thermal oxidation, with an increase in the percentage of the stabilizer, the yield of all detected gaseous degradation products decreases markedly (Figs. 8, 9). For example,

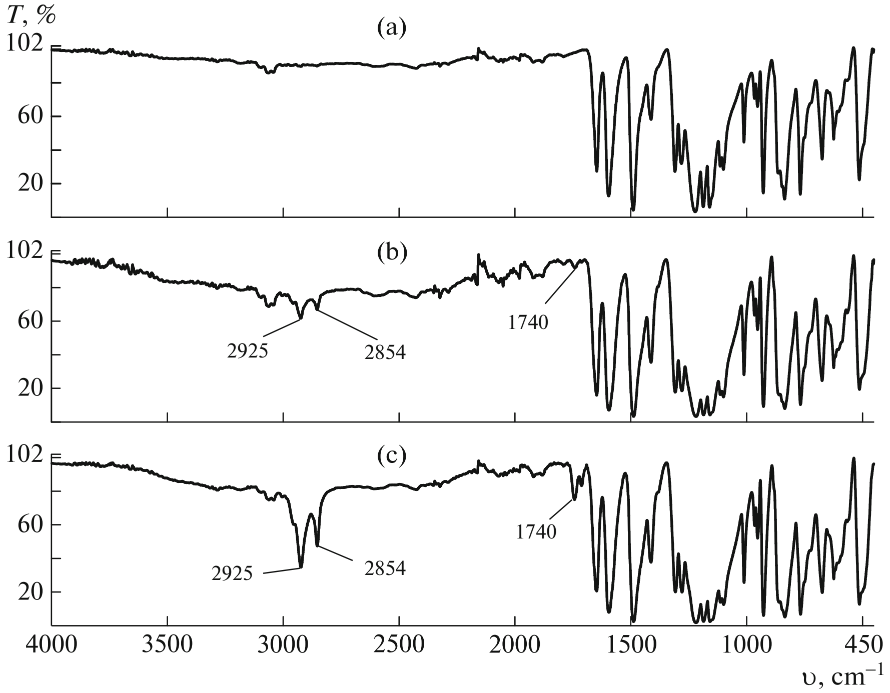


Fig. 5. IR spectra of PEEK (a) without heat treatment and PEEK kept for 30 min at 400°C in (b) argon and (c) air.

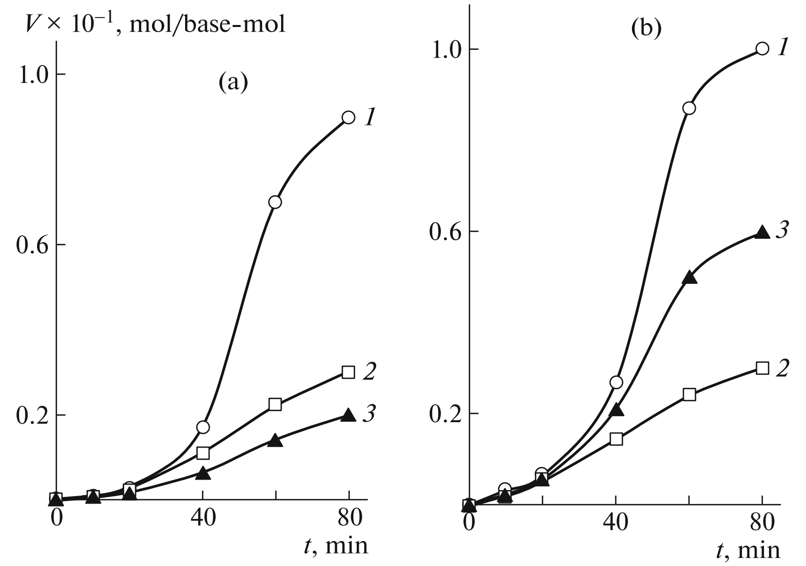


Fig. 6. Kinetic curves for the formation of (a) CO and (b) CO_2 during thermal degradation and at $T = 500$°C for (*1*) PEEK, (*2*) PEEK + 0.3% stabilizer, and (*3*) PEEK + 0.5% stabilizer.

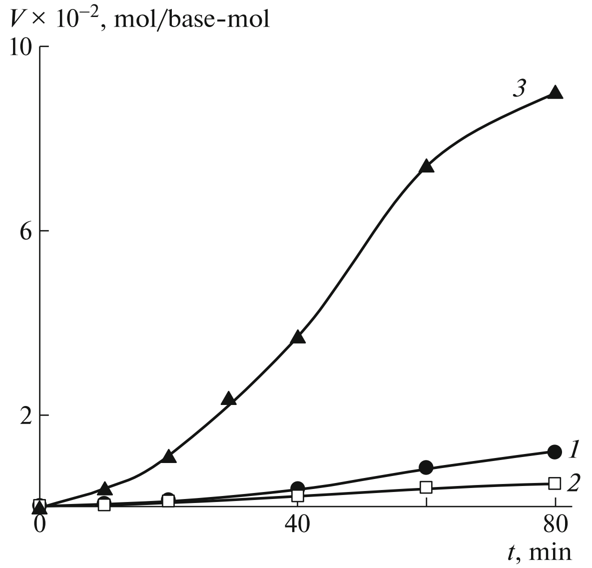


Fig. 7. Kinetic curves of hydrogen formation during thermal degradation and at $T = 500$°C for (*1*) PEEK, (*2*) PEEK + 0.3% stabilizer, and (*3*) PEEK + 0.5% stabilizer.

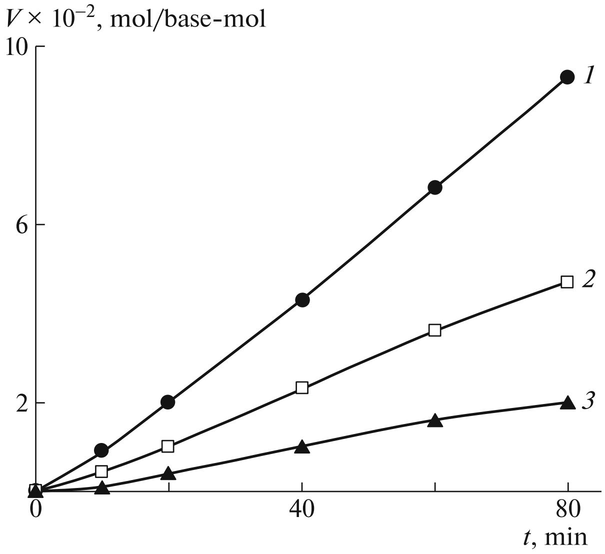
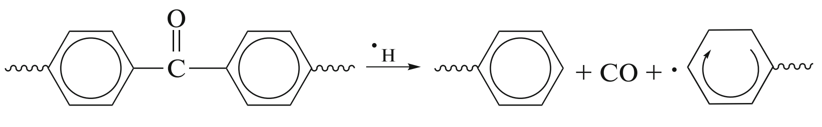


Fig. 8. Kinetic curves of hydrogen release during thermo-oxidative degradation and at $T = 400$°C for (*1*) PEEK, (*2*) PEEK + 0.3% stabilizer, and (*3*) PEEK + 0.5% stabilizer.

the yield of hydrogen for stabilized PEEK (curve *3*) decreased by 5 times (Fig. 8) compared with the original one (curve *1*); the time of pyrolysis was 80 min.

The linear pattern of the hydrogen evolution curves indicates that simple reactions of branching and cross-linking of the main polymer chain of PEEK occur. At the same time, for the PEEK + 0.5% stabilizer sample, the yield of hydrogen and CO decreases by almost an order of magnitude.

The observed effects indicate that the stabilizer binds active hydrogen atoms, which reduces the degree of their participation in the rupture of the main polymer chain; this assumption is confirmed by reduction in the released CO:



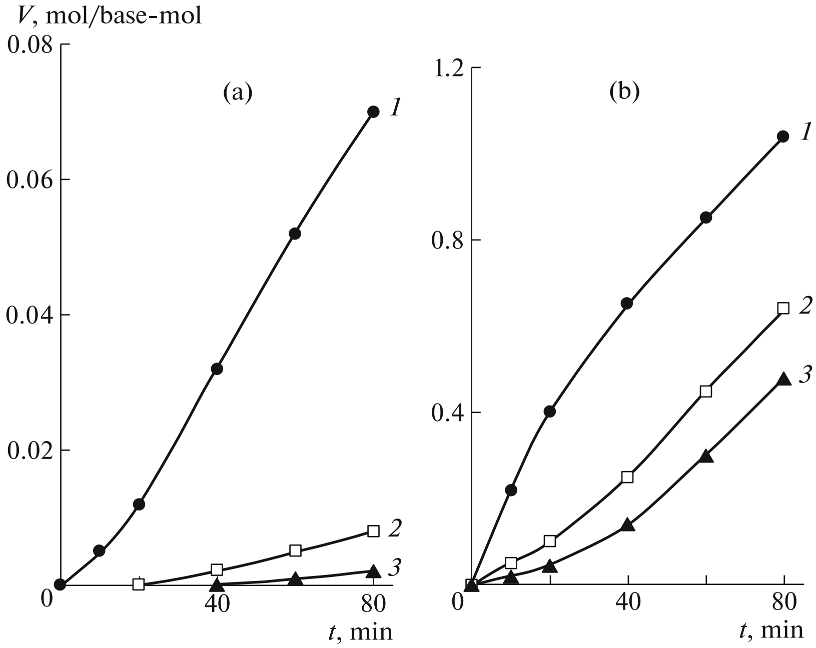


Fig. 9. Kinetic curves for the release of (a) CO and (b) CO_2 in thermo-oxidative degradation and at $T = 400°C$ for (*1*) PEEK, (*2*) PEEK + 0.3% stabilizer, and (*3*) PEEK + 0.5% stabilizer.

In general, the revealed patterns show that the depth of the processes of thermal degradation of PEEK can be controlled to ensure its processing without the risk of deterioration of the main technological and operational characteristics.

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