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Polymeric Chemical Fibre-reinforced Composite Materials with Reduced Combustibility

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The present state of research in the field of the thermal degradation and combustion of fibre-reinforced polymeric composite materials is examined. Special attention has been devoted to questions of the inter-relation between the chemical compositions of the reinforcing fibres and the polymeric binders as well as their thermophysical and thermochemical properties, on the one hand, and the processes occurring on pyrolysis and combustion of the materials, on the other.
The bibliography includes 99 references.

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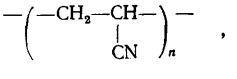
I. INTRODUCTION

Polymeric composition materials (PCM) are at the present time to a large extent responsible for the acceleration of the scientific and technical progress in many branches of the National Economy. The PCM with reduced combustibility, used, for example, in the construction of blocks of flats and public buildings, in transport, etc., are of special interest.

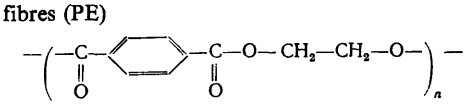
In world practice, polymeric thermoplastic or thermoreactive binders for the synthesis of PCM are reinforced with glass, asbestos, boron, and carbon fibres, aromatic polyamide fibres, and filamental metal oxide, carbide and nitride crystals.[1]

The possibility of reinforcing synthetic resins with chemical fibres manufactured on an industrial scale has attracted the attention of investigators in recent years.[2-22] This is associated with the fact that chemical fibres possess a whole series of specific features which make it possible to extend greatly the range of properties of materials for constructional building purposes: the mass of the articles and components can be greatly reduced, their resistance to vibrations can be increased, they can be stabilised in relation to corrosive media, their antifriction properties can be improved, etc.

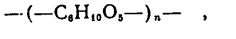
The problem of improving PCM possessing a set of specific physicomechanical properties and reduced combustibility and which are at the same time light, strong, and relatively cheap, can be solved by reinforcing resins with modified chemical fibres produced by the chemical industry on a wide scale, such as polyacrylonitrile fibres (PAN)



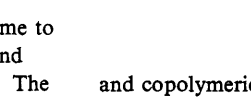
polyester fibres (PE)



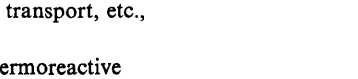
viscose fibres (VF)



poly(vinyl chloride) fibres (PVC)



and copolymeric fibres based on copolymers of acrylontrile and vinyl chloride (AN/VC)



Non-conditioned fibres,[22] which are available both in the chemical fibres industry and in the processing branches of industry (textile, light, etc.),[23] can also be used for this purpose.

II. METHODS OF REDUCING THE COMBUSTIBILITY OF POLYMERIC COMPOSITE MATERIALS

The majority of fibre-filled PCM are combustible materials, which holds back the growth of their manufacture and narrows the region of their applicability and effectiveness. The reduction of the combustibility of PCM is achieved mainly in two ways. The combustibility can be reduced by employing resins containing phosphorus, halogen, nitrogen, etc., compounds which retard or fully suppress combustion and are usually referred to as antipyrenes. Antipyrenes are introduced into the binder at the stage involving the synthesis of oligomers or directly in the formation of the material.[22-34] The second way involves the application of reinforcing systems resistant to combustion: inorganic fibrous fillers (glass, boron, and asbestos fillers); carbon fibre fillers; incombustible thermally stable fibres comprising aromatic polyamides, polyimides, and polyimidoamides; chemical fibres fire-proofed by various antipyrenes.

However, the application of incombustible reinforcing systems without antipyrenes does not solve the problem, because almost the entire polymer matrix burns up in the combustion of the material.[35,36] For example, epoxide PCM containing 60 wt.% of glass fibre

lose up to 40% of their weight when subjected to a test by the "fire tube" method in accordance with GOST 17088-71 [a USSR government standard (Ed.of Translation)].[35]

The reinforcement of combustible polymeric binders with chemical fibres containing an antipyrene makes it possible to improve the resistance to combustion of not only the fibre by itself but also of the polymer matrix.[35–38]

Questions concerning the theory and technology of the preparation of the antipyrene-modified, so called fire-proofed fibres have been described in numerous publications and inventions.[39–83] It is possible to differentiate the following methods whereby resistance to combustion can be imparted to chemical fibres: surface treatment of the fibres with antipyrenes, the introduction of antipyrenes into the polymer before the formation of the fibres, and chemical modification. Various phosphorus-, chlorine-, bromine-, and nitrogen-containing compounds or their synergistic mixtures are used for this purpose.

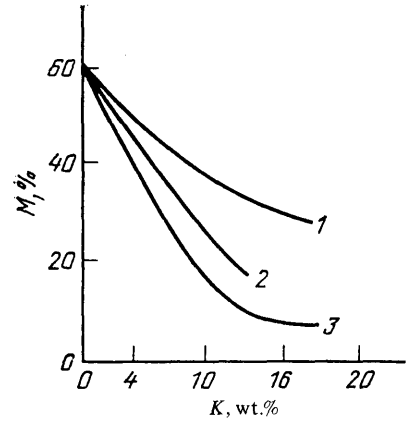


Figure 1. Dependence of the weight loss by the PCM (M) on the amount of inhibitors (K):[37] 1) PAN fibre + SF-342A composition modified with DBPP, Br + P being present in the binder; 2) AN/VC fibre + SF-342A, Cl forming part of the composition of the fibre; 3) PAN fibre modified with DBPP + SF-342A, Br + P being present on the fibre.

The employment of synthetic resins for reducing the combustibility of PCM reinforced with combustible chemical fibres (PAN, VF, PE) is relatively ineffective, since it requires the introduction into the material of large amounts of an antipyrene, which increases its cost and at the same time impairs its physicomechanical properties. In such compositions, it is desirable to introduce the antipyrene not into the polymeric binders but together with the reinforcing fibre.[35–38,84–91] For example, PCM based on anilino-phenol-formaldehyde resin SF-342A and PAN fibres fire-proofed by impregnation with dibromopropyl phosphate (DBPP) is characterised, compared with other materials containing the same amount of DBPP in the binder, by a weight loss smaller by a factor of two (Fig.1, curves *1* and *2*), a lower rate of propagation of the flame, an ignition point higher by 20 K, and an increase in the oxygen index (OI), characterised by the minimum oxygen content in the oxygen–nitrogen mixture ensuring the candle-like combustion of materials and expressed in volume percentages (or volume fractions), from 28 to 34%.

Analogous results have been obtained for phenolic compositions containing antipyrenes with different efficiencies. The Br + P mixture of combustion inhibitors, which is more effective than Cl, reduces the weight loss to a greater extent following the ignition of materials in air when these antipyrenes are introduced into the composition together with the reinforcing fibre [Br + P was introduced with the PAN fibre modified by DBPP, while Cl was introduced together with the reinforcing system comprising a mechanical mixture of PAN and the AN/VC copolymer fibres (Fig.1, curves *2* and *3*)].

However, the Cl entering into the composition of the reinforcing fibre reduces the combustibility of PCM to a greater extent than Br + P introduced into the phenolic resin as part of the composition of DBPP (Fig.1, curves *1* and *2*).

The greater inhibition of the combustion of PCM after the introduction of the antipyrene with the fibre can be explained by the fact that the antipyrene permeates from the fibre to the layer of polymer matrix, protecting thereby both the fibre itself and the polymeric binder against combustion. This has been confirmed experimentally on model PCM specimens prepared by casting in ED-20 epoxide resin lavsan fire-proofed with tricresyl phosphate (TCP).[37] The study of the specimens by scanning electron microscopy combined with X-ray spectroscopic analysis revealed the presence of phosphorus in the boundary layer of the polymer matrix adjoining the fibre over distances exceeding the maximum thickness (5 μm) of the layer of binder in PCM produced by the direct pressing method. The number of pulses recorded over a period of 30 s and characterising the phosphorus content in the specimen was 34 in the reinforcing fibre itself and on moving away from the surface of the fibre into the layer of polymer matrix to distances of 1, 7, 10, 17, and 40 μm the numbers of pulses were respectively 32, 28, 23, 16, and 0.

The antipyrene introduced with the binder permeates into the structure of the reinforcing fibre less effectively and inhibits mainly the combustion of the polymer matrix.[86] This is indicated by the increased weight loss in the combustion of PCM observed when the content of the PAN fibre is increased from 30 to 60% with an unchanged content of the antipyrene introduced into the composition together with the binder (Table 1).

III. INTER-RELATION BETWEEN THE CHEMICAL COMPOSITION OF THE REINFORCING FIBRES AND POLYMERIC BINDERS, AND THE THERMAL STABILITY AND COMBUSTIBILITY OF THE POLYMERIC COMPOSITE MATERIALS

The dependence of the thermal stability and combustibility of unfilled polymers on their chemical structure has been noted in a number of studies.[92–94] It has been shown that (a) there is a correlation between the yields of the coke residue (CR) formed on pyrolysis and the OI of the polymers not containing inhibitors of flame reactions:[92]

$$OI \times 100 = 17.5 \pm 0.4\,CR;$$

(b) the tendency towards the formation of coke is an additive characteristic of the polymer and can be estimated from the

contributions of the functional groups constituting the polymer units:[92]

$$CR = \frac{\sum(TFC)_i \times 12}{M} \times 100\%,$$

where TFC is the tendency of the group i to form coke expressed in carbon equivalents per polymer unit and M is the molecular weight of the unit; (c) there is a relation between the OI and the heat of combustion per gramme of the test substance:[92]

$$OI = 1.9/\Delta h_{comb},$$

but the relation does not hold for a series of materials, including cellulose, polyacrylonitrile, etc.;[92] (d) there is a relation between the OI and the elemental composition of the polymer.

Table 1. Weight losses in the combustion of PCM containing bromine and phosphorus introduced with the binder.[86]

Br + P content in binder wt.%	Weight loss (%) in different compositions		
	60% PAN fibre + 40% SF-342A resin	50% PAN fibre + 50% SF-342A resin	30% PAN fibre + 70% SF-342A resin
0	60	59	52
2	58	57	46
5	58	50	36
10	49	38	27
15	45	31	—

The thermophysical and thermochemical properties of the fibres have a decisive influence on the characteristics of the thermal degradation and combustion of composite materials reinforced with chemical fibres, such materials constituting multicomponent systems. For example, the temperature of the degradation of the PCM reinforced with PVC and PAN fibres, a mechanical mixture of PAN (60 wt.%) and PVC (40 wt.%) fibres, and AN/VC copolymer fibre is higher by 20–50 K than the temperature of the degradation of the unfilled epoxide resin. The degradation temperatures are directly related to the thermal stabilities of the reinforcing fibres, which can be arranged in the following sequence in terms of this parameter: PAN > PAN + PVC mixture > AN/VC copolymer > PVC.[38]

One of the main characteristics of combustion is the rate of the latter. It can be expressed as the mass velocity characterising the burning up of the material. The rates of pyrolysis of materials under different conditions, including the temperature regimes which obtain on combustion, have been determined from the mass velocity of the degradation reduced with respect to the current mass of the specimen for which the given mass velocity has been found, i.e. with respect to the quantity $\dot{m}/m$, where $\dot{m} = dm/d\tau$, m is the current mass of the specimen in grammes, and τ is the duration of the test in seconds.[38]

The introduction of fibres into epoxide compositions lowers by a factor of 1.5–2 the rate of their pyrolysis and increases by a factor of 2–3 the yields of coke. On the other hand, the presence of fibres in phenolic PCM increases the rate of pyrolysis by a factor of 1.5–3 and lowers the yield of coke by 30–50%. However, the rate of pyrolysis of the material is determined to a large extent by the chemical composition of the fibres, which follows from the fact that the rate of pyrolysis of the unfilled epoxide resin is higher by a factor of 4 than that of the phenolic resin, while the rates of pyrolysis of PCM based on these binders differ by only 20–50%. The same character of the variation of the rate of pyrolysis and of the yield of coke can then be noted for both epoxide and phenolic PCM reinforced with identical chemical fibres (Table 2).[38,87]

Table 2. The mass velocities of the pyrolysis of PCM and the yield of coke at different temperatures:[38]

Reinforcing fibre	Temperature, K				
	673	773	873	973	1073
	Epoxide PCM				
PAN	0.64; 60.0	0.98; 31.0	1.54; 30.0	1.96; 26.5	2.44; 25.0
PVC	0.5; 56.0	0.94; 21.5	1.26; 16.0	1.8; 15.0	2.22; 14.0
AN/VC copolymer	0.65; 47.0	1.15; 27.0	1.75; 23.5	2.4; 21.5	3.0; 20.0
PAN + PVC mixture	0.4; 56.0	0.9; 35.0	1.4; 30.0	1.9; 28.0	2.35; 25.0
ED-20 without fibre	0.4; 53.0	2.5; 25.0	2.8; 9.0	3.35; 9.0	3.9; 9.0
	Phenolic PCM				
PAN	0.45; 79.0	0.78; 64.5	1.1; 61.5	1.4; 58.0	1.6; 55.0
PVC	0.35; 68.5	0.65; 64.5	0.98; 60.0	1.3; 55.0	1.5; 50.0
AN/VC copolymer	0.35; 73.0	0.8; 51.5	1.3; 49.5	1.8; 48.0	2.3; 46.0
PAN + PVC mixture	0.4; 71.0	0.7; 58.0	1.0; 54.0	1.3; 52.0	1.6; 50.0
SF-342A without fibre	0.08; 85.0	0.2; 80.0	0.4; 76.0	0.8; 60.0	1.0; 87.0

*The first figure represents the mass velocity of pyrolysis (s^{-1}) and the second the yield of coke (wt.%).

The chemical composition of the fibres in PCM influences also the temperature in the flame zone, which depends to a large extent on the composition of the pyrolysis gases from the reinforcing fibres.[38] For example, the flame temperature in the combustion of PCM based on PAN fibres is higher by 30 K than in the combustion of the unfilled epoxide resin. The observed dependence of the flame temperature on the amount of chlorine in the reinforcing fibres is complex (Fig.2): in the combustion of materials reinforced with the AN/VC copolymer fibre containing 13% of chlorine, it is higher than in the combustion of PCM based on the mechanical mixture of PAN + PVC fibres (60 and 40 wt.% respectively), containing 9% of chlorine. This is associated with the higher content of the combustible HCN in the pyrolysis gases of the AN/VC fibre compared with the gases evolved on pyrolysis of the mechanical mixture of PAN + PVC fibres (Fig.3).[89] These data show that the combustibility of the material depends not only on the composition but also on the structure of the reinforcing systems.

The ignition delay time is determined by the heat changes accompanying the degradation of the reinforcing fibres.[88] The unfilled epoxide resin has an ignition delay time of 1.3 s. The introduction of PAN fibres into the composition lowers the ignition delay time to 1.0 s, since the degradation of the fibre itself is characterised by an appreciable heat change (Fig.4, curve *3*). The ignition delay times of the PCM reinforced with chlorine-containing fibres, a mixture of

PAN and PVC fibres, which are degraded with smaller heat changes than the PAN fibre (Fig.4, curves *1* and *2*), are longer and amount to 1.8 and 2.2 s respectively. The maximum ignition delay time (2.6 s) is characteristic of PCM with the AN/VC copolymer fibres, whose degradation in the initial stage takes place endothermically (Fig.4, curve *4*).[88]

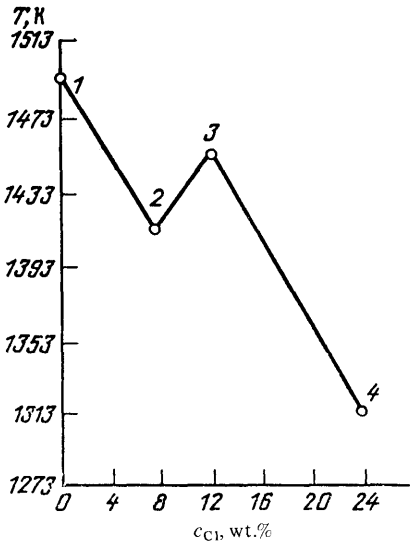
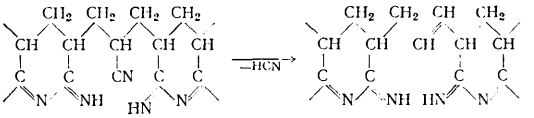


Figure 2. Dependence of the flame temperature (T_{fl}) of epoxide PCM on the chlorine concentration c_{Cl} in the reinforcing fibres:[38] 1) non-reinforced ED-20 epoxide resin; 2) PAN + PVC; 3) AN/VC; 4) PVC.

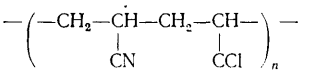
IV. REDUCTION OF THE HCN TOXICITY OF THE PYROLYSIS GASES FROM POLYMERIC COMPOSITE MATERIALS REINFORCED WITH POLYACRYLONITRILE-CONTAINING FIBRES

The polyacrylonitrile-containing fibres used to reinforce resins evolve toxic gases, including HCN, on pyrolysis.[95-97]

A decrease in the HCN toxicity of PCN can be attained in several ways. Thus the amount of HCN evolved from the PAN fibres can be reduced by using graft copolymers of PAN with cellulose. In the pyrolysis of such fibres, the yield of HCN is appreciably reduced owing to a change in the mechanism of the thermal decomposition of PAN: the water evolved on pyrolysis of cellulose hydrolyses the nitrile groups, as a result of which NH_3 is evolved instead of HCN.[98] The AN/VC copolymer fibres used for reinforcement afford an even higher yield of HCN than the PAN homopolymer fibres (Fig.3, curves *1* and *2*).[89] This phenomenon has been explained by the fact that heating of PAN fibres entails complex chemical reactions and structural transformations: cyclisation, aromatisation, and depolymerisation,[97] while the evolution of HCN in the temperature range 473–823 K takes place mainly from the uncyclised sections of the chain with formation of double bonds via the reaction[99]



The introduction of chlorovinyl groups into the polyacrylonitrile molecule,



prevents its cyclisation, since steric hindrance due to the appearance of unconjugated nitrile groups arises. This increases the amount of uncyclised sections and hence the yield of HCN.[89]

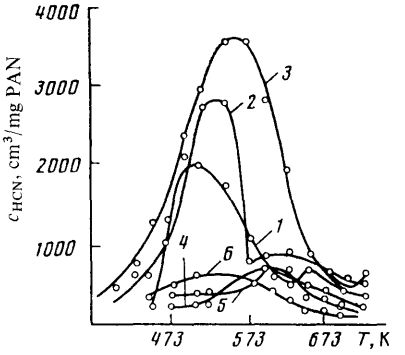


Figure 3. Dependence of the yield of HCN c_{HCN} on the pyrolysis temperatures of various fibres and composite materials based on them:[89] 1) PAN fibre; 2) AN/VC fibre; 3) PCM based on the AN/VC fibres; 4) mechanical mixture of PAN + PVC fibres; 5) PCM based on the PAN + PVC mixture of fibres; 6) PAN fibre modified with 2,3-dibromopropyl phosphate.

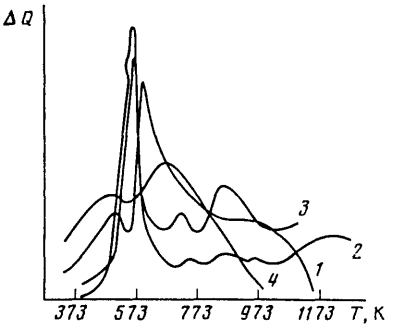


Figure 4. Differential thermal analysis curves for different fibres (Q are the heat changes):[89] 1) PVC fibre; 2) PAN + PVC mechanical mixture; 3) PAN; 4) AN/VC copolymer fibre.

The second method of reducing the yield of HCN involves the use of a mechanical mixture of the PAN + PVC fibres.[92] Thus the yield of HCN from a mixture of 60 wt.% PAN and 40 wt.% PVC fibres is lower by a factor of ~6 compared with the AN/VC copolymer fibres with the same content of polyacrylonitrile (Fig.3, curves *2*

and *4*). In this reinforcing system, PVC accelerates catalytically the cyclisation of PAN, which reduces the evolution of HCN.[89] The yield of HCN from phenolic PCM reinforced with a mixture of PAN + PVC fibres is close to that observed in the pyrolysis of the reinforcing mixture of fibres (Fig.3, curves *4* and *5*). On the other hand, the yield of HCN from PCM reinforced with the AN/VC copolymer fibres is higher than for the reinforcing fibres (Fig.3, curves *2* and *3*). This has been explained by the different chemical mechanisms of the degradation of the above reinforcing systems, leading to a difference between the degradation reactions of the PCM based on them.

According to differential thermographic (DTA) data (Fig.4), an exothermic peak characteristic of the PAN cyclisation process is observed in the thermal degradation of both PAN fibres and the mixture of PAN + PVC fibres in the same temperature range.[89] For an AN/VC copolymer fibres, an endothermic peak characteristic of the dehydrochlorination processes is observed in the same temperature range, while the exothermic peak corresponding to cyclisation is displaced towards higher temperatures. Since the degradation of the phenolic resin occurs at higher temperatures compared with the AN/VC fibres, the HCl evolved in the dehydrochlorination process accumulates in the bulk of the material, leads to the depolymerisation of PAN, and increases the yield of HCN compared with that observed from the AN/VC fibres alone.[89]

An effective method of reducing the amount of HCN involved consists also in modifying the PAN fibres with dibromopropyl phosphate $(CH_2-Br-CHBr-CH_2O)_3PO$ (Fig.3, curve *6*).

Table 3. The yield of water and HCN in the pyrolysis of fibres.[86–88]

Fibre	c_{H_2O}, cm^3/mg PAN at different temperatures, K				c_{HCN}, cm^3/mg PAN at different temperatures, K			
	423	523	623	723	523	623	723	823
PAN	155	210	150	80	1050	2600	480	180
PAN + 11 wt.% (Br + P)	75	520	710	320	310	750	220	55

V. THE MECHANISM OF THE ACTION OF ANTIPYRENES IN POLYMERIC COMPOSITE MATERIALS

It has been established[93] that various compounds containing isotypical combustion inhibitors have different types of influence on the combustibility of polymers. Bromine-, chlorine-, and phosphorus-containing antipyrenes or their synergistic mixtures exert an inhibiting effect on a series of specific PCM.[37,38,84–89]

The bromine + phosphorus system introduced into the composition of the PAN fibres fire-proofed with dibromopropyl phosphate acts on phenolic PCM [86–88] and alters the course of the reactions in both condensed and gas phases. The composition of the pyrolysis gases changes under these conditions—the water content c_{H_2O} increases and the HCN content c_{HCN} diminishes (Table 3), the amount of heat evolved is reduced, which slows down the reaction in the gas phase, the flame temperature T_{fl} diminishes, the ignition temperature T_i increases, and the yield of coke falls slightly (Table 4).

Table 4. Characteristics of the thermal degradation and combustion of PCM (1 : 1 fibre : resin ratio).[86–88]

Composition	Coke residue (%) at different temperatures, K					T_i, K	T_{fl}, K	OI, %
	673	773	873	973	1073			
PAN + SF-342A	79.0	64.5	61.5	58.0	55.0	1383	1537	27
[PAN + 11 wt.% (Br + P)] + SF-342A	71.0	60.1	56.5	55.0	54.0	1437	1483	34

The introduction of antimony trioxide (Sb_2O_3) into PVC fibre + epoxide resin + polyethylenepolyamine compositions slows down the smoke formation process, increases the yield of coke, lowers the weight loss on combustion, and increases the OI and the ignition temperature (Table 5).[90,91]

Table 5. The influence of Sb_2O_3 on the characteristics of the combustion of epoxide PCM reinforced with PVC fibre.[93,94]

Combustion inhibitor and its content, wt.%	OI, %	Weight loss, %	T_i, K	Yield of coke (%) at different temperatures, K		
				773	873	973
Cl (23.9)	29.0	67.0	1392	21.5	16.0	15.0
Cl (23.9) + $+Sb_2O_3$ (10)	38.0	10.5	1440	29.0	25.0	23.0

In compositions with a phenolic resin reinforced with the AN/VC copolymer fibres, the action of Sb_2O_3 is manifested by an increase (almost by a factor of 2) in the amount of coke residue, a decrease in smoke formation, and a decrease in the weight loss on combustion.[86,88]

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