Epoxy Polymer Gasification under Combustion

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Abstract

The processes taking place in the preflame zone at flame spread over the surface of epoxy polymer have been investigated in the present work. It has been shown that heating of yet unignited polymer ahead of flame spreading over the thermally thick samples is done mainly by the heat conduction through condensed phase. The compositions of highly- and hardly-volatile products of gasification are determined in conditions of the preflame zone. It is shown that the main combustible product of gasification is CO (ca. 85 %). The mass rates of gasification and the linear velocities of an injection of gasification products into gas phase of preflame zone have been determined. The complicated aerodynamic structure of the preflame zone with a vortex formation is shown to exist. As a result oxygen gets a free access to a polymer surface and can participate in gasification processes. Experimental simulation of the epoxy polymer gasification processes was carried out in the oxygen-18 enriched atmosphere. The main oxygen-containing product of gasification is shown to be generated both as a result of pyrolysis, and a result of thermooxidation. More than 75 % of carbon dioxide is formed only due to thermooxidative destruction, and 75 - 90 % of carbon oxide is formed only due to pyrolysis. It has been shown that in a course of epoxy polymer gasification in preflame zone the main mass of combustible products is generated by pyrolysis, but an energy for this is mostly supplied by simultaneously occurred exothermal processes of thermooxidation of the near-surface layers of epoxy polymer.

Introduction

A lot of works is dealing with research of polymer combustion. A considerable attention is given to a research of flame spreading over the surface of polymers, as this process represents the special interest for solution of a number of problems concerning fire-safety.

Polymers in usual conditions in themselves are not burning, so that in flames only gas phase products of polymer destruction can burn. Therefore for the beginning of burning it is necessary, that the polymer has got hot up to decomposition temperature, and the destruction products should pass into gas phase. The gasification processes of polymers in preflame zone, therefore, play a dominating role in the mechanism of flame spread over a surface of polymers. According to [1,2], polymer combustibility mainly depends on an amount and composition of products of polymer gasification under conditions of burning and on creation [4] of charring layer on a burning surface of

polymer.

In many works the flame spread over a surface of polymers was suspected to be accompanied by oxidative processes in the preflame zone in a number of cases. As for char-forming polymers, which typical specimen is epoxy, the reality of such a supposition was proved only by indirect experiments [1].

The examination of energy balance at an edge of flame spreading over a surface of epoxy polymer has shown [2] that this balance cannot be reduced disregarding contribution of exothermal reactions of thermooxidative destruction of polymers in gasification processes in preflame zone. But it is impossible practically to find the size of such contribution in conditions of the real flame spread by experiment. Even in conditions of experimental simulation of researched epoxy polymer gasification the direct determination of thermooxidative destruction products quantities cannot be carried out because during pyrolysis and thermooxidative destruction of epoxy polymer there are formed one and the same oxygen-containing products CO, CO_2, H_2O. Therefore it is need in using of

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«tracer atoms» method.

Thus, the purposes of work consist of the following:

1. The determination of the dominating mechanism of heat transfer into the preflame zone of epoxy polymer at flame spread over the surface;

2. The investigation of gasification products composition of epoxy polymer in the preflame zone;

3. The determination of gasification kinetic parameters and linear velocities of an injection of gasification products into a gas phase of preflame zone;

4. The elucidation of the role of oxygen as an oxidizing mixture component in gasification processes of epoxy polymer in preflame zone.

Heat transfer and gasification in preflame zone

For the description of combustion process the information concerning structural characteristics of flames (composition and temperature profiles, profiles of gas stream velocities, mechanisms of chemical transformation of substances in combustion wave etc.) is very important. Besides combustibility of polymers greatly depends on an amount and composition of gasification products under conditions of burning, on creation of charring layer on a burning surface of polymer [2,3,6]. The composition of gasification products and tendency to charring under burning is determined by a chemical structure of macromolecule, by a permolecular structure and additives, i.e. depend on specific properties of polymer. For researches the typically char-forming epoxy polymer obtained by curing the diglycidil ether of bisphenol A (from the commercial epoxy resin ED-20) with m-phenylenediamine was selected. The choice is caused by not only broad application of it in construction, microelectronics etc., but also by that the combustion of char-forming polymers is investigated a little. Besides at the polymers with the fire-retardant additives the enhancement of charring of a burning surface is observed, than, at least is partial, the reduction of their combustibility is explained.

From a practical point of view the flame spreading over a surface of polymers represents of the greatest interest. Theoretically to describe such process it is very complicated, as it requires a joint solution of systems of the nonlinear equations of a chemical kinetics, heat- and mass-transfer. Therefore it is necessary to resort to various simplifications and assumptions, which regularity is checked up only by experiment.

In work [5] when studying of temperature distribution in the preflame zone it had been found that on a distance of 1 mm ahead of the flame front the temperatures in a gas phase and on a surface of polymer increased uniformly. But nearer to flame front the temperature in a gas phase increases faster. This means, that the heat flux acting from a gas phase on a surface get a considerable size only close to an edge of a flame. It is characteristic that the width of a "melt" zone ahead of the flame also amounts to 1 mm. For the contribution of the heat transfer through the gas phase by convection, radiation, heat conduction and that of the heat transfer through the condensed phase in gasification process to compare the experiments concerning the flame skipping over inert spacers have been carried out [3]. The flame spreading in a stationary mode is stopped for a time when coming to the incombustible spacer. Then a bit later the flame makes appearance on the backside of the spacer also and both joint parts of the flame are propagating further with a former velocity. The flame delay time depending on a thickness of a spacer was determined as visually as on temperature measurements by means of oscillograms.

The conclusion was made from these measurements and from data of work [7] that ahead of the "melt" zone the heat proceeding from a flame is spent, in main, for an oxidizing mixture heating up, and gasification is carried out, with energy being supplied by thermal conduction through condensed phase. Otherwise there would be no delay of a flame before incombustible spacers. Certainly, the direct flux of heat from a gas phase to a polymer surface introduces the certain contribution in the surface temperature rise, but it begins to play a noticeable role only at a leading edge of a flame and inside a visible flame.

At gas phase in the preflame zone are present, in main, CO, CO_2, H_2O, CH_2O. The detection CO closer to the flame front as compared with CO_2, with the latter concentration passing through a maximum on a distance of 1 mm from the leading edge of the flame, is of interest.

At the flame edge the oxygen concentration makes up only 9 %, i.e. the most of O_2 is consumed already in the preflame zone (the initial concentration of oxygen is 80 %). Such intense consumption O_2, presence of a "melt" zone and composition of the gas phase are pointing at the fairly intense processes of thermooxidation ahead of the flame front to take place.

The further study of oxidative pyrolysis processes happening in the preflame zone immediately during propagation of a flame without its essential violation

is extremely complicated. The possibility of such experiments was opened, with studying the flame skipping over incombustible spacers [3], when the process of heat transfer through condensed phase and that of flame spread appear separated in time. Nevertheless, and in these conditions in view of short period of process (some seconds) it have appeared impossible to realize a direct sampling of gasification products by some microprobe for the flame is heavily perturbed in such case. Therefore oxidative pyrolysis was studied by means of special installation in which conditions of a flame skipping over incombustible spacers were reproduced (there was no only flame) [4].

Among gasification products CO, CO_2, H_2O predominate. In smaller amounts there are C_1-C_3- hydrocarbons, CH_2O, C_6H_6, alcylbenzenes, phenols, cresols. The determination of product composition was made by methods of mass-spectrometry and IR-spectroscopy [4].

On the basis of mass-spectral analyses it is shown, that the main combustible product of gasification is CO (about 85%), i.e. detected amounts of CO are quite sufficient to provide a stable flame propagation. Proceeding from the experimentally observed (in the mentioned conditions) mass losses of the epoxy polymer samples from the unit of the surface area dependently on heating time of it for various rates of temperature increase there were calculated the gasification mass rates. To calculate these values the original curves of mass loss dependencies on the time of heating were differentiated numerically by means of piecewise-linear approximation. As a first approximation the process of gasification was considered as a single-stage reaction of zeroth order with a simple kinetius equation

$$q = k_0 \cdot \exp[-E/RT] \qquad (1)$$

Rearrangement of plots q = f (T) in Arrhenius coordinates shows the occurrence of low-temperature and high-temperature regimes of this process. The transition temperature between them changes within 520 to 560 K, growing with the increase of the heating rate. The least-squares technique was used to evaluate effective reaction rate constants and activation energy of gasification processes in the preflame zone conditions [4]. The effective kinetic parameters calculated [4] by this method are represented in Table 1.

Table 1

Effective kinetic parameters of the equation (1) for gasification of epoxy polymer films (for confidence limit of 95%)

Average rate of heat, K/s	Low-temperature region		High-temperature region	
	$lg\ k_0$, $g \times cm^{-2} \times s^{-1}$	E, kJ/mole	$lg\ k_0$, $g \times cm^{-2} \times s^{-1}$	E, kJ/mole
47.5	-0.08±0.09	32.6±3.8	1.85±0.46	52.3±7.0
40	-0.60±0.03	39.3±2.3	6.92±0.94	104.2±10.6
34	-0.12±0.09	38.5±3.3	7.06±0.86	115.2±11.0
30	-0.60±0.37	25.4±3.4	6.97±0.80	100.7±8.2

In low-temperature region E_{eff} makes up ~34 kJ/mole, that corresponds to activation energy of diffusion processes [6] and close to data [8] for thermooxidation of epoxy polymer films in low-temperature isothermal conditions. In high-temperature region (except for heat rate of 40 K/s) E_{eff}, on the average, are equal to 106 kJ/mole, that also is close to data [9,10] for isothermal conditions. Then it is possible to assume, that for the heat rate above 40 K/s in our conditions the gasification passes in a linear pyrolysis regime, of which the decrease of effective activation energy twice [6] is characteristic. However it is known [11] that the comparison of activation energies found in isothermal and unisothermal conditions is true only in that case, when characteristic time of a heating-up τ_h is much less than characteristic time τ_g of polymer gasification. In our experience, according to the made calculations, $\tau_h \ll \tau_g$ up to 600 K, i.e. gasification takes place in internal kinetic area, for which the macroscopic kinetics coincides a true kinetics of a reaction of decomposition in volume [12].

Above 600 K the gasification rate at first sharply

drops, that for heat rate of 47.5 K/s is reflected in decreasing k_{0eff} approximately to 10^5 times, though it is largely compensated by a simultaneous diminution approximately twice to effective activation energy (see Table 1). As a result there is $\tau_h << \tau_g$ again. Therefore it is impossible to accept, that the process passes in a linear pyrolysis regime, where there should be $\tau_h >> \tau_g$ and $q \sim \exp[-E/2RT]$. More probably, the given outcome is explained by features of epoxy polymer gasification and is observed because the higher temperatures are reached in heating with high rates during experiment, and in that case the gasification mass rate is sharply reduced. Really, according to data [13], just in this region of temperatures during thermooxi- dation of epoxy polymer the rate of loss of a mass sharply decreases, and simultaneously exothermal effect is exhibited. It usually refers [6] to an enhancement of processes of structurization of charred residue by cross-linking accompanying with appropriate decrease of a rate of gas emission.

By using data of Table 1, it is possible to evaluate the injection velocities distribution of highly-volatile products of the epoxy polymer gasification into gas phase along the preflame zone in spreading of the flame over this polymer's surface. Within the limits of a «melt» zone at a distance 0.6-0.8 mm ahead of the leading edge of flame the injection velocity sharply increases up to 17 cm/s. Closer, within 0.4-0.6 mm, due to the processes of carbonized residue structurization by cross-linking the velocity of injection is somewhat decreased and then again sharply grows, reaching 33 cm/s near the leading edge of flame.

Hence, in the gas phase of the preflame zone ahead of a leading edge of a flame an intense flow of gasification products blows, and that is perpendicular to an oxidizer flow. It means, that the structure of the gas phase preflame zone is actively effected by aerodynamic factors creating conditions for vortex formation, a boundary layer detachment from a polymer surface, and intense mixing of gasification products with an oxidizer.

The oxygen, however, is incompletely pushed by flows of gasification products from a polymer surface: above a leading edge of the flame, for example, according to data [14], at height of 0.5-0.9 mm the linear velocity of a diffusion O_2 to a surface exceeds 80 cm/s, i.e. it is more than velocities of an injection. Under the flame the arrival of oxygen to a polymer surface relaxes, but the heat flux from a gas phase is increased. As a result a thermal decomposition of polymer is accelerated, which in a «zone of violent

gasification» proceeds practically in the bulk of the polymer layer heated-up.

The demonstrated picture of distribution of gasification products flow velocities is also more of fundamental importance. All theoretical researches of a flame spread over a surface of polymers usually carry out because of an idea of a boundary layer, supposing, that a gasification starts step-wise immediately under a leading edge of a flame, that the mixing of combustibles with an oxidizer is carried out, mainly, by a molecular diffusion, that ahead of a flame it is possible to neglect by a gas flow velocity component directed perpendicularly to a polymer surface, etc. If the found picture of distribution of linear velocities of gasification products flow will appear have the rather large generality, many of listed ideas will be induced to reconsider.

The contribution of thermal and thermooxi-dative destruction into gasification of epoxy polymer

Thus, as is said in the previous section, as a result of vortex formation the convective mixing intensifies, and the oxygen receives a free access to the gasifying polymer surface. However, in the consent with existing ideas [6], at first we had assumed [4], that in burning the role of oxygen in a preflame zone is reduced only to after-oxidizing of pyrolysis products, and a limiting stage of gasification processes is pure thermal destruction of deep underlying layers of polymer, but is not thermooxidation of its surface.

For validity of these assumptions to test in the same work [4] we have set some experiments with respect to gasification by having applied gaseous oxygen, labeled by isotope ^{18}O. The obtained results definitely specified a simultaneous course pyrolysis and thermooxidation of the epoxy polymer under conditions of the preflame zone. However, in view of severe contamination of used oxygen, enriched with ^{18}O, by carbon oxide, carbon dioxide and water vapors also containing lots of the ^{18}O atoms (and all four substances have unequal isotopic ratio of oxygen), and in the absence at that time of the calculation procedure developed the half-quantitative evaluation of a thermooxidation role in gasification has appeared understated. An incorrect conclusion also was made that the most of carbon dioxide was generated by polymer pyrolysis, while more than half of carbon oxide was generated in course of thermooxidation. Though the other conclusions of work [4] are quite correct,

but after all these experiments one kept nevertheless incomprehensible, how the thermooxidation products are forming - by oxidation of the epoxy polymer in itself or its pyrolysis products (under conditions of experiment the last variant seems less probable).

Therefore, to check up a potential participation of oxygen in thermooxidative destruction of the epoxy polymer itself, it is necessary to know whether an absorption of oxygen by a condensed phase happens. The authors of works [15,16] have shown, that in epoxy polymer there is absorption of oxygen by the condensed phase in the preflame zone and that the average concentration of «excessive»oxygen (as compared with the pure polymer itself) in condensed phase varies from 1.9 up to 2.4 % mass in the layer by a thickness about 0,4 mm, decreasing with depth of a penetration [16]. At the same time in the underflame zone a level of excessive oxygen little differs from zero. These results conform to data [17]; other data in the literature are absent.

The technique of experiments described in [4] is unnecessarily complicated and is time-consuming. Besides in carrying out of isotopic experiments [4] one of conditions of epoxy polymer gasification simulation had been violated − there was no flow of an oxidizing mixture along a surface of a sample. Therefore the experimental unit completely reproducing conditions, prescribed in [4], was developed. In it using of membrane microcompressor ensures a circulation of gas mixture with necessary velocity. This unit, which is used both for isotope dilution of an oxidizing mixture, and for realization of epoxy polymer gasification experiments with labeled oxygen, is very compact. The requirement of compactness of the unit is very strict, as it is necessary to ensure a very small consumption of the expensive oxygen-18 in carrying out experiments and very small losses of that when preparing experiment. Besides preparation of an oxidizing mixture is realized for more short time. The analysis of chemical and isotope composition was carried out by using the mass-spectrometer MI-1201B and standard technique [18].

In general the experimental procedure is following [19]. Before experiment the oxidizing mixture enriched with oxygen-18 is agitated until the homogeneous composition is obtained. Then the sample of an oxidizing mixture is taken for the analysis of isotope ratio of oxygen in all constituents. After the analysis is over, the experiment itself is conducted, and through 2-10 s the gaseous sample is again taken for the analysis of isotope ratio of oxygen in all gasification products. In

details the procedure of calculations isotope composition gasification products , the formulation of the equations to calculate of the contributions of thermooxidative destruction process and pyrolysis process in polymer gasification in the preflame zone are described in [19].

The calculation of the concentration ratio of isotopes $^{18}O/^{16}O$ in an initial oxidizing mixture was made according to equation:

$$a = \frac{2I_{36} + I_{34}}{2I_{32} + I_{34}} \qquad (2)$$

where a - concentration ratio of isotopes $^{18}O/^{16}O$ in molecular oxygen; I_{36}, I_{34}, I_{32} - intensities of lines with m/e 32, 34, 36, corresponding to ions of $^{16}O_2^+$; $^{16}O^{18}O^+$; $^{18}O_2^+$ in mass-spectra of an oxidizing mixture (after subtracting of intensities of the same lines of background mass-spectra). In this equation (and following) corrections for ^{17}O isotope content were not made, as it was less than measurement error of heights of mass-spectral peaks (1-2 %) [18].

The analysis of isotope ratio of gasification products was made a little differently. Because of noticeable contamination of an oxidizing mixture by carbon oxide and dioxide both containing the isotopes ^{16}O and ^{18}O also, it is necessary to know precise amounts CO and CO_2, liberated during experiment. For that reason the normalization of mass-spectra of an oxidizing mixture (after a subtraction the intensities of lines of background mass-spectra) with respect to the internal standard ($^{16}O_2$, $m/e=32$) was being taken. Then the normalized intensities of lines CO and CO_2 in mass-spectra of an initial oxidizing mixture were subtracted from the normalized intensities of lines CO and CO_2 in mass-spectra of gasification products. For further calculations just these difference values, obtained for peaks with mass numbers 48, 46, 44, 30 and 28, are using. The limiting relative error of a normalization procedure, according to our evaluation, makes less than 0.5 %.

Besides before calculations of isotope composition of oxygen in CO being based on the difference values one was taken account of superposition on peaks with m/e 30 and 28, caused by appropriate fragment ions, which arose from molecular ions CO_2^+ with m/e 48, 46, 44. The necessary coefficients of fragmentation were taken from calibration mass-spectra recorded in identical conditions by using this same mass-spectrometer. The limiting relative error of this procedure in an approximation of an additivity achieves 2-3 %.

The final calculation of oxygen isotope ratios in gasification products was made by the following formulae:

$$u = \frac{I_{30}}{I_{28}} \qquad (3)$$

$$v = \frac{2I_{48} + I_{46}}{2I_{44} + I_{46}} \qquad (4)$$

where u and v - concentration ratio of isotopes $^{18}O/^{16}O$ in CO and CO_2, correspondingly; $I_{48...}I_{28}$ - difference values for peaks with m/e 48...28, correspondingly, corrected for superpositions of peaks. However, from the comparison of values of a, u and v it is possible only to make a conclusion about participation of oxygen-18 in gasification processes. But that does not allow yet to determine separately the contributions of thermooxidation and pyrolysis in total amounts of carbon oxide and dioxide which are generated during gasification [19].

For the calculation i, representing the ratio of an amount of CO, formed as a result of thermooxidation, to an amount CO, formed as a result of pyrolysis, equation (2), (3), (4) after simple algebraic transformations, while taking into account the correction for a natural ratio of oxygen isotopes in epoxy polymer, give the following expression in closed form:

$$i = \frac{1+m}{1+a} \bullet \frac{a-u}{u-m} \qquad (5)$$

where m - a natural ratio of oxygen isotopes $^{18}O/^{16}O$, characteristic of oxygen, contained in polymer. The similar calculation j, representing the ratio of an amount CO_2, formed as a result of thermooxidation, to an amount CO_2, formed as a result of pyrolysis, after algebraic transformations gives expression:

$$j = \frac{1+m}{1+a} \bullet \frac{a-r}{v - [m(1-s)/(2+r)]} \qquad (6)$$

where $\quad r = \dfrac{I_{46}}{I_{44}} \quad (7) \text{ and } \quad s = \dfrac{I_{48}}{I_{44}} \quad (8)$ [19]

The molecules of carbon oxide and dioxide released from polymer in its thermooxidation are generated during some total reaction of interaction between polymer and gaseous oxygen. The formation rates of its varieties containing different isotopes of oxygen are directly proportional to concentrations of these isotopes in oxygen of an oxidizing mixture and effective rate coefficients of appropriate chemical reactions.

According to the equations of the theory of a transient state and theory of collisions, as a first approximation, the proportion of rate coefficients of the same reactions of molecules $^{16}O_2$ and $^{16}O^{18}O$ will make magnitude close to 1,03 [20], i.e. the oxygen molecule including only light isotopes, will react faster to 3 %. Since the total errors of experiment are evaluated by magnitudes up to 10 %, it is possible to neglect this difference between chemical reaction rate constants and, correspondingly, overestimate of the contents of an isotope ^{16}O in thermooxidative destruction products of polymer.

In our case also, apparently, it is possible to neglect the corrections for isotope exchange reactions. According to [21,22,23], a high barrier of activation delays the direct exchange of isotope atoms between molecules, but the isotope exchange can happen and as a result of chemical reactions. However it is known [15,22,23], that in a gas mixture which has a composition as being similar to our compositions, the isotope equilibration of oxygen in all substances, even at the presence of the catalyst, needs high temperatures (more than 1200 K) and takes long time (about two hours). Under our experiment condition the temperatures as high as 700 K are observed on a small length of the installation during less 10 s, i.e. the isotope exchange can be neglected. In favor of this conclusion indicates the fact of existence of distinguishing isotope compositions at all gasification products while being sufficient the reproducibility of measurement. The errors in determining of isotope structure, most likely, depend on random factors - in particular, on not quite identical conditions of sample heating and of gas probe taking. The limiting relative errors of isotope ratio determinations of a, u, v, on our evaluation, are equal $\delta_a = 3$ %; $\delta_u = 21$ %; $\delta_v = 20$ %. The limiting relative errors of calculations by the formulae (4) and (5) will increase up to: $\delta_i = 39$ %; $\delta_j = 32$ %.

The thermooxidation contribution to water formation can be determined by the same equations, which are used for calculation of the thermooxidation contribution to formation of CO. However, the known difficulties of a mass-spectral measurement of small amounts of water in gas probes result in sharp increase of experimental errors. Attempt to develop other calculation scheme based on the account of iso-

tope ratio variations only in water vapors has reduced to a set of equations from a class Diophantine, i.e. the number of unknowns has exceeded the number of the equations. This fact forces to limit in case of water only by approximate evaluation of the thermooxidation contribution making use of the received inequality for an upper bound of it. Such evaluation gives value very close to zero. Therefore, in accordance with [24-27 etc.], practically all water vapors during gasification will be formed only due to pyrolysis.

It is possible to divide the experimental results on epoxy polymer gasification in an oxidizing mixture, enriched with the isotope oxygen-18, into two groups (Table 2), but, with our estimations of relative errors of measurements and calculations by formulae making allowance for, such division is necessary to recognize rather arbitrary. Nevertheless, the data from Table 2 demonstrate completely obvious and unambiguous, that in a course of epoxy polymer gasification the thermal destruction (pyrolysis) and thermooxidative destruction are realized simultaneously.

Table 2

The thermooxidation contribution into the formation of CO and CO_2 during the epoxy polymer gasification

№	Rate of temperature rise, K/s	Final temperature of heating, K	The thermooxidation contribution into formation of CO, %	The thermooxidation contribution into formation of CO_2, %
1	66	>730*	5**	86**
2	131	>730	11**	_***
3	135	>730	10	78
4	70	>730	8	96
5	70	>730	9	53
6	38	665	_***	76
7	43	443****	20****	72****
8	60	715	29	_***

*In experiment № 1 there was a self-ignition of gasification products.
**In experiments № 1, 2 calculations were made for two of oxidizing mixtures and two samples of gasification products (the average values are indicated).
***In experiments № 2, 6, 8 it was not possible to calculate the proportions of carbon oxide or carbon dioxide, resulting from thermooxidative destruction, by reason of errors of mass-spectra recording.
****In experiment № 7 the mass of a specimen was not changed (a residual has not changed its color and has not charring).

Among the experiments of first group, in which are observed the higher rates of temperature rise and higher final temperatures of heating (in one experiment even there was a flash), average proportion of CO_2, resulting from thermooxidative destruction, makes 79 %. At the same time average proportion of CO, resulting from thermooxidative destruction, is not so great - only 8 %.

The second group of experiments is characterized by smaller rates of temperature rise and lower final temperatures of heating. Among those the average proportion of CO_2, resulting from thermooxidative destruction, is less a little and makes 74 % that within the limits of the indicated relative error of calculations differs a little from the proportion found by first group

of experiments. However, the average proportion of CO, resulting from thermooxidative destruction, increases significantly, apparently, and makes 25 %.

In the second group there is distinguished the experiment № 7, in which the sample in appearance under small final temperature of heating (443 K) seems to be not changed and the noticeable loss in mass is not observed. In this experiment the proportion of CO_2, resulting from thermooxidation, makes 72 %, and analogous proportion of CO makes 20 %. According to [13], thermooxidation of epoxy polymer, really, are starting at lower temperatures, than pyrolysis, and from the very outset of thermooxidation the mass losses are not observed. In an interval of temperatures 420 - 450 K the mass loss due to gasification seems to be

compensated practically completely by absorption of oxygen [13].

Summarizing experiments with labelled oxygen, it is possible to conclude that CO_2 is formed mainly as a result of the thermooxidation, and CO is not its precursor, being formed, in main, only by the thermal destruction (pyrolysis). As to the water our evaluation indicates that it is possible to neglect the thermooxidation contribution into formation of one.

The conditions of the first group of experiments approach nearer to conditions to realize immediately on the backside of the incombustible spacer in skipping of a flame spreading over epoxy polymer surface. Those also are close to conditions to realize at the preflame zone of a freely spreading flame. According to [28] CO_2 is a main product ahead of a leading edge of a flame, that agrees with data of tab. 2 and means an occurrence of an intensive thermooxidation in the preflame zone of a freely spreading flame. The contribution of thermooxidation into formation of CO_2 reaches 79 %, i.e. CO_2 near to flame edge is formed by polymer thermooxidation in preference. But among volatile products of epoxy polymer gasification CO dominates (about 80 % vol.) [4], more than 90 % of which is formed as a result of thermal destruction.

The products of only thermal destruction of polymer predominate among products of gasification also integrally as concerns a mass. Therefore, the known correlations between combustibility of polymers and compositions (and amounts) of pyrolysis products are quite fair. Most mass of gasification combustible products, in the consent with [29], to be provided a flame spread is evolved into gas phase by pyrolysis. But energy for it is supplied, however, mainly by simultaneously occurring exothermal processes of thermooxidation in the near-surface layers of the polymer, for the most part - by processes of formation CO_2, that is in agreement with data of work [30]. Apparently, it is necessary to assume, at least - for polymers, that thermooxidation of ones generally is always accompanied by only thermal destruction, but contributions of both processes into polymers gasification can strongly depend on certain conditions of gasification and nature of the polymer under study.

Conclusions

An experimental study of flame spread over the surface of epoxy polymer was performed to obtain knowledge of gasification processes of a char-forming polymer in the preflame zone and the following conclusions were derived.

Heating of yet unignited polymer ahead of flame spreading over the thermally thick samples is done mainly by the heat conduction through condensed phase.

The compositions of highly- and hardly-volatile products of gasification are determined in conditions of the preflame zone. The main combustible product of gasification is CO (ca. 85 %).

The mass rates of gasification and the linear velocities of an injection of gasification products into gas phase of preflame zone have been determined. The complicated aerodynamic structure of the preflame zone with a vortex formation is shown to exist. As a result oxygen gets a free access to a polymer surface and can participate in gasification processes.

Experimental simulation of the epoxy polymer gasification processes was carried out in the oxygen-18 enriched atmosphere. The main oxygen-containing products of gasification are generated both as a result of pyrolysis, and a result of thermooxidation. More than 75 % of carbon dioxide is formed only due to thermooxidative destruction, and 75 - 90 % of carbon oxide is formed only due to pyrolysis. Practically all water vapors during gasification are formed only due to pyrolysis.

In a course of epoxy polymer gasification in preflame zone the main mass of combustible products is generated by pyrolysis, but an energy for this is mostly supplied by simultaneously occurred exothermal processes of thermooxidation of the near-surface layers of epoxy polymer.

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