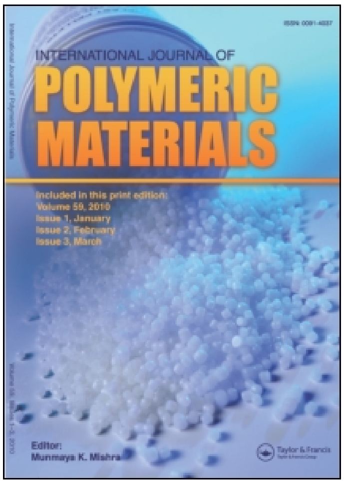

International Journal of Polymeric Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

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To cite this Article Khalturinskii, N. A. and Berlin, A. A.(1990) 'On Reduction of Combustibility of Polymeric Materials', International Journal of Polymeric Materials, 14: 1, 109 — 125
To link to this Article: DOI: 10.1080/00914039008041077
URL: http://dx.doi.org/10.1080/00914039008041077

Intern. J. Polymeric Mater., 1990, Vol. 14, pp. 109–125
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Printed in the United Kingdom

On Reduction of Combustibility of Polymeric Materials

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On the basis of broad experimental material, the authors made the following conclusions: inert fillers influence the combustion of polymeric materials strongly only at high weight content; the fillers, that decompose into volatile products as CO_2 and H_2O can more strongly influence the combustion of composite compounds; the effective methods of reducing the combustibility of polymers are chemical modification of the thermoreactive matrix, or modification of filling fibers, that can cause increased coke formation.

KEYWORDS: Combustibility, polymeric materials, inert filling agents, ignition, heat balance, polyolefines

A major factor restraining introduction of various polymeric materials is their combustibility.

Combustibility is a complex parameter of material or construction that is comprised of ignition or self-ignition parameters; rate of burn-out and propagation of flame across the surface; limiting parameters of conditions allowing for self-sustained process of combustion, e.g. atmosphere analysis (oxygen index) or temperature (temperature index).

It should be said that the above shown combustibility parameters are contradictory and improvement of one of the parameters may cause deterioration of another one. Besides, application of additives impeding combustibility of polymeric materials usually leads to a certain deterioration of physical, mechanical, dielectrical and other performance and technological characteristics and increase of cost of material. Thus the problems of limitation of polymeric materials combustibility are the optimization problems.

It is accepted that inert filling agents are the filling agents that do not exert considerable influence on the composition and amount of polymeric materials pyrolysis products in gaseous atmosphere and the amount of coke residue under the conditions of combustion. These filling agents can be divided into two parts only conventionally, since it depends upon the polymeric matrix:

1) Inert non-combustible filling agents, resistant up to 1000°C—oxides of metals, potassium fluoride, lithium fluoride, silicates, industrial carbon, powdered metals etc.

2) Inert non-combustible substances that decompose at temperature below 400–500°C with heat absorption and, as a rule, carbon dioxide liberation and/or water vapor and ammonia liberation—hydro-oxides, carbonates, hydrocarbonates of metals, phosphates etc.

It is obvious that theoretic treatment of principal stages of the process should be done to analyse the process of combustion and to indicate exterior factors defining different parameters of combustibility. Still it is not feasible now. Existing models comprise a number of hardly reasonable restrictions and hardly match experimental data.

The approximate analysis used in the given review is based on the condition of heat balance in the leading edge of the flame, i.e. in the area adjacent to the gasifying surface. It should be mentioned that combustion parameters, e.g. completeness of combustion, heat of combustion etc. may be different for the leading edge of the flame and for the whole flame. The bigger the tongue is, the greater those differences are.

Analysis and final formulae of the existing model used in this review are based on the heat balance equation for the leading edge of the flame presented in the form of reagent flows towards the reaction zone:

$$(T_g - T_0)(c_{O_2}\dot{m}_{O_2} + c_{N_2}\dot{m}_{N_2}) + c_T\dot{m}_T(T_g - T_s) = Q\dot{m}_T - L\dot{m}_T - Q_{NOT}$$

where T_g, T_s, T_0—temperature of flame, of the surface of the burning body and environment respectively;

c—average specific heat;

$\dot{m}$—mass flow;

indices O_2, N_2, T—referring oxygen, nitrogen of the environment and gaseous combustible products of polymer destruction (fuel) respectively;

Q, L—combustion heat and polymer gasification;

Q_{NOT}—flow of heat losses.

Besides, heat losses due to filling agent were taken into consideration. Further on, it was foreseen in the model:

1) analysis of the oxidant that gets into the flame coincides with the analysis of gaseous media:

$$m_{O_2} = \frac{Y}{1 - Y} m_{N_2},$$

where Y—mole (volume) fraction of oxygen in the environment;

2) fuel and oxidant react in stoichiometrical ratio, $m_{O_2} = rm_T$ where r—mass stoichiometrical factor of combustion;

3) temperature in the leading edge of the flame for the candle-type combustion of polymeric materials, as it was seen through experiment, changes within the limits from 700°–800°C to 1200–1300°C. That is why we accept that for limiting conditions $T_g - T_0 = \text{const} = 1000°\text{C}$. This assumption was proved in an indirect way in practice.

As a result we get the following expression for the oxygen index of polymeric materials with fillers of the first two groups:

$$\frac{100}{O.I.}=\frac{Q-L-c_T(T_g-T_s)-\dfrac{Q_{\mathrm{NOT}}}{\dot{m}_T}-\kappa q_H}{c.r.(T_g-T_0)} \tag{2}$$

where $c \approx c_{N_2} \approx c_{O_2} \approx 1.088 \times 10^3$ J/kg × K (calorie/g × °C – 0.26); κ—filling agent fraction of the total mass; q_H—heat absorbed by filling agent mass unit.

For the first group of filling agents:

$$q=c_H(T_s-T_0)$$

For the second group:

$$q_H=c_H(T_P-T_p-T_c)+(1-\gamma)c'_H(T_s-T_p)+q_p+c'_{\mathrm{H_2O,CO_2}}\gamma(T_g-T_p) \tag{3}$$

in that case c_{H}, c'_H—specific heat of the filling agent and solid products of its decomposition; q_p, T_p—specific heat and decomposition temperature of the filling agent; $c_{\mathrm{H_2O,CO_2}}$—average specific heat and fraction of the total mass of the gaseous products of decomposition.

Average specific heat of the fuel may be accepted equal to 2.09 J/kg × K.

Effect of "inert" filling agents on combustibility of polymers is the subject of several researches.[1,2,3,4,5-7] Data on the effect of inert filling agents are given in Table I.

It is clear from the above shown data that these filling agents exert practically no influence on the value of oxygen index in the studied range of concentrations.

Some researches point out the increase of combustion rate of polymeric materials armoured with glass fibre.[8,9] For example, when the contents of glass in composition with polymethylmethacrylate increased up to 70% of the composition mass, combustion rate increased three times if compared to unfilled polymethylmethacrylate. This is explained by higher thermal conductivity of glass fibre and spalling of binder from the fibre.

On the basis of experimental data and heat balance calculation researches[10] come to the conclusion that introduction of inert fillers can not cause a considerable increase of flame-resistance of polymeric materials. It is stated in the research that introduction of quartz sand into epoxy resin (up to 95% of the composition mass) will increase oxygen index only by 38%.

It is seen from the shown data that to achieve a considerable decrease of polymer combustibility by way of introduction of inert non-combustible filling agents is possible only if the filling agents constitute over 80% of composition mass. It is explained by low heat input for the heating of filling agents to the temperature of the burning materials surface in the total heat balance. At such high degrees of filling the material becomes too fragile, its physical and mechanical characteristics usually do not meet necessary requirements. The only exception is some construction materials manufactured by compaction and caking. Due to high viscosity of the melt such materials usually are unfit for treatment by extrusion and dye casting.

When fibre filling agents are applied, such additional factors as orientation of

TABLE I

Effect of inert filling agents on the value of oxygen index of polymers according to Refs. 3, 4, 5

Polymer	Oxygen index
1. Polycarbonate	30
2. Polycarbonate + 20% of glass fibre	29.8
3. Polycarbonate + 40% of glass fibre	29.3
4. Polysterene	18.2
5. Polysterene + 30% glass fibre	18.5
6. AV	18.8
7. AV	
+ 29% of glass	21.6
8. Polyacetals	14.9
9. Polyacetals + 30% of glass fibre	15.6
10. High pressure polyethylene	17.7
+ kaolin 5%	17.9
10%	17.9
20%	18.1
+ chalk 5%	17.9
10%	17.9
20%	18.1
+ glass fibre 10%	17.5
20%	17.9
30%	17.9
11. Polypropylene	
+ kaolin 5%	17.9
10%	17.9
20%	19.8
+ chalk 5%	17.7
10%	17.9
20%	18.1
+ glass fibre 10%	17.7
20%	18.8
30%	18.4
12. Shock-proof polystyrene	18.1
+ kaolin 5%	18.8
10%	19.2
20%	19.2
+ chalk 5%	18.4
10%	18.8
20%	19.2
+ glass fibre 10%	18.8
20%	19.0
30%	19.0

fibres and relationship between the size of fibres and the heated layer of polymeric matrix acquire great importance. This fact is vividly illustrated by the data shown on Figure 1 for polymethylmethacrylate armoured with copper wire of different diameters. Thickness of polymeric film and the size of heated layer ratio becomes very important for stratified constructions. Temperature conductivity of the base has a major effect on propagation of flame for thermically thin materials.

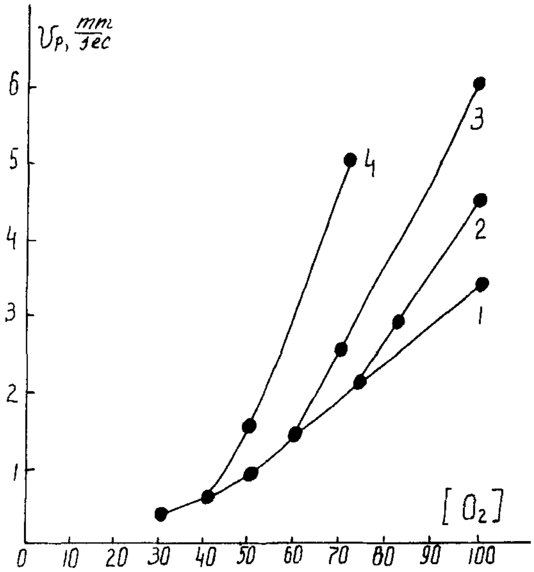


FIGURE 1 Relationship vetween concentration of oxygen and the rate of propagation of PMMA across the surface; 1—not armoured PMMA; PMMA armoured with copper wire, diameter 2—0.15 mm, 3—0.23 mm, 4—0.35 mm.

The experiments set to make clear the effect of dimensions on limiting characteristics revealed that under certain conditions decrease of thickness of a specimen causes flame-out. For the combustion of polymers on thermal conductor base the critical thickness of combustion equals: 0.3–0.5 cm for polysterene, 0.15–0.2 cm for polymethylmethacrylate (PMMA), 0.03 for celluloid.[11] For combustion of PMMA the limit thickness of combustion between thermal conductivity plates equals 1.7 cm.[11] Limit dimensions are relevant due to additional heat losses both from gaseous and condensed phases. Limit dimensions of combustion will decrease as the concentration of oxygen in the ambient air increases.[12] It can be explained by the decrease of thickness of the heated layer in the condensed phase and increase of heat release rate in the gaseous phase. Combustion of polymer films on copper wires and glass fibres of different diameters is studied in researches.[13,14] It was shown, that the value of critical thickness of polymer film for copper wires first increases in proportion to the diameter and then reaches its limit values. For glass fibres, increase of critical thickness occurs only for small values of d.e. films on fibre glass may be thinner than on copper wires, essentially for downward combustion. Critical parameters of PMMA combustion on copper wires and glass fibres are shown in Table II.

Let us consider the effect of inert filling agents on other parameters of combustibility. As it is shown in research work,[15] critical sizes of combustion of filled polymers increase due to introduction of heat-conductivity filling agents.

When the effect of inert filling agents on ignition parameters was studied,[16] it was stated, that their introduction exerts practically no influence on the ignition temperature of polymeric compositions up to 40% of filling. At a higher degree of

TABLE II

Type of filament 1	Direction of combustion 2	Diameter mm 3	Critical thickness of film, mm 4	Rate of combustion 5
Copper	downwards	0.15	0.030	1.29
		0.03	0.055	0.70
		0.7	0.115	0.35
	horizontal	0.15	0.04	1.31
		0.3	0.08	0.70
		0.7	0.165	0.36
	upwards	0.25	0.11	0.30
		0.35	0.11	0.21
		0.5	0.11	0.16
Glass	horizontal	0.25	0.065	0.064
		0.35	0.65	0.46

filling the ignition temperature rises due to decrease of gasification rate and depletion of combustible mixture at the gaseous phase.

Another parameter of ignition is the ignition delay or the duration of contact of the heat source and the polymer while the duration of the combustion itself tends to infinity. After this effect the composite specimen may burn independently, without the exposure to external source. According to the thermal theory of ignition,[17] when the polymer is exposed to constant heat flow ignition delay time is determined from the following formula:

$$\tau = \pi c \rho \lambda \frac{(T_s - T_0)^2}{4q_0^2} \qquad (6)$$

When all other conditions are the same, ignition delay time is determined by variations of composit heat activity. For example, it was discovered[18] that the period of ignition induction increases with the increase of the volume fraction of filling agents in case of ignition of stratified metallic and polymeric composite materials with the burner flame. As the product increases, the rate of heat required to create critical conditions increases as well; these conditions are realized in stationary combustion of polymers. The period of the ignition induction is described by the following equation:

$$\tau = \tau_0\left[1 + \frac{\lambda_M Y_M}{\lambda_0(1 - Y_M)}\right] \qquad (7)$$

where τ_0 is the period of ignition induction of the unfilled polymer; λ_M, λ_0—heat conductivity of metal and polymer; Y_M—volume fraction of metal in composite materials.

On the contrary, during the research of propagation of flame across the surface of composites, the rate of propagation along the oriented filling agents will be higher than for the propagation of flame perpendicular to the filling agents fibres orientation or the pure polymer due to bigger fraction of heat transfer through the condensed phase.

TABLE III

Relations between ignition delay time (τ_3) of polyurethanes of different density

ρ g/cm^3	$\lambda \frac{\mathscr{E}_T}{\text{mK}}$	$c \frac{J}{g\,°\text{C}}$	$\lambda_{c\rho} \frac{\text{J}^2}{\text{cm}^2 \cdot \square° \cdot \text{cm}^4} 10^3$	t_3, c
0.91	0.119	0.96	1.04	2.5
0.77	0.102	0.81	0.64	1.5
0.59	0.082	0.62	0.30	0.8
0.48	0.070	0.51	0.17	0.4

For the dispersive spheric filling agents:

$$\lambda = \lambda_n \frac{2\lambda_n + \lambda_H - 2\varphi(\lambda_n - \lambda_H)}{2\lambda_n + \lambda_H + \varphi(\lambda - \lambda_H)} \tag{8}$$

This expression is correct for heat conductive fillers and for foam plastic type porous system. Relations between ignition delay time (τ_3) for polyurethanes of different density[16] are shown in Table III.

The similar relationship can be traced for heat conductivity filling agents. Data for the epoxy resin filled with calcium carbonate and copper powder are shown in Table IV.

If we introduce into the composite of the 2nd type "inert fillers", we would be able to subdue combustibility much more efficiently. Figure 2 shows the comparison of filled polymers oxygen index and concentration of filling agents of the first and the second groups. Only very large amounts of filling agents of the first group (over 80%) make it possible to bring down the combustibility of the material.

As it can be seen from Figure 2, the same filling agent would be more efficient at smaller values of stoichiometric factor. It is related to different inputs of endothermic effects into heat balance in the edge of the flame (see Table V). It can be seen from the table that endothermic effect for POM* equals 25% of heat balance, while for polyethylene it is only 10%. That's why TGOA* is much more efficient in case of POM.

Combustion parameters for polyolefins compositions[19] are shown in Table VI.

TABLE IV

Relationship between ignition time delay of epoxy resin and the degree of filling

Composite	τ_3, sec	$\lambda \times 10^4 \frac{\text{calories}}{\text{cm} \times \text{sec} \times °\text{C}}$	$c \frac{\text{calories}}{g \times °\text{C}}$
Unfilled resin	0.6	4.5	0.3
Resin + 12% $CaCO_3$	0.9	5.24	0.31
Resin + 32% $CaCO_3$	1.2	6.8	0.32
Resin + 45.5% $CaCO_2$	1.6	8.29	0.33
Resin + 55.6% $CaCO_3$	2.6	9.76	0.34
Resin + 64% $CaCO_3$	3.5	11.3	0.35
Resin + 40% Cu (powder)	0.95	5.6	0.34
Resin + 80%	4.1	11.73	0.48

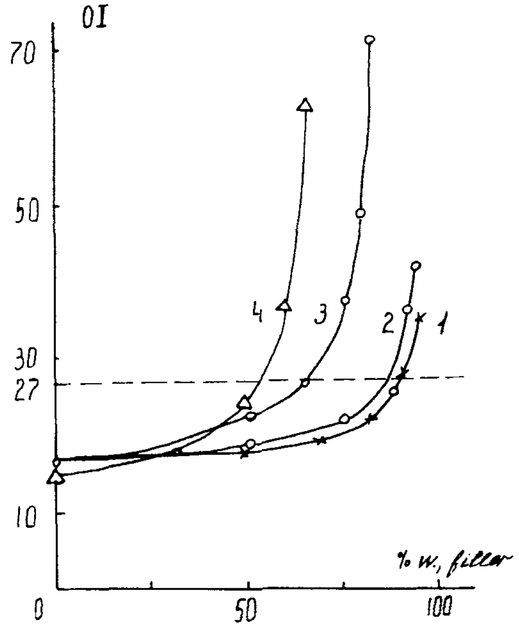


FIGURE 2 Relationship between OI and content of filling agents 1—Al_2O_3 + PE; 2—PO + PE; 3—$Al(CH)_3$ + PE; 4—$Al(OH)_3$ + PF.

As it can be seen from the table, ignition time increases in proportion to endothermic effect of TOA* decomposition, while the rate of combustion decreases.

The above studied groups of filling agents are regarded "inert", but some reports point out their effect on processes of the condensed phase. For example, in work[20] the effect of industrial carbon on combustibility and destruction of polychloroprene is described. In Ref. 19 effect of "inert" TGOA* on condensed

TABLE V

Heat balance for polymer combustion with air

Heat effect cal/g	PE*	PF*	PMMA
Combustion	11000	4040	6400
Completeness of combustion	0.66	0.7	0.7
Gasification	550	580	390
Warm-up of polymer	450	300	350
Warm-up of air	6250	1390	3570
Radiation	100	—	160
Heat losses	7350	2810	4470
Heating of A_2O_3, $3H_2O$ 50% filling	700	700	700

*—Transliteration.

TABLE VI

Combustion parameters for polyolefin compositions

Polymer	Weight proportion of TOA* (%)	Ignition time, sec	Linear rate of combustion, sec	TOA* destruction heat, kJ
SEVA*	0	5	24	—
	20	7	23	17
	30	10	21	25
	40	13	18	33
	50	15	15	42
	60	17	12	50
	70	23	11	58
High pressure polyethylene	0	4	22	17
	20	6	17	25
	30	8	15	33
	40	8	12	42
	50	8	11	
	60	10	10	50
	70	12	8	58
Polypropylene	0	5	22	—
	20	5	21	17
	30	6	18	25
	40	9	16	33
	50	9	15	42
	60	10	12	50
	70	15	10	58

*—Transiliteration.

phase destruction processes is marked. Evidently, this effect for such filling agents is insufficient.

The effective method of reduction of combustibility of materials with inert filling agents is modification of polymer matrix by introduction of chemically active admixtures—antipyrines, and modification of the main polymer chain.

For example, introduction of halogen compounds reduces combustibility of polyolefins, polysterene and its copolymers. Many researches supposed that halogen atoms in gas flame act as inhibitors of chain oxidation of hydrocarbons. Still there are doubts[21] about this fact if it is treated on the basis of thorough kinetic analysis. It can be added that polymer combustion flame has thermal nature and the proportion of chain processes is not high. It was shown for the direct modelling of polymer combustion in diffusive gas flame[22] that such agents as HCl and CCl_4 exerts minimal effect on fuel combustion oxygen limit. Actually, their action can be described rather well by the plain inert dilution of mixture. In that case, chlorine additive will cause only some changes in heat balance due to heat expenditures for its heating up to the temperature of flame. Nitrogen injected with fuel has the analogous effect.

Important information about mechanism of effect of chloroparaffins contains in Ref. 23. Relationship between chloroparaffin oxygen index (OI) and molecular mass with the same content of chlorine (55% of mass) is shown in Figure 3. It appears, that if during heating chloroparaffin evaporates with destruction and

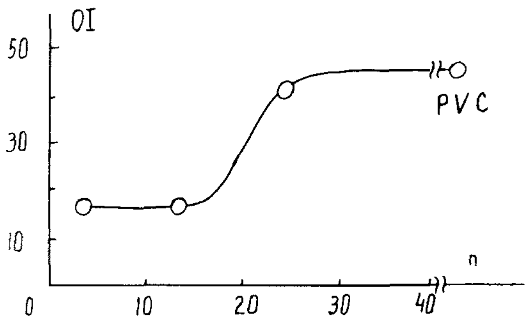


FIGURE 3 Effect of molecular mass of chloroparaffins on the value of OI.

then it undergoes all other changes in gaseous phase, then the effect of chlorine is insufficient. If chloroparaffin destructs in condensed phase, then OI is rather high. In that case the content of gas getting into flame considerably changes. For low molecular chloroparaffins the content of gas as to proportion of carbon and hydrogen coincides with chemical composition of parent material. When high molecular chloroparaffin is decomposed in condensed phase, a considerable amount of coke is produced that does not get into gas flame. The latter is explained by carbon and, consequently, ratio of combustible gas (hydrocarbon) and inert HCl. In that case the effect of thermal dilution of small amounts of combustible gas and large amounts of HCl is quite considerable. Quantity assessments prove that this reason for variations of combustibility of such compositions is correct. Thus changes of the direction of destruction becomes a major factor that influences upon combustible-non-combustible substances ratio in gaseous phase.

Compositions of antimony are often used as antipyrine. Many editions touch upon the problem of synergetic effect of halogen hydrocarbons and antimony trioxide. It is stated that when it is exposed to flame, antimony trioxide interacts with hydrogen halide (HCL or HBr) that is produced as a result of halogen compound decomposition; as a result of this interaction chlorine (bromine) oxide and trichlorine (tribromine) antimony are produced. A conclusion is made[24] that generation of hydrogen halide (and not Cl_2 or Br_2) after the destruction is a vital condition for combustion inhibition.

There are different suppositions as to action of the generated antimony compounds. It is supposed that antimony chloroxide promotes carbonization in condensed phase, while trichlorine antimony sublimates, gets into gas flame, where it is oxidized and is converted into fine dispersive antimony trioxide. There is a consideration that antimony compounds in gaseous phase catalyzes the destruction of radical, thus inhibiting gaseous phase combustion. We are of the opinion that most reliable theory is based on merely thermal analysis, i.e. increase of heat losses due to sublimation, heating to flame temperature, and increase of flame radiation due to the increase of its luminous emittance.

One of the most efficient inhibitors of combustion and smouldering of polymers is phosphorus and its compounds. Effect of phosphorus antipyrenes is usually explained in the following way.

During pyrolysis of polymers containing phosphorus compounds phosphoric acid and its anhydrides are produced to catalyze dehydration and dehydrogenation, to stimulate carbonization.

Phosphorus compounds pyrolysis products inhibit gaseous phase reactions due to active radicals deactivation in the flame. Inhibition of flame, probably, takes place as a result of hydrogen atoms destruction by the following formula:

$$H^{\cdot} + PO + M \rightarrow HPO + M$$

$$HPO + H^{\cdot} \rightarrow H_2 + PO^{\cdot}$$

Destruction of active centers leads to the decrease of reaction rate in the gaseous phase and, consequently, to the decrease of heat release and maximal temperature of flame. Authors[25] dwell upon the formation of protective carbonized film on the surface of the pyrolyzed polymer. This film may impede outgoing combustible products of destruction and, besides, it acts as the thermal screen reducing polymer heat input.

Author of work[26] supposes that polyphosphoric acids and unhydrides also reduce penetrability of foam coke forming on the surface of the burning polymer.

The question whether phosphoric compounds show stronger inhibiting qualities in condensed or in gaseous phase is still unsolved. Obviously, different polymers have different patterns of inhibition. Thus, it is shown that in case of PMMA and PE phosphorus is active mainly in the gaseous phase, while in case of epoxy compositions it remains in condensed phase, increasing the output of carbonized residue compared to pure polymer.

It is suggested in work[27] to use polymeric phosphorus antipyrine instead of low molecular antipyrenes for inhibition of polymers. These polymeric additives provide better compatibility, decrease polymeric antipyrene migration and are characterized by high resistance to external actions, that makes such low phosphorus additives quite efficient as antipyrenes. Thermal analysis data made it possible for the authors to say that as a rule the action of phosphorus is meant to form heat resistant structures in polymer condensed phase and thus to decrease the output of combustible gaseous destruction products.

The possibility of acquisition of thermal resistance by the compositions containing normal resins by way of reinforcing them with "flame-resistant" phosphorus fibres (i.e. fibres that are modified by phosphorus compounds) is shown in work.[26]

Heat resistant qualities of organic fibres may be improved by increasing the amount of flame-resistant fibres in the composition or content of antipyrene in fibres.

If phosphorus fibres are applied as the filling agent, the decrease of combustibility caused coke formation on the surface of the burning polymer.

In recent years oxides and hydroxides of different metals, salts of organic and inorganic acids and gelatin complexes were used efficiently as antipyrenes. A major advantage of such antipyrenes is the fact that they are used in concentrations that are much less than phosphorus and halogen compounds. As a rule, mechanism of action of metal compounds in gaseous phase is related to inhibition of radical reactions of oxidation in the flame due to increase of the rate of kinetic chain break by way of recombination of active radicals.

Intensification of processes of coke formation is stressed by the researches studying the effect of metal additives on the condensed phase reactions. As it was stated above, processes of coke formation that take place in condensed phase of polymer combustion exert much influence on combustibility parameters. A layer of coke on the surface impedes the process of heat and mass exchange on the surface of burning polymer and reduces the rate of ingress of combustible products of pyrolysis at the gaseous phase. Acetylacetonates Fe^{2+}, Mo^{6+}, Cr^{3+}, Zn^{2+} in halogenated polymers increase the output of coke residue. In case of polybromstyrene, increase of carbonization degree in the presence of pyrometallate of zinc occurs due to inhibition of polymer destruction and acceleration of the processes of lacing. Lewis-type acids were used as efficient catalyst of coke formation for polystyrene.[29] Author thinks that Lewis-type acids promote substitution reactions in aromatic ring, and oxidizer of $CuCl_2$, V_2O_5, PbO_2 type facilitates proton detachments. If polystyrene is destructed without formation of coke, then in the presence of $Fe_2O_3 + CuCl_2$ output of coke will increase by 14%. Efficiency of metal additives as coke formation catalysts depends upon the polymer structure. For example, zinc pyrometallitate during the pyrolysis of polybromstyrene obstructs splitting out of bromine due to complex formation, while in case of PVC it, on the contrary, catalyzes dehydrochlorination; still in both cases carbonization is accelerated.

Type of compound that introduces metal into polymer also play a major part in formation of coke. Thus acetylacetonates Fe^{3+}, Mo^{6+}, Zn^{2+} in halogenated polymers accelerate formation of the coke, while their phenates and oxides do not. At the pyrolysis of polybrom styrene the increase of coke residue is caused only by zinc pyromellitate while zinc oxide and zinc pyromellitate unhydride do not affect the formation of coke.

One of the efficient means of combustibility decrease is physical and chemical modification of material surface. In cause of thermal treatment of epoxyamine compositions[30] high values of OI of material were attained without introduction of antipyrene additives.

OI and some mechanical parameters of the studied epoxyamine compositions before and after thermal treatment are shown in Table VII.

One of the trends that was most thoroughly developed in recent years is the introduction of antipyrene additives in microcapsules into polymeric compositions.

Antipyrenes can be divided into two groups: 1) high boiling, with boiling temperature higher than the temperature of opening of microcapsules; 2) low boiling, with boiling temperature much lower than the temperature of opening of microcapsules. The first group is comprised, for example, of trichlororethylphosphate and tridibrompropylphosphate. The action of these antipyrenes and their efficiency in microcapsules are the same as in case when they are introduced into polymer as usual additives. Their main effect is the intensification of the process of coke formation, increase of the amount of coke, its porosity and lower

TABLE VII

No.	System	$\sigma =$ GPa	ε, %E	GPa	σGPa	ε, %E	GPa	OI
	Before heat treatment:							
1.	DGER + MFDA* (1:1)	0.12	5.4	2.8	0.13	10	2.3	29.5
2.	DGER + MFDA (1:1.33)	0.11	5.3	3.7	—	—	—	27.4
3.	DGER + 4,4-DADFS (1:1)	0.10	6.0	—	—	—	—	27.6
4.	DGER + PEPA (8:1)	—	—	—	—	—	—	24.6
5.	ED − 20 + MFDA (1:1)	—	—	—	—	—	—	27.3
6.	ED − 5 + PEPA (8:1)	—	—	—	—	—	—	23.0
	After heat treatment:							
1.	DGER + MFDA (1:1)	9.11	4.5	3.2	0.14	11	2.45	56.5
2.	DGER + MFDA (1:1.33)	0.11	3.1	3.8	—	—	—	53.8
3.	DGER + 4,-DADFS (1:1)	—	—	—	—	—	—	44.0
4.	DGER + PEPA (8:1)	—	—	—	—	—	—	40.5
5.	ED − 20 + MFDA) (1:1)	—	—	—	—	—	—	55.1
6.	ED − 5 + PEPA (8:1)	—	—	—	—	—	—	23.0

penetrability of coke by combustible liquid and gaseous products of polymer destruction.

Compounds of the second group are characterized by a brand new and quite efficient mechanism of action. These compounds in microcapsules bring down combustibility of polymeric compositions much more efficiently than in its usual form (see Figure 4). OI of the composition depends a great deal upon the dimensions of microcapsules. The value of the optimal dimensions depended upon the nature of antipyrene and varied within the limits of 40–160 μm.

It was found that the liquid within microcapsules by the moment of opening is

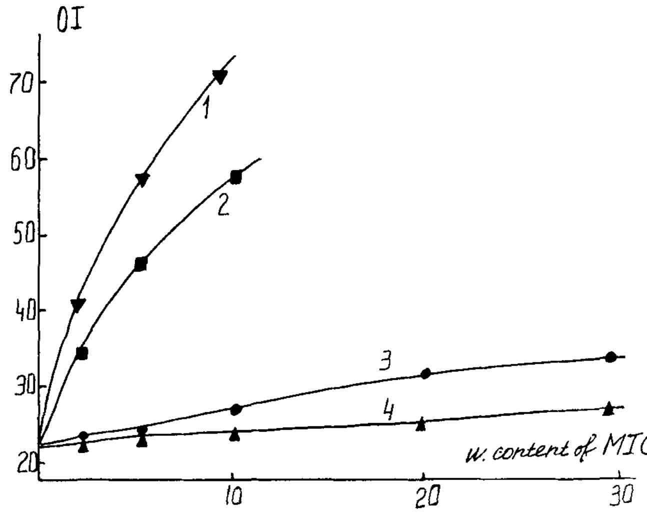
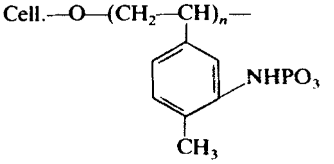
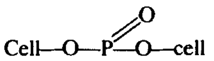
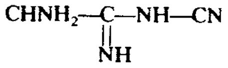
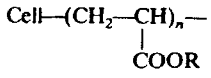
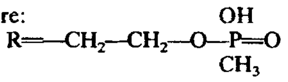


FIGURE 4 Effect of MIK* antipyrene content on OI of epoxy polymer (ED − 20 + PEPA), 4—CCl_4 (in the form of plasticizer); 3—MIK trisdibrompropylphosphate; 2—MIK tetrafluorinedibromethane; 1—MIL CCl_4.

overheated a great deal. Stable (metastable) overheated state of the liquid within microcapsules is determined by the lack of nucleation. When temperature reaches microcapsule membrane destruction value, defects can be seen on its surface; these defects are the nucleus of the gaseous phase. And if at this moment the liquid is overheated, the pressure rises sharply and the microcapsule explodes. The more overheated the liquid is, the bigger is the explosion. These microexplosions lead to the dispersing of polymer matrix: particles of the polymer detach from the main bulk and leave the flame zone. Thus, the organic polymer, that is pyrolyzed by flame under normal conditions forming combustible gaseous products, as a result of dispersing is carried over in the form of solid particles surrounded by a gaseous cloud of antipyrene. Efficiency of dispersing depends also upon the state of polymer matrix in the moment of microcapsule opening.

Besides polymer matrix modification, another trend has been developed in recent years. It is connected with introduction of antipyrene into the composition with the help of chemically active filling agent.

TABLE VIII

Parameters of the material	Type of bond antipyrene fibres	Amount of antipyrene in fibres	Amount of antipyrene in composition, %	
			calculated	found
1	2	4	5	6
viscose fibre + 15%$(NH_4)_2HPO_4$	no	P—7.0 N—6.2	P—3.5 N—3.1	P—3.4
OZV*—PMVP HPO_3	salt	P—7.0 N—1.8	P—2.2 N—1.1	P—2.1
				
Resin + OZV—OP	chemical	P—3.2	P—2.4	P—2.6
 $\text{Cell—O—}\overset{\displaystyle O}{\overset{\|}{P}}\text{—O—cell}$		N—4.8	N—2.6	
 $CHNH_2\text{—}\underset{\displaystyle NH}{\underset{\|\|}{C}}\text{—NH—CN}$				
Resin + OZV—FEM	chemical	P—3.2	P—2.2	P—2.3
 $\text{Cell—(}CH_2\text{—}\underset{\displaystyle COOR}{\underset{\|}{C}H}\text{)}_n\text{—}$				
where:  $R\text{=—}CH_2\text{—}CH_2\text{—O—}\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{P}}\text{=O}$				

Possibility of making compositions with usual resins flame-resistant with the help of armouring them "fire-resistant" phosphorus fibres is studied in work.[22]

The following viscose fibres were studied:

To produce incombustible composite materials with the help of epoxy resin minimal amount of OZV—OP* fibres that make the composition incombustible in the air equals 60% of mass. When the epoxy resin is armoured with flame-resistant OZV—OP viscose fibres with different content of antipyrene in fibres, fire-resistance of both compositions increases as the amount of fibres in the composition increases. Determination of the content of phosphorus in epoxy compositions with fire-resistant fibres containing different amounts of antipyrene demonstrated that the value of OI directly depends upon the amount of phosphorus in the composition. Consequently, fire-resistance of organic fibre materials may be increased with the increase of amount of the fire-resistant fibres in the composition or increase of antipyrene content in fibres. Assessment of the value of OI of materials armoured with unmodified viscose fibres shows that as the content of viscose fibres in composition increases, combustibility of organic plastic materials increases as well. Increase of the content of glass fibres in composition up to 60% of mass of the composition does not lead to any considerable increase of OI (Figure 5).

If phosphorus fibres are applied as the filling agent, then, as in cases shown above, combustibility decrease is caused by formation of coke on the surface of the burning polymer.

The following conclusions can be made on the basis of the above shown data:

1) Introduction of inert filling agents into composite materials in moderate concentrations does not exert much influence on their combustibility. Their effects are obvious at higher degrees of filling, still in that case parameters of the compositions deteriorate considerably.

2) One of the methods of combustibility reduction is application of filling

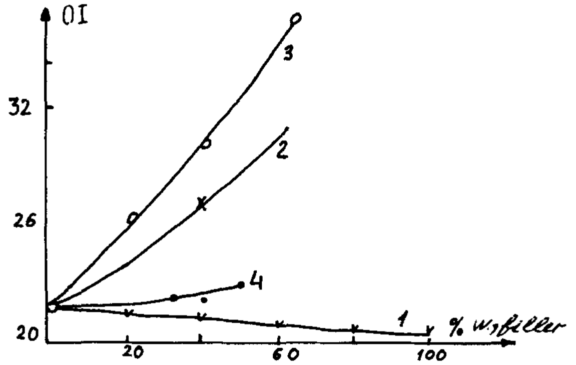


FIGURE 5 Relationship between epoxy materials OI and content of filling agents in the composition: 1—unmodified viscose fibres; 2—"fire-resistant" viscose fibres containing 2.85% of phosphorus; 3—the same, 7.5% of phosphorus; 4—glass cloth.

agents that decompose at 300–400°C into volatile "inert" products, such as CO_2, H_2O, H_3, etc.

3) Halogenized compounds together with other compounds causing the effect of synerism are applied to reduce combustibility of thermoplastic polymer matrix. In the majority of cases their action reveals in gaseous phase.

4) Modification of thermoreactive polymers and matrix, based on these polymers, is to be carried out for the sake of intensification of coke formation processes in the condensed phase.

5) One of the methods of modification of surface is the introduction of low boiling antipyrenes in microcapsules that are quite efficient in decreasing combustibility.

6) To preserve the features of polymeric matrix and decrease combustibility of the composite it is possible to use modified by antiperenes chemical fibres.

The shown trends of combustibility decrease of the composite materials do not exhaust the entire problem. New researches of possibilities of combustibility reduction are quite necessary; amoung these researches the most important part is reserved for the studies of reactions that take place on the surface of the burning polymer.

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