

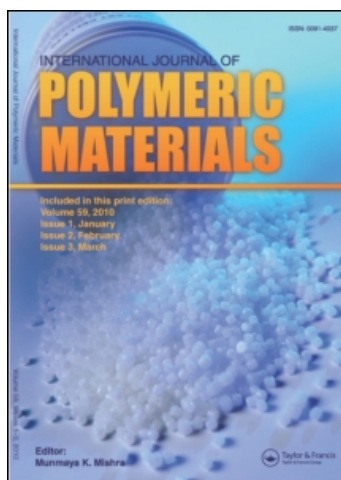
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Burning of the Carbonized Polymers

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The paper discusses the influence of the carbonized layer and the effect of its separate characteristics upon polymer combustibility. The expressions relating burning rate with carbonized layer thickness and some properties of degradation products are presented and main directions of lowering carbonized materials combustion have been shown. They are to increase viscosity of pyrolysis products and to decrease coke penetrability.

KEYWORDS: Combustion, carbonized layers, polymer combustibility, coke yield, mechanism of quenching

Under the influence of fire a carbonized layer is formed on the surface of some polymers, contributing to the decrease in combustibility.^{1,2} Recently there appeared also empirical formulas, which connect polymer combustibility with the coke yield.^{3,4} The mechanism of quenching of polymer burning connected with the formation of carbonized residue is usually explained by the fact that the surface coke layer hinders the diffusion of oxygen and active flame particles to the decomposing polymer and impedes the outflow of the destruction products into the combustion zone. These reasons however have no practical confirmation, being of tentative and descriptive character.

In the present paper, the influence of the carbonized layer has been considered and the effect of its separate characteristics upon polymer combustibility has been estimated.

Heat from the flame upon combustion is spent on heating and decomposition of a polymer and if the coke residue is present, additional losses of thermal energy are indispensable for heating of such coke residue and pyrolysis products, passing through the coke. It is reasonable to single out two surfaces for the coking polymers: the surface of the carbonized layer, being in contact with the gaseous phase, and the surface of the decomposing polymer, being in contact with the coke the thermal balance upon the combustion of the carbonized polymers in quasi-stationary conditions can be expressed by the following equations:

$$U_m = \frac{\alpha(T_f - T_{S_1}) + \delta \mathcal{E}_f T_f^4 - \delta \mathcal{E}_{S_1} T_{S_1}^4 + Q_{oxc}}{K[C_c(T_{S_1} - T_{S_2}) + q_{gas c}] + C_p(T_{S_2} - T_0) + q_{pyr} + G[C_g(T_{S_1} - T_{S_2})]}$$

where U_m —mass burning rate

α —heat transfer coefficient

T_f —temperature of the flame

$Q_{ox.c.}$ —oxidation heat of the coke

δ —Steven-Boltzmann's constant

$\mathcal{E}_f, \mathcal{E}_{s_1}$ —radiation capability of the flame and the coke surface

T_{s_1}, T_{s_2} —temperature of the coke surface and the decomposing polymer

C_c, C_p, C_g —average heat capacity of the coke, polymer and volatile destruction products, $q_{gas.c.}, q_{pyr}$ —gasification heat of the coke and of polymer pyrolysis, K —a part of the polymer transformed into coke

G —a fraction of gaseous products, formed upon the polymer decomposition (K and G are connected by the ratio $K = 1 - G$). A numerator of the expression comprises heat in flow from the flame by way of connection and radiation, along with a member reflecting dispersal of the absorbed thermal energy by the surface due to radiation.

Heat losses represented in the denominator comprise polymer heating, its gasification and energy of chemical transformations, heating of the volatile decomposition products, the formed coke and its volatilization energy.

An analysis of the Eq. (1) shows that to decrease the decomposition rate and in accordance with the combustibility of the polymer, it's reasonable to increase the coke surface temperature. In this case, the heat flow from the flame drops: firstly, due to the decrease in the connective heat inflow, because $T_f - T_{s_1}$ decreases, secondly, due to the increase in the heat outflow in the environment by the surface radiation.

Heat losses on heating of the carbonized layer and especially volatile compounds passing through this layer also increase so as their heat capacity can exceed the heat capacity of the condensed substances by a factor of two. Gas injection into the combustion zone shields the polymer material also from the

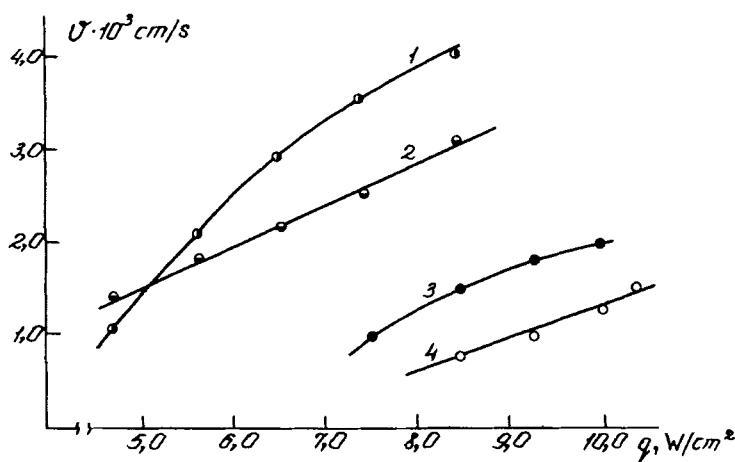


FIGURE 1 The effects of the nature of the heat flow on the rate of linear pyrolysis: 1, 2—radiant; 3, 4—convective (1, 3 without 2, 4—with porous plate (thickness 2.8 mm)).

connective heat energy from the flame. This is obviously seen by the linear pyrolysis data of polymethylmethacrylate samples, covered with plates of porous material, under the action of radiational heating and in the flows of heated air (Figure 1).

In a number of experiments, we have attempted to model out the process of polymer burning by using porous plates of heat-resistant materials: (foam-ceramics, foaming glass), which have been applied to cover the polymer under study. Then such samples have been submitted to the unilateral effect of radiant or convective heat flows.

Figure 2 shows the linear effect of the radiant flow power upon the rate of the linear pyrolysis of polymethylmethacrylate samples, covered by porous plates of different thickness. It is seen that with an increase in the heat effect power, the rate of polymer decomposition increases, and an increase in the plate thickness results in decrease of the rate of polymer decomposition. Variation in the temperatures of plate surfaces has shown that an increase in the plate thickness and flow density results in an increase in the temperature of the external plate surface. Thus, with the plate thickness of 0.38 cm, the temperature upon which flows 4.5 w/cm^2 and 8.5 w/cm^2 possess the values of 920°K and 1100°K respectively, and an alternation of the foam material height from 0.21 to 0.46 cm upon the radiation power of 8.5 w/cm^2 results in an increase of the surface temperature from 1070° to 1150°K . However, according to the experimental data the pyrolysis rate of the polymer increases with an increase in the heat flow power more than it does in the calculations.

Such a discrepancy is connected with the lift of the liquid destruction products and polymer melts up the porous layer, that has been shown earlier.^{1,5} It is noteworthy that in all the experiments described above, the temperature of the internal plate side, i.e. on the border foam-layer-polymer, has been constant and equal to 650°C .

The coke formed upon polymer combustion has a porous structure, and the

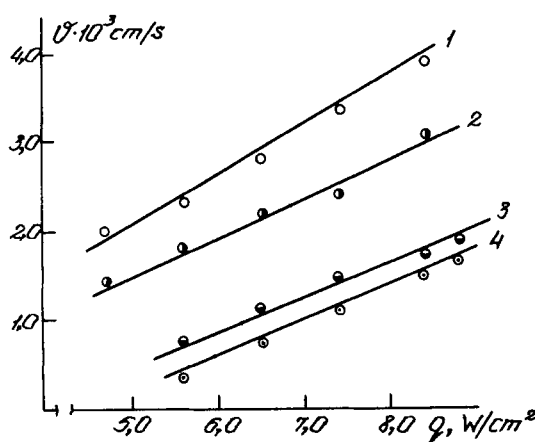


FIGURE 2 The influence of the power of the heat flow upon the rate of linear pyrolysis under different thickness of porous plate (mm): 1—2.1; 2—2.8; 3—3.8; 4—4.6.

gaseous destruction products pass from the depth of the condensed phase through the carbonized layer to the combustion zone. For liquid products the coke can play a role of a "fuse" by which they raise up to the surface and maintain burning.

The burning rate of the carbonized polymers is determined by the coke gasification rate and the rate of the liquid and gaseous destruction products passing through the carbonized layer. Taking into account that the flow rate of liquids and gases through the porous materials is described by Darcy's law, the expression for the burning rate of the polymers on the surface of which a carbonized residue is formed can be presented as follows:

$$U_m = U_k \cdot k + (1 + k) \left(\frac{K \cdot \rho_g}{\eta_g \cdot l} \Delta P + \frac{K \rho_l}{\eta \cdot l} \right)$$

where U_m —the mass burning rate

U_k —the mass gasification rate

k —the part of the polymer, transforming into the coke

K —Darcy's constant

l —the thickness of the carbonized layer

ρ_g, ρ_l —densities of the gaseous and liquid products

η_g, η_l —viscosities of liquids and gases

ΔP —the difference between the external layer and underlayer of the coke.

As far as the motion of the pyrolysis liquid products through the carbonized layer can be realized due to the capillary forces, the Eq. (2) in accordance with Laplace's law can be represented as follows:

$$U_m = U_k \cdot k + (1 + k) \frac{K}{l} \left(\frac{\rho_g}{\eta_g} \Delta P + \frac{\rho_l 2\delta}{\eta_l R} \right)$$

where δ —the surface tension

R —the radius of the porous material.

It follows from the Eq. (3) that with an increase in the yield of the carbonized residue an amount of the destruction liquid and gaseous products flowing into the combustion zone, decreases, and the burning rate within the limit can be determined by the paralysis rate of the carbonized layer. In this case, the burning rate of the polymer can be described by the coke outburning rate. However, the straight lines of the penetrability measurement of the coke have showed that the Darcy's constants obtained for different polymers under different conditions are considerable and they can change over the wide range.

Thus, Darcy's constants of the cokes formed upon the pyrolysis of phenol-formaldehyde raises the temperature range from 670 to 770°K altered from 80 to 600.

The calculations shows that with such values of Darcy's constants the carbonized layer even of considerable thickness cannot hinder the outflow of the volatile decomposition products into the combustion zone, and besides the gases formed upon pyrolysis cannot create substantial excessive tension neither under the layer of the coke nor inside the layer of the coke. The presence in the carbonized layer through thin canals contributes to the motion of the liquid destruction products through the coke.

It has been found from the experimental data of the coke penetrability determination, obtained from phenol-formaldehyde resin, that $\frac{1}{3}$ of the overall amount of pores possess small diameter. Through these pores, liquids can raise due to the capillary forces. The calculation shows that upon such a structure of the coke low-viscous liquids can move at a considerable rate through the carbonized material. In the experiments of measurement of outburning rate of acetone, ethanol, benzene in quartz tubes, corked by the layer, it has been found out that the burning rates of these liquids don't alter despite the alternation of the thickness of the carbonized layer (from 1.0 to 5.0 cm), and are equal to the outburning rates of these liquids, which have been determined upon their own free burning, i.e. it has been shown in these experiments that the rates of motion of these liquids through the porous material exceed the rates of their outburning and that's why the alternation of the thickness of the carbonized layer in the known limits doesn't effect the burning rate.

The thickness of the carbonized layer can effect the polymer combustibility according to the Eq. (2), upon the formation of viscous liquids. For instance, upon the coke thickness of 1 cm, epoxy resin, which has viscosity of 1200 cP (343) at 45°, burns, and with a decrease in the temperature down to 30° viscosity increases up to 7000 cP, and burning ceases.

The calculations shows that upon burning polymer melts can also penetrate through the surface carbonized layer. It has been confirmed experimentally in experiments with polystyrene plates, covered with foamed coke, affecting them by the heated air flow. Upon rapid cooling of the sample by nitrogen after ignition polystyrene of molecular mass of 9×10^4 has been found in the foamed coke. Maybe it can also account for combustibility of highly filled polymer materials and glass reinforced plastics. Polyolephines can be an example of it.

So far as upon combustion of polyolephines coke is not formed, the filler which is capable to form coke upon heating has been used for estimation of the carbonized layer. A mixture: pentaerythrite-phosphate diammonium-melamine has been used as such a filler. The data of variation of the oxygen index of polyethylene and polypropylene with different amount of the filler are presented in Table I. It is seen that upon small filler concentrations polymer combustibility decreases insignificantly the formation of the foamed coke layer affecting the combustion of polyethylene to a lesser degree than that of polypropylene.

In the experiments with polyolephines, filled with foamed additions one can observe the same phenomenon as in the case of combustion of polystyrene

TABLE I
Combustibility of polyethylene and polypropylene upon different concentrations of the foamed filler

C of the filler, %	O.I. of polyethylene	O.I. of polypropylene
—	17.5	17.5
10.0	19.5	19.0
20.0	21.0	23.0
30.0	24.5	32.5
40.0	28.0	48.0

samples, covered with the plates of foamed coke, i.e. under the coke layer of the porous structure, a partially destroyed polymer melt is formed, which passes by the canals of the porous carbonized layer to the surface and maintains combustion. So far as melting temperature and viscosity of the polypropylene melt is higher than that of polyethylene, the latter possesses higher level of the melt raising through the foamed coke. It affects also the height of the foamed coke layer: low temperature of the polyethylene melt hinders heating-up of the foamed filler, and no intensive formation of the foamed coke. It is noteworthy that the liquid products can attain the surface of the carbonized layer depending on the coke structure, thermal conductivity of the coke, the thickness of the carbonized layer, as it has been shown in the experiments of measurement of the combustion rates of liquids, the formation of the coke insignificantly affecting combustibility combustion in this case. With an increase in the heat flow density and the thickness of the carbonized layer, the surface temperature and the area of the intensive gasification displaces in the depth of the porous material. Thermal conductivity plays also a significant role in the temperature distribution in the coke layer, that follows from the problem solution of cooling of a porous plate by liquids—the rate of liquid feed for necessary cooling of a porous plate decreases with an increase of the plate thickness and a decrease in its thermal conductivity. On the basis of the obtained data a model of combustion of the carbonized polymers can be presented, which is done schematically in Figure 3.

Estimating separate parameters of the heat and mass transfer processes upon polymers combustion with the formation of the surface coke layer, one can single out the following main directions of lowering their combustion:

— an increase in the yield of the carbonized residue, that decreases an amount of the carbon-containing fuel entering the combustion zone;

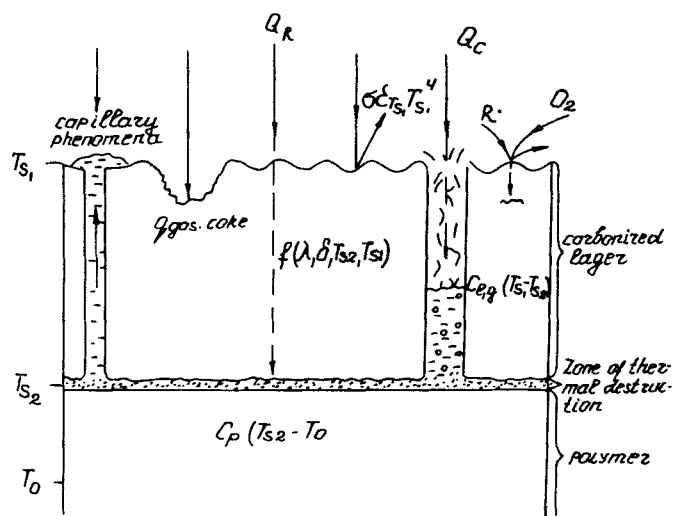


FIGURE 3 Scheme of charring polymers combustion.

– an increase in the coke heat-resistance, resulting in an increase in the surface temperature, which contributes to a decrease in the connective heat inflow, an increase in heat energy dissipation due to the surface radiation and an increase in the losses on heating of the gaseous destruction products, passing through the carbonized layer occupying a special place. The presence of the heat-resistant coke on the surface creates a barrier for a heat-flow on the flame that's why an increase in the thickness of the carbonized layer and a decrease in its thermal conductivity are desirable;

– penetrability of the carbonized layer should be low to limit the lift of the liquid pyrolysis products. The second way is to increase viscosity of these products, for instance, due to the linkage reactions.

Phosphorous-containing compounds are widely applied as combustion retardants, contributing to the coke formation.

It has been found out that phosphorous substances also causes a decrease in penetrability of the carbonized residues. Thus, upon the treatment of the coke obtained upon the pyrolysis of phenol-formaldehyde resin, by phosphoric acid and its subsequent treatment at 600°K the Darcy's constant decreases by a factor of 4. The similar phenomenon is observed also upon introduction of other phosphorous-containing compounds, contributing to the lowering of the polymer combustibility. Figure 4 presents the data of the oxygen indexes of polymers covered by the "cap" of the foamed coke, obtained upon the pyrolysis of phenol-formaldehyde resin with different contents of monoammonium-phosphate. It is seen that the presence of a phosphorous compound results in a decrease in the coke penetrability and provides accordingly a decrease in the polymer combustibility. The values of the oxygen indexes for epoxy resin samples are higher than that for polystyrene because the destruction products of epoxy

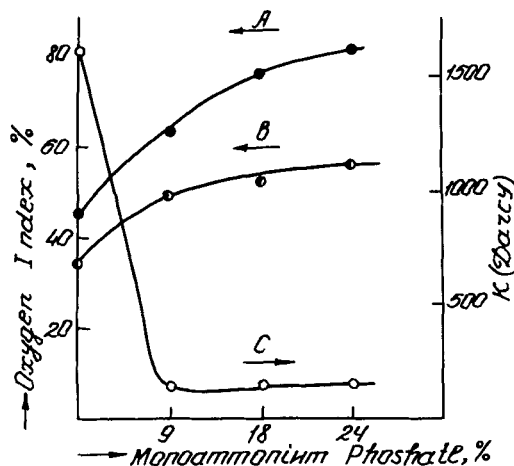


FIGURE 4 Combustibility of opoxide resin (A) and polysterene (B) samples coated with the carbonized layer $1 \cdot 10^{-3}$ with different penetrations (C). The coke has been obtained upon P.F.N. pyrolysis monoammonium phosphate additions.

resin are likely to interact with phosphoric acid with the formation of substances of high viscosity.

The data of X-ray radioscopical and electron microscopical analysis have shown that the coke microstructure of phenol-formaldehyde resin in the absence of phosphates is characterized by open porosity and amorphous disorder. After adding of monoammonium-phosphate more regular diffusion of micropores in the coke bulk is observed and some ordered crystalline areas appear.

Some boric compounds similarly affect the carbonized residue.

Figure 5 presents the data of penetrability of the carbonized residues of phenol-formaldehyde resin with boric acid, obtained at different temperatures and the O.I. values of epoxy resin samples covered by layers of these cokes. It is seen from the same figure that the coke penetrability decreases with a temperature increase and attains its minimum value at 450°C, and then increases again that accordingly affect combustibility. It is known that boric acid is decomposed upon heating in water and boron oxide which viscosity is higher at 350°C, slowly lowering the increase of temperature at 450°C boron oxide becomes a low-viscous liquid, which is likely to cover the coke pores and contributes to a decrease in penetrability. With a temperature increase there occurs a decrease in viscosity of films of boron- and phosphorous-containing compounds. The surface of the carbonized material opens and its outburning occurs.

The results of investigations by X-ray examination and electron microscopy have allowed to establish that the coke structure optimum by its homogeneity, is observed for a sample by which is heated up to 450°C. For the coke obtained at pyrolysis temperature of 350°C, two types of pores structure of micro- and macroelements are observed. An increase in the pyrolysis temperature contributes to the stabilization of the coke structure. In the coke pyrolyzed at the temperature of 500°C, a decomposition of the coke and a qualitative change of the structure occur.

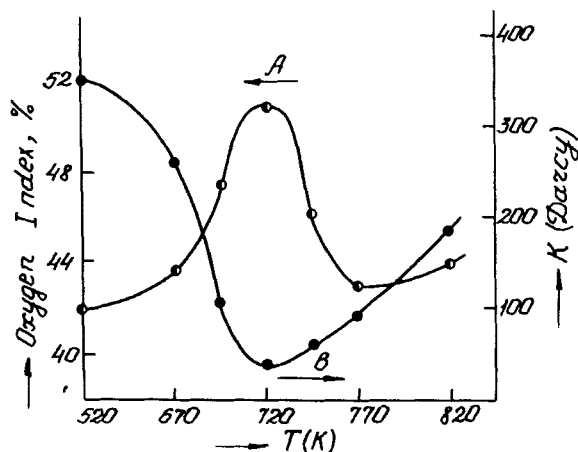


FIGURE 5 Combustibility of polystyrene (A) samples coated with the carbonized layer of $1 \cdot 10^{-3}$ m with different penetrations (B). The coke has been obtained upon pyrolysis of P.F.N. (100%), B_2O_3 (20%) and hexamethylene-tetramine (6%) at different temperatures.

To estimate such an effect upon the coke penetrability of the compounds in question, it has been supposed that polyphosphoric acids formed at high temperatures and boric oxide possess high viscosity and fill pores of the carbonized residue. This hypothesis has been put to test in the experiments using plates of foamed ceramics, treated by boric acid at different temperatures. Porous material held at 720°K has penetrability 10 times higher than that at 620°K, and the oxygen indexes of polystyrene, covered by the plates of these materials, has values of 40% and 51%.

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