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Polymeric composite materials reinforced with polyacrylonitrile fibres

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ABSTRACT. The results of studies of the influence of polyacrylonitrile fibres on structure formation in and the properties of polymeric composite materials are surveyed. The new modification methods which have been developed, studies on the properties, and possible applications of such polymeric composite materials are described.

The bibliography includes 74 references.

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I. Introduction

The needs of the National Economy require the creation of new building and constructional materials which would make it possible to reduce sharply the use of metals in finished articles and would increase the strength and anticorrosion properties of constructions and would reduce their mass.[1]

A tendency towards the replacement of components made of traditional materials (wood, metals, ceramics, and glass) in the construction of buildings by polymeric materials has arisen. The requirement for metal is reduced sharply in the first place in those cases where the operating conditions do not involve the application of high pressures and temperatures and where the finished articles are subject to corrosion. Polymeric composite materials (PCM), which are fairly strong and long-lived and are lighter and more resistant to corrosion and erosion than metals, are promising in this instance.[2]

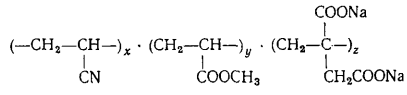
PMC reinforced with chemical fibres (carbon, aramide, etc. fibres) constitute a new class of materials distinguished by a set of valuable properties. PCM based on cheap polyacrylonitrile (PAN), polyester, viscose, polyamide, and other fibres, produced industrially on a large scale, are extremely promising for different branches of the National Economy.[3]

Although the industrial forms of chemical fibres have not been until recently a valuable reinforcing material because of their low strength, relatively low modulus of elasticity, and low heat resistance and thermal stability, nevertheless the possibility of varying their properties widely by modification as well as the set of the specific properties of PCM based on such fibres suggest that in the next few years their application in the reinforcement of plastics will become one of the effective ways of regulating the properties of PCM in accordance with the requirements of different branches of industry.

This review concentrates mainly on PCM reinforced with industrial PAN fibres in view of the increasing scale of their manufacture[4] and their specific properties: low density (1170–1190 kg m^{-3}), low water absorption (0.5–1%), a relatively high thermal stability (200–250 °C), the presence of reactive groups, and a fairly high strength.

Various methods for the modification of both the polymer matrix and the reinforcing fibre system are being developed in order to solve the problem of imparting to PCM the required properties in conformity with their functional purposes.

In the present review, an attempt is made to survey the results of studies and developments concerning different methods for the modification of PCM based on industrial PAN fibres obtained from the ternary copolymer



(0.92% of PAN, 6.3% of methyl acrylate, and 1.7% of sodium itaconate), formed under different conditions, and distinguished by specific physicomechanical properties.

II. Changes in the properties of polyacrylonitrile fibres on formation of polymeric composite materials

The technology of the manufacture of PCM based on chemical fibres differs in many respects from the technology of PCM with mineral fillers, such differences being associated with the specific features of the structure of the chemical fibres and the character of the physicochemical processes occurring at the polymeric fibre–polymeric binder interface.

The formation of PCM on the basis of polymeric fibres is accompanied to a greater or lesser extent—depending on the nature of the selected fibres and binders and the conditions in the pressing of the material (temperature, duration, and pressure)—by the mutual diffusion of the components: of the binder into the fibre and of low-molecular-weight components from the fibre into the polymeric binder.[5] Chemical fibres are structurally inhomogeneous and consist of an oriented high-density shell with an increased degree of crystallinity and a relatively loose core containing crystalline and amorphous sections. Longitudinal folds, 15–200 Å pores, 100–500 Å cracks,[6] and other defects may be present on the surfaces of the fibres.

Since the rate of diffusion into the amorphous regions of the polymers is appreciably higher than the rate of diffusion into the crystalline regions, the components of the binder penetrate the surface layers of the fibres, filling non-uniformly principally the microdefects.[3] This alters the structure of the surface layers of the fibres and hence their properties.[5,7–14]

Depending on the type of fibres and binders chosen, these changes can be both positive and negative.[3,15–18] The change in the supermolecular structure of highly oriented polyamide fibres under the influence of epoxide binders and their components has been investigated[18] by X-ray diffraction.[19] The different character of the interactions of the polyamide fibres based on poly-*p*-phenyleneterephthalamide (PPTA) and on poly-*p*-amidobenzimidazole (PABI) with the components of the EDT-10 and EKhD-MK binders has been established. The chlorine-containing EKhD-MK binder and its principal component, the EKhD resin, impair the structure of the bulk phase of the binders of both types when they interact with them.

The impregnation of nitron, lavsan, and vinol by the latexes of the SKD-1 and SKN-40-1 GP elastomers loosens the fibrillar structures as a result of the diffusion of the elastomer into the surface layer of the fibres.[16]

When technical viscose thread is treated with epoxide and phenolic binders, the strength of the thread is reduced[20] as a result of the penetration of the oligomer molecules into the fibre, the extent of the molecular interaction is diminished, and a disorder in the structure of the fibre is observed.

For poly(vinyl alcohol) (PVA), polyester, and viscose fibres[21] and also for heteroarylene[22] and highly-modular CBM fibres,[23] a plasticisation effect has been observed on treatment with various thermoreactive binders and their components.

After a correct choice of the PCM components and optimum contact conditions between them, it is possible to achieve the improvement of the physicomechanical properties of the fibres. First, under the influence of an epoxide resin accompanied by an increase in temperature up to 180–200 °C, the strength and rigidity of lavsan increase somewhat (by 15–20%). The nature of the hardener in this case has little influence on the rigidity of the fibres, but, up to 100 °C, it does promote an increase in their strength. At temperatures above 100 °C, there is a sharp decrease in the strength of lavsan under the influence of the hardener.

X-Ray diffraction analysis of PAN fibres treated with ED-20 epoxide oligomers, polyethylenepolyamine (PEPA), and a binder based on them showed that impregnation of the PAN fibres leads to the diffusion of the epoxide oligomer and PEPA into the bulk of the fibre, as a result of which the structure[24] and the strength[25] of the fibre change. The change in structure is indicated by the decrease in the intensity of the X-ray reflections: the intensities of the X-ray reflections for unimpregnated PAN fibres and TAN fibre treated with EG-20, PEPA, and binders based on them are respectively, 1, 0.34, 0.41, and 0.08 relative units.

The strength of fibres depends on the nature of the components, the temperature, and the duration of their contact. Thus treatment of PAN fibre with an epoxide oligomer and PEPA for 0.25 h at 80 °C (which corresponds to the PCM pressing conditions) hardly affects the strength and elongation of the fibres, while further increase in temperature and in the duration of treatment of the fibre by the binder components induces its elongation and greatly reduces its strength (Table 1). Consequently, in the making of PCM from chemical fibres, it is necessary to take into account the influence of the binder on the structure and properties of the fibres and to select the appropriate resin–fibre pairs and formation parameters, being guided by the principles formulated by Mashinskaya[3] and Artemenko,[15] which make it possible to bring out most fully the strength properties of reinforced fibres.

Table 1. The change in the strength and elongation of PAN fibres after their treatment with the epoxide oligomer and polyethylene polyamine.

Binder components	Change in properties on heat treatment, %			
	80 °C; 0.25 h		100 °C; 3 h	
	strength	elongation	strength	elongation
ED-20	+8.5	0	−46	+58
PEPA	+1.6	−7.9	−22	+53

III. The structure and physicomechanical properties of polymeric composite materials

1. The influence of polyacrylonitrile fibres on the hardening of polymeric binders

A characteristic feature of PCM reinforced with polymeric fibres is the presence of a diffuse transition layer on the polymeric binder—polymeric fibre interface, arising as a result of the different rates of diffusion of the components of the binder into the amorphous and crystalline sections of the fibres.[5,7–10]

The structure and properties of this layer differ from those of the PCM component. Their different structural organisations are characterised by different molecular mobilities, which is reflected in the rates of relaxation processes.

For example, it has been shown[26] that new levels of structural organisation arise in the bulk phase of an organoplastic based on very strong organic fibres and the epoxyphenol binder. Their molecular mobility is manifested by α'_1- and α'_2–relaxation processes in the region of 453 and 503 K respectively (Fig. 1). The manifestation of a multiplicity of relaxation processes in organoplastics is caused, according to the authors, by the presence of four macroscopic structural organisation levels associated with the binder in the bulk phase of the plastic and in the region remote from the surface of the fibre (α_1), with the binder at the surface of the fibre (α'_1), with the surface layer of the reinforcing organic fibre (α'_2) modified by the diffusing component of the binder, and with the structure of the fibre core (α_2).

Under the influence of the fibres, the conformations of the binder molecules in the transition layer differ from the conformations in the bulk of the polymer, which leads to a non-monotonic variation of the packing density of the macromolecules and going away from the interface.[10] The increase in the order of the arrangement of the epoxide oligomer under the influence of the fibre during the hardening process is confirmed by the increase in the density of the PCM from 1162 to 1319 kg m^{-2} [27] and by the presence on the surface of the fibrous filler of a macrolattice repeating its layered organisation.[25,28] Thus when the fibre is impregnated with the epoxide binder, a diffuse transition layer arises at the fibre–resin interface. The orientation of the globular resin formations at the

surface of the PAN fibre and a decrease in the size of the globules can then be clearly seen. Furthermore, on the fibre (in a unidirectional PCM) the macromolecules of the epoxide binder are oriented on the fibre surface, while in the bulk of the polymer they have a globular structure, which indicates the influence of the surface of the fibre on structure formation in the binder.

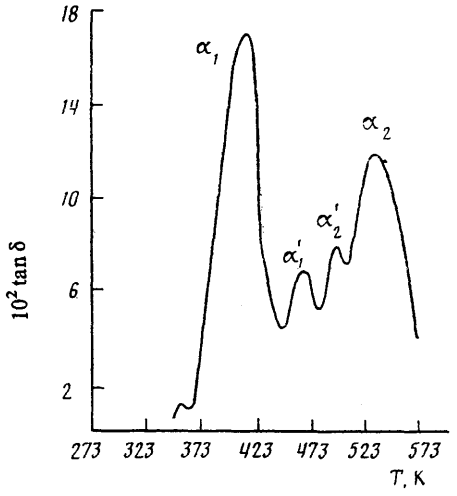


Figure 1. Temperature dependence of the mechanical losses coefficient tan δ of an organic plastic based on an epoxyphenolic binder.

Yet another cause of the formation of a transition layer is the adsorption of one component on the surface of another.[29] A change in the concentration of the cross-linking agent (PEPA) on the surface of the filler as a function of the nature of the chemical fibre has been demonstrated.[30,31] The redistribution of PEPA in the epoxide binder takes place as a result of its selective sorption by chemical fibres.

The structural changes occurring in the binder under the influence of polymeric fibres cannot fail to influence the kinetic parameters of the binder hardening process.

It has been shown[15,29–34] that the introduction of chemical fibres into polymeric binders affects the kinetics of the hardening of the latter in different ways: acetate, polypropylene, and polyamide fibres accelerate while modified viscose fibres retard the hardening process. The retarding effect of the viscose fibre on the hardening of anilinophenol-formaldehyde resin can be explained by the large surface area of the viscose fibre with active hydroxy-groups promoting the sorption of the oligomer and its fairly strong retention on the surface of the fibre. Part of the reactive groups of the oligomer blocked in this way do not participate in the formation of the three-dimensional structure, which diminishes the rate of reaction and lowers the degree of hardening of the polymer.

Lavsan and PAN have a dual effect on polymeric binders. Lavsan retards the hardening of the phenolic binder at 120–140 °C, while at 170 °C it accelerates it. The influence of the PAN fibre is determined by its content in the composition. The introduction of small amounts (up to 5 wt.%) of the PAN fibre into the epoxide binder accelerates the hardening process, while following an increase in its content to 20 wt.% and above (50 wt.%) the formation of the three-dimensional network is retarded both for the epoxide[30] and for the phenolic binders (Fig. 2). Fig. 2 shows that staple fibre exhibits the greatest inhibiting effect, which is due to its high sorption capacity (the specific surfaces of staple fibre and technical twisted cord, determined by gas chromatography, are respectively 7.4 and 4.6 $m^2 g^{-1}$).

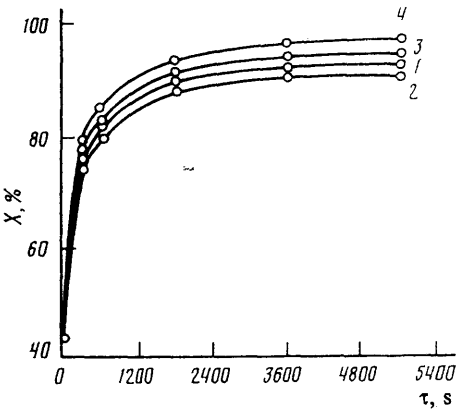


Figure 2. The influence of staple (curves *1* and *2*) and technical PAN fibre on the degree of hardening *X* of SF-342A resin: (*4*) unfilled resin; (*1*) and (*3*) PCM based on PAN fibre (50 wt.%) washed free of the lubricant; (*2*) ditto for the unwashed PCM.

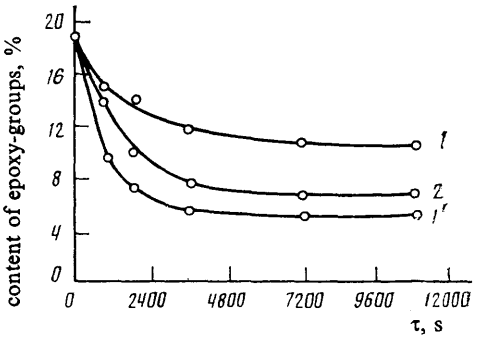


Figure 3. The influence of PAN fibre and temperature on the content of epoxy-groups in an epoxide oligomer: (*1*) and (*1'*) ED-20; (*2*) PCM based on PAN fibre (10 wt.%) [(*1*) and (*2*) at 20 °C; (*1'*) at 100 °C].

The rate and degree of hardening are also influenced by factors such as temperature and pressure.[15,24,33] An increase in temperature from 20° to 100 °C accelerates the hardening of the epoxide binder (Fig. 3). Thus the residual content of epoxy-groups 900 s after the start of the polycondensation process is 14.4% at (20 °C) and 9.8% (100 °C), while 7200 s from the start of the polycondensation process the residual contents are 11.6% (20 °C) and 5.2% (100 °C). The

introduction of PAN fibre into the composition also diminishes the content of epoxy-groups. When 7200 s has elapsed from the start of the polycondensation process, their residual content in the unfilled binder is 11.6%, while in PCM it is 6.8%, which indicates the influence of the fibre on the degree of cross-linking of the epoxide binder.

Thus, by altering the formation parameters and the amount of fibre in the composition, it is possible to regulate specifically the topological structure of the polymeric matrix and hence the properties of the PCM.

2. Methods for the modification of polymeric composite materials based on polyacrylonitrile fibres

Under the conditions of the dynamic scientific and technological development of the National Economy, the regulation of the properties of polymeric composite materials is important in order to meet to the optimum extent technological, operating, and economical requirements of industry. The properties of PCM are regulated by the formation of their specific chemical and physical structure, which is achieved by the modification, using various methods, of both the polymeric matrix and of the reinforcing filler.

Various PCM ensure a wide range of valuable properties—chemical stability, electrical conductivity, mechanical strength, etc. There is much scope for the improvement of the properties of PCM.

One of the most important factors influencing the properties of PCM is internal stresses arising both in the bulk of the binder and, especially, at the binder–chemical fibre interface, caused by the differences between the temperature coefficients of the linear expansion of the polymer and the filler and also by the contraction of the binder during the hardening process.[35,36]

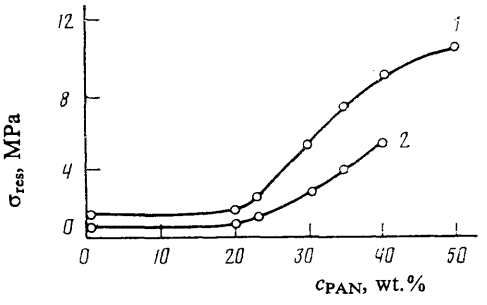


Figure 4. Dependence of the residual internal stress in the initial (curve *1*) and Thiokol-plasticised (curve *2*) composite material on the content of PAN fibre.

The residual internal stresses in the PCM reinforced with PAN fibres have been determined by the polarisation-optical method[37] on model PCM specimens containing between 0.5 and 50 wt.% of the fibre and consisting of transparent films 0.1–0.3 mm thick.

It has been established[25] that a more strained structure compared with the structure of the unfilled resin is produced in epoxide compositions under the influence of the PAN fibre: the introduction of 50 wt.% of PAN fibre into the composition increases by a factor of more than 5 the residual internal stresses [for the unfilled resin and the PCM, the internal stresses amount respectively to 1.8 and 10.3 MPa (Fig. 4, curve *1*)]. This is associated with the fact that fibres have a negative linear expansion coefficient, while the polymeric binder has a positive coefficient. The rigid compression of the fibres by the polymeric matrix prevents the free variation of the volume of the binder during its hardening.

As a rule, the introduction of different plasticisers facilitates the occurrence of relaxation processes in the polymer network being formed, which reduces the residual stresses.[38–40]

A polysulphide rubber (Thiokol) is an effective plasticiser for PCM reinforced with PAN fibre. The introduction of 15 wt.% of Thiokol into the composition makes it possible to reduce greatly the residual internal stresses (Fig. 4, curve *2*)[25] and, with increase in the content of the fibre in the composition, the influence of Thiokol on the internal stresses is enhanced.

The diminution of the residual internal stresses in the PCM following the introduction of Thiokol entails an increase in the impact and water resistance of epoxide PCM and in their strength (Table 2).[41] The phenomenon of "antiplasticisation", expressed by an increase in the bending strength (σ_b) and tensile strength (σ_t) by a factor of 1.2, in impact strength (a_{sp}) and the modulus of elasticity (E_e) by a factor of 1.5, and in elasticity ε by a factor of 1.8 is observed for such systems.[42]

Table 2. The influence of the plasticisation of the epoxide oligomer on the physicochemical characteristics of the PCM.

Plasticiser	Content of plasticiser, wt.%	Physicomechanical properties of PCM					
		σ_s, MPa	σ_b, MPa	a_{im}, kJ m^{-2}	$10^3 E_e$, MPa	ε_{rel}, %	W, %
Without plasticising agent	0	89	140	50	5.2	4.6	0.3
Dibutyl phthalate	10	60	30*	78	4.4	9.7	0.48
	20	—	60*	110	2.2	11.6	0.9
Thiokol	15	100,6	170	73	7.6	8.3	0.106

* The bending moment corresponding to the bending of the specimen by an amount equivalent to 1.5 times its thickness is presented.

The mechanism of "antiplasticisation" in network polymers, especially in unfilled epoxide binders, has been investigated.[43–46] It was established that "antiplasticisation" is the result of the simultaneous alteration of the structure and properties of the matrix and the plasticiser associated with their compaction, which in fact improves the mechanical and other properties.

For PCM reinforced with PAN fibre and plasticised with Thiokol, the increase in strength characteristics and the decrease in water absorption may be associated with the formation in the individual units of the three-dimensional structures of flexible transverse bridges, which promotes the formation of a more close-packed and less strained structure:

$$2R{-}CH{-}CH_2 + HS{-}R'{-}SH \rightarrow R{-}\underset{OH}{CH}{-}CH_2{-}S{-}R'{-}S{-}CH_2{-}\underset{OH}{CH}{-}R.$$
$$\quad\ \backslash O /$$

As a result, a better compatibility of such polymeric matrix with the fibre is ensured and the operational effectiveness of the PCM as a whole is improved. This is also indicated by the character of the

break. The plasticised material breaks without the separation of the reinforcing component and of the polymeric matrix at high loads (101 MPa) and for large elongations (8.3%), whereas the usual PCM gives rise to a serrated break for lower loads (90 MPa) and elongations (4.6%).

In the plasticisation with Thiokol of PCM reinforced with caproic thread, an increase in the modulus of elasticity and in strength was not observed.[47] On the contrary, in this case the classical plasticising effect was noted, being manifested by an increase in impact strength and in the relative elongation on rupture and by a decrease in the modulus of elasticity.

Thus the plasticising effect of Thiokol in PCM reinforced with chemical fibres is manifested in different ways depending on the nature of the reinforcing fibres.

The method involving modification with small amounts of additives of different chemical nature has been used in recent years for the specific regulation of the properties of various polymers.[49–59]

The modification of polymers by acting specifically on structure formation processes as a rule extends only over the region of physical transformations and all positive effects are achieved as a result of the change in the character of the intermolecular interaction.[53]

The modification of a PCM reinforced with PAN fibre by the introduction of the optimum (2 wt.%) amount of an alloying additive — oligo-oxypropylene glycol (OOPG) — makes it possible to increase the bending strength of the PCM by 50%, the impact strength by 40%, and the tensile strength by 20% (Fig. 5). The alloying additive, which increases the mobility of the polymer chains, stimulates their closer packing, as a consequence of which the free volume diminishes and the viscosity of the system rises.

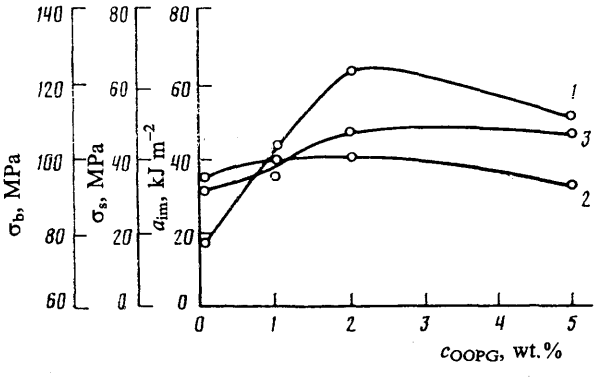


Figure 5. Dependence of the bending (σ_b) (curve *1*) and stretching (σ_s) (curve *2*) breaking stresses and of the impact strength (a_{im}) (curve *3*) of the composite material on the content of the alloying additive.

The increase in the viscosity of the system under the influence of the alloying additive is indicated by the fact that the capacity of the modified oligomer for wetting (determined by the capillary rise method[53]) is impaired.[25]

Furthermore, PCM containing 2 wt.% of oligooxypropylene glycol swells much less in acetone compared with the initial material: the equilibrium degrees of swelling of the modified and unmodified PCM are 15 and 225 mg g^{-1} respectively.

The results obtained show that the modification of PCM reinforced with PAN fibre and small amounts of added organic substances, in particular oligooxypropylene glycol, makes it possible to increase the strength of the material, probably as a result of the better compatibility of the polymeric matrix and the reinforcing fibre.

One of the disadvantages of PCM based on PAN fibres is high combustibility, which limits their applications in branches of industry such as aeroplane construction, building, etc.

The possibility of reducing the combustibility of PCM based on PAN fibres by introducing into them a ternary system comprising bromine-, chlorine-, and phosphorus-containing compounds has been demonstrated.[53] It was established that the efficiency of the modifying additives (combustion inhibitors) is greater if they are introduced into the reinforcing fibre and not into the polymeric binder.

The decrease in the combustibility of such PCM leads to additional possibilities for their use in various branches of industry. Different inorganic additives, in particular antifriction and other additives (graphite, carbon black, molybdenum disulphide, metal powders, etc.) are used nowadays to modify PCM in order to impart to them specific properties.[55,56] However, in most cases the introduction of disperse carriers lowers the strength of the compositions.[57] One of the ways of simultaneously increasing the strength and of improving the antifriction properties of polymeric materials for the manufacture of various sliding components involves the use of hybrid compositions containing both fibrous and disperse fillers.[58] The modification of polymeric materials by such hybrid compositions impart to the PCM a series of new specific properties and the cost of the material is also reduced. Thus the introduction of antifriction additives (molybdenum disulphide and graphite) into the PCM based on PAN fibres in an amount up to 5% not only reduces the coefficient of friction μ but also increases the hardness and bending strength of the material[59] (Table 3). Table 3 shows that the replacement of flaky graphite by highly disperse graphite leads to an additional reduction of the coefficient of friction of the PCM and to an increase in its strength and hardness.

Table 3. Dependence of the coefficient of friction and the physicomechanical properties of the PCM on the type and content of additives.

Additive	Content, wt.%	Physicomechanical properties of PCM			μ
		σ_b, MPa	σ_s, MPa	N_B, MPa	
Initial PCM	0	87	67	28	0.25
Molybdenum disulphide	1	103	54	36	0.18
	3	98	53	38	—
	5	83	50	40	—
Flaky graphite EUT-1	1	99	59	30	0.21
	5	72	62	35	0.20
	10	50	56	38	0.18
Highly dispersed graphite	1	132	—	41	0.14
Acetylene carbon black	1	80	64	—	0.2
	5	84	57	—	0.12
	10	57	48	—	0.13

Although a further increase in the content of antifriction additives in PCM (> 5 wt.%) does in fact reduce the coefficient of friction of the materials, yet at the same time it increases the porosity of the PCM and leads to a decrease in their strength.[59,60]

The antifriction properties of PCM reinforced with PAN fibre depend on temperature. On heating such PCM, the coefficient of friction passes through a maximum (Fig. 6) and the maximum value of the coefficient of friction is observed in the region of the glass point of the polymer (100 °C). (Tests were carried out at a slip rate of 7.5×10^{-3} m s^{-1} and a pressure of 1.5 MPa.) This can be explained by the decrease in the hardness of the material, which increases the area of the actual contact. The hardness of the PCM, both initial and of the material containing 1% of molybdenum disulphide, decreases by 76 and 64% respectively on heating to 100 °C.

The fibres present in the surface layer of the specimen exhibit an additional resistance to friction, which is associated with the transition of the PAN from the vitreous to the highly elastic state. Further increase in temperature leads to an appreciable local overheating of the friction surface, entailing partial degradation of the polymer, as a result of which a charred film is produced, playing the role of a lubricant which reduces the coefficient of friction.

PCM containing graphite behaves differently on heating: on raising the temperature, the coefficient of friction hardly changes (Fig. 6, curve *4*). In all probability, the introduction of even small amounts of graphite (in the given instance 1%) promotes the formation on the friction surface of a layer of graphite, which plays the role of a lubricant.

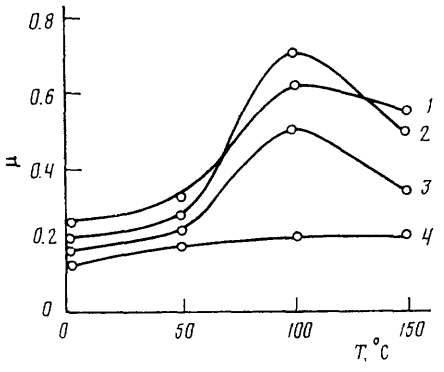


Figure 6. Temperature dependence of the coefficient of friction: (1) initial composite material; (*2*) and (*3*) composite material with molybdenum disulphide [(*2*) reinforcing fibres perpendicular to the friction surface; (*3*) reinforcing fibres parallel to the friction surface]; (*4*) composite material with graphite.

One of the promising aspects of the development of PCM is the creation of hybrid materials, i.e. blends containing three or more components of different chemical composition.[2,61,62] By combining fibrous fillers of different chemical nature, it is possible to obtain PCM with a high resistance to fatigue and the required anisotropy of the properties—in other words it is possible to create materials with the planned properties. The use of polyfibrous fillers makes it possible to obtain materials with the optimum combination of mechanical characteristics, which cannot be achieved in a monoreinforced PCM.

PCM based on inorganic and organic highly modular fibres have been most thoroughly investigated. Questions concerning the classification of the structures, the decomposition mechanisms, and the prospects for the development of such PCM have been described in reviews.[58,62]

One of the features of hybrid PCM is the presence of a hybrid (synergistic) effect. The introduction into PCM reinforced with PAN fibre of viscose (VF) and caproic (CF) fibres, differing from the PAN fibre by their strength and rigidity, makes it possible to reduce the brittleness of the material.

Polyfibrous compositions have been obtained by the joint impregnation of threads of different chemical nature with the binder. The threads were subsequently cut up.

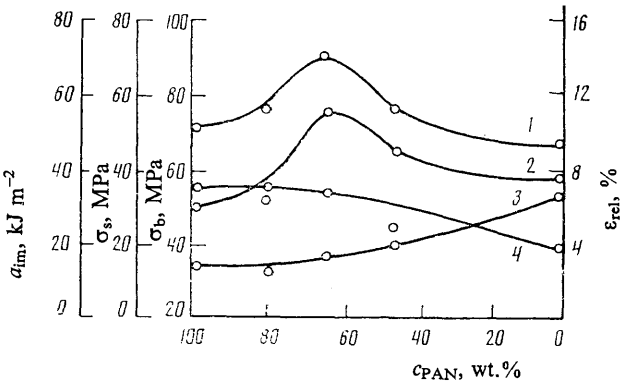


Figure 7. Dependence on the bending (curve *1*) and stretching (curve *4*) breaking stresses, the impact strength (curve *2*), and the relative elongation on rupture (curve *3*) on the ratio of the PAN and caproic fibres in the hybrid filler.

Table 4. Weight losses by hybrid PCM during dynamic heating.

Ratio of PAN and viscose fibres in hybrid filler, wt.%	Weight losses (%) at different temperatures			
	300° C	360° C	400° C	500° C
100:0	10	14	17	25
75:25	12	19	23	32
50:50	14	24	28	38
38:62	13	26	30	41
0:100	35	40	49	59

In the manufacture of polyfibrous compositions based on a mixture of PAN and caproic fibres, the strength of the fibres is not of decisive importance:[63] PCM reinforced with the stronger caproic fibre (62 cN tex^{-1}) has smaller bending and tensile strengths than PCM based on the weaker (41 cN tex^{-1}) PAN fibre as a result of the difference between the elastic properties and the coefficients of thermal expansion of the fibres and the polymeric matrix (Fig. 7).

The combination of these fibres in the PCM in proportions of 65:35 (wt.%) increases appreciably the resistance of the PCM to bending and impact as well as its elasticity. The appearance of a synergistic effect is then observed: the experimental bending and impact strengths of the PCM exceed the additive values on average by 40 and 70%.

A synergistic increase in strength (Fig. 8) and thermal stability (Table 4) has also been noted for polyfibrous compositions containing viscose and PAN fibres taken in equal amounts (50 wt.%) as the reinforcing system: the experimental bending strengths of the PCM exceed by 20% the additive values, while the weight losses, determined by thermogravimetric analysis, exceed the additive values by 5–10%.

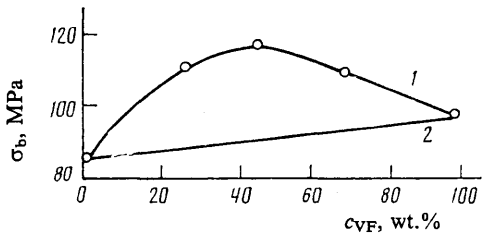


Figure 8. The synergistic increase in the bending strength of the composite material reinforced with a mixture of PAN fibres and viscose thread: (*1*) experimental curve; (*2*) additive curve.

In the preparation of hybrid PCM, the scheme employed for the reinforcement of the polymer matrix with the polyfibrous filler is very important. For example, when fabrics made up of chemical fibres of different chemical nature were impregnated separately with the binder and were subsequently arranged in alternate layers in the composition, the appearance of a synergistic effect was not observed regardless of the type of binder (Table 5).

Table 5. Dependence of the properties of the PCM on the ratio of different fibres in the hybrid filler (on the basis of fabric sheets).

Binder	Ratio of PAN and viscose fibres (wt.%)	Physicomechanical properties of PCM			
		σ_b, MPa	σ_s, MPa	a_{im}, kJ m^{-2}	ε_{rel}, %
Epoxide	100:0	114	58	20	3.8
	50:50	142	88	30	7.0
	0:100	178	130	50	10.2
Phenolic	100:0	104	62	12	4.0
	50:50	119	87	25	5.0
	0:100	190	138	6	—

Thus the combination of PAN fibre with other chemical fibres differing from it in strength and elastic properties makes it possible to increase bending and impact strengths of PCM by 30–40% and their thermal stability by 15–30%.

The fact that the PCM reinforced with PAN fibre combined with viscose fibre has a lower density and a higher resistance to water compared with the PCM reinforced with the viscose fibre alone is fairly important.

A vigorous search has been prosecuted in recent years for new polymeric materials with a high electrical conductivity. Electrically conducting plastics are obtained either by synthesising polymers containing free or mobile electrons, responsible for the semiconducting properties of the plastics, or by introducing electrically conducting additives into polymers.[57] Both powdered and fibrous electrically conducting fillers are usually employed: carbon black, metallic powders, metallic fibres, metallised glass fibre, carbon fibre, etc.[56,57,65,66] However, in order to ensure sufficiently effective electrically conducting properties of the PCM, it is necessary to introduce into the composition an appreciable amount (30–55 wt.%) of a powdered additive, which usually weakens the mechanical properties of the PCM. The introduction into the composition of the PCM of additional carbon and other fibres eliminates this disadvantage but increases significantly the cost of the material (for example, the cost of carbon fibres amounts to between 20 and 200 dollars per kilogram[57]).

A promising aspect of the manufacture of antistatic and electrically conducting PCM involves the introduction into the binder of a fibrous reinforcing filler modified by the method in which metal salts are included (metal salts are incorporated into the structure of the freshly formed fibres).[67,68]

The PCM fibres modified by the inclusion of nickel salts with their subsequent reduction, which ensures a uniform distribution of nickel in the fibre, make it possible to obtain PCM which are fairly strong and have fairly high electrical conductivities in the presence of a very small (2–3 wt.%) metal content.[69]

Table 6. Comparative properties of composite materials based on normal and nickel-containing PAN fibres.

Properties	PAN fibre	
	initial	nickel-containing
Strength of fibre, cN tex^{-1}	22	23
Breaking stress (MPa) in		
bending	110	120—130
stretching	59	54
Impact strength, kJ m^{-2}	16	18
Bulk-phase electrical resistivity, Ωm	$1.9 \cdot 10^{11}$	$4.4 \cdot 10^{6}$
Tangent of dielectric losses angle	0.43	0.004
Electrical strength, kV mm^{-1}	15	3

Thus the introduction of a nickel-containing PAN fibre into an epoxide binder increases the electrical conductivity of the PCM (Table 6). The bulk phase resistivity of such PCM is then reduced compared with the unmodified material by a factor of 10^5 (from 1.9×10^{11} to 4.4×10^6 Ωm), the electrical strength diminishes by a factor of 5, and the tangent of the dielectric losses angle increases by a factor greater than 2. The physicomechanical properties of the modified PCM are then not impaired and a 25% increase in the bending strength is actually observed. The increase in the electrical

conductivity of the PCM indicates the current conducting role of nickel distributed in the fibre in the form of a polyatomic layer. With increase in the weight fraction of the modified fibre in the PCM and also with increase in the nickel content in the fibre structure, the electrical conductivity of the PCM rises as a result of the increased content of the current-conducting component (Table 7). The bulk phase resistivity of the PCM containing 50 and 60 wt.% of the nickel-containing fibre is 4.4 × 10^6 and 8.5 × 10^5 Ωm respectively. The same parameters for the PCM containing fibre with 2.5 and 3.2 wt.% of nickel and respectively 8.5 × 10^5 and 7.1 × 10^3 Ωm.

The dependence of the decrease in the bulk phase resistivity of the PCM on the content of the current-containing component can be explained from the standpoint of the theory of chain conductivity,[65,66] according to which the electrical conductivity is ensured by the significantly greater number of contacts between the electrically conducting elements.

Table 7. Dependence of the electrical properties of the PCM on the content of the nickel-containing fibre (nickel content in fibre 2.5 wt.%).

Content of PAN fibres in PCM, wt.%	Properties of PCM		
	ρ_v, Ωm	E_{br}, kV mm^{-1}	tan α
40	$1.2 \cdot 10^{10}$	7	0.075
50	$4.4 \cdot 10^{6}$	3	0.094
60	$8.5 \cdot 10^{5}$	2	0.90
60*	$7.1 \cdot 10^{3}$	—	—

*The fibre contains 3.2 wt. % of nickel.

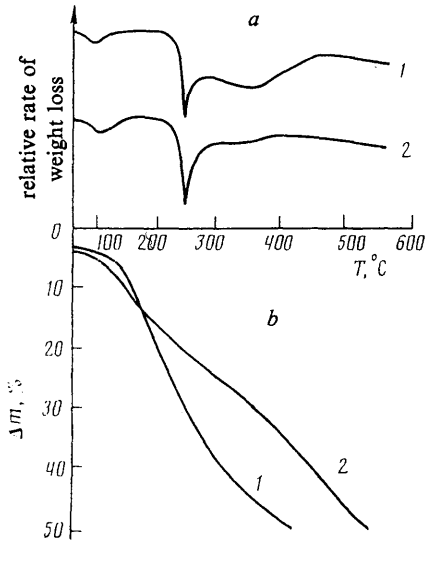


Figure 9. Thermogravimetric analysis of PCM based on the initial (curve *1*) and nickel-containing (curve *2*) PAN fibre: (*a*) relative rate of weight loss; (*b*) weight loss.

Under the influence of the nickel-containing PAN fibre, a more thermally stable PCM structure is formed: the mechanism of the degradation of the modified material is different from that of the initial material and is characterised by the presence of a single peak at 272 °C, whereas the presence of two maxima on the weight loss rate curve is characteristic of the unmodified PCM—at 260° and 348 °C (Fig. 9*a*).[25]

The introduction of nickel into the structure of the PAN fibre increases the stability of the PCM in relation to thermooxidative degradation: the weight losses by the modified PCM are appreciably lower at all temperatures above 160 °C than the weight losses of the initial material (Fig. 9*b*). This is also indicated by the greater stability of the strengths of the PCM after the exposure to different temperatures: the residual strengths of the unmodified and modified PCM after heating the latter for 7 h at 200 °C are respectively 65 and 83% (Fig. 10).

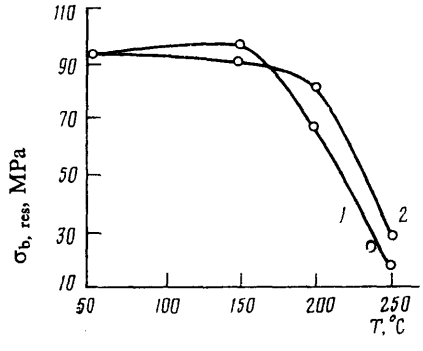


Figure 10. The change in the residual bending strength of the PCM based on the initial (curve *1*) and inclusion-modified (curve *2*) nitron after heating.

On the basis of the data obtained, the PCM reinforced with nickel-containing PAN fibre can be classified as a member of the group of antistatic materials,[65] which can be used to prepare current-conducting elements and also as a facing material for the covering of walls and ceilings.

3. The influence of external media on the properties of polymeric composite materials

The introduction of fibre-fillers into PCM affects not only the character of the structure formation in the filled polymer but also its behaviour on exposure to different external influences. When PCM come into contact with corrosive liquids and their vapours, the latter penetrate into the material owing to the presence of structural defects and the properties of the reinforcing fibres and of the polymeric matrix. Such penetration is accompanied by a change in the weight and strength of the material.

Thus when PCM reinforced with viscose fibre is treated with a reagent capable of inducing appreciable changes only in the polymeric matrix (acetone), the decrease in the strength of the composition is determined by the structure and properties of the three-dimensional network and the hardened polymeric binder.[70]

When PCM is exposed to water, the change in its strength is now limited by the behaviour of the fibres, since the strength of the polymeric matrix, determined by the character of the three-dimensional network, hardly changes under these conditions.

The reinforcement of PCM with hygroscopic viscose fibre, which has a porous surface, leads to appreciable swelling of the PCM in water and to a change in its strength: the decrease in the bending strength and the increase in the mass of the PCM specimens after exposure to water for 1000 h are respectively 30% and 58.3 mg g^{-1}.[7] The modification of the surface of viscose fibre by the chemical grafting of polystyrene, which reduces its sorption capacity, increases the resistance of the PCM to the action of corrosive media.[71]

The same effect is observed when PCM is reinforced with hydrophobic fibres. For example, in phenolic compositions based on kapron and lavsan, the increase in the mass of the material is much smaller than in the PCM reinforced with unmodified viscose fibre.[72]

Table 8. The change in the weight of the specimens after treatment with corrosive media.

Composite material	Medium			
	H_2O	CCl_4	3% H_2SO_4	1% NaOH
Epoxide	−1.4	0.2	−7.5	−1.9
Phenolic	0.4	0.02	0.5	0.4

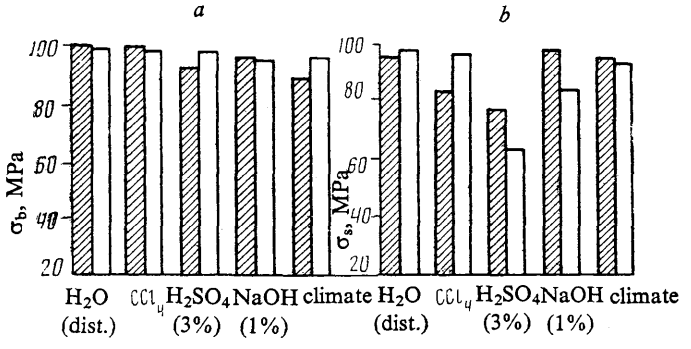


Figure 11. The residual bending strength (*a*) and tensile strength (*b*) of epoxide (shaded columns) and phenolic (unshaded columns) PCM after treatment with corrosive media.

The exposure of PCM based on PAN fibre for a long time (120 days) to corrosive media does not induce an appreciable change in the mass and strength of the specimens (Table 8, Fig. 11). Sulphuric acid is an exception, its action reducing the mass of the epoxide PCM by 7.5% (as a result of some decomposition) and its tensile strength by 22%. The effect of sulphuric acid on phenolic PCM reduces its tensile strength by 36%.

Carbon tetrachloride and dilute alkali do not induce an appreciable change in the strength, mass, and external appearance of such PCM.

The effect of natural climatic factors (climate) during the same period reduces only slightly the strength of the PCM (by 5–10%) (Fig. 11), but there are no changes in the linear dimensions, mass, and external appearance of the specimens under these conditions.

Thus the behaviour of PCM (reinforced with chemical fibre) on treatment with various corrosive media is determined by a whole series of factors, the most important of which are the nature of the fibre and the structure of the PCM surface and also the nature of the binder.

IV. The possible applications of polymeric composite materials

The composite material based on PAN fibre has effective technological properties: the rate of spreading of the moulding material and the fluidity (thickness of the disc), determined by the method of Dyukhin and Stavrov,[73] are respectively 0.25 mm × s^{-1} and 1.6 mm.[74] Articles made from this material have a pleasant external appearance and a shiny surface and can be subjected to all kinds of mechanical treatment: milling, drilling, turning, polishing, etc.

The PCM which have been developed have a set of specific properties: an increased resistance to bending and impact loads, a low density, a fairly high atmospheric and chemical stability, an improved thermal stability, and antifriction properties.

The results obtained show that it is useful to employ PCM based on PAN fibre in chemical machine construction and also as building materials for the protection of constructions against corrosion.

In the building industry, PCM are used to prepare facing materials and sanitary-technical articles, in particular, for the manufacture of various connecting components used in the assembly of pipelines. Articles made of PCM have a number of advantages over metallic articles. These include primarily corrosion resistance and low density.

Industrial tests on facing plates made of PCM reinforced with PAN fibre demonstrated the possibility of using them to cover industrial environments.

No changes in the physicomechanical characteristics of the PCM and its external appearance on treatment with water and acetic acid vapour were observed during the tests.

A modified PCM containing graphite (1%) can be usefully employed as an antifriction material. Tests on experimental specimens (inserts in slip bearings) showed that metal-PTFE inserts can be usefully replaced by inserts made from antifriction PCM. The intrinsic cost of the components is then reduced and their useful operating life is increased. In addition, the possibility of employing PCM with added graphite in dry friction components makes it possible to abandon the use of scarce and expensive lubricating materials.

The PCM which have been developed, reinforced with PAN fibres, can be recommended for the manufacture of components and constructions withstanding impact loads, for example, for the manufacture of the shells of shuttles in looms.

Industrial tests on experimental specimens demonstrated that PCM reinforced with chemical fibres are economical and their application is technically and socially useful. In the first place the intrinsic cost of the material is reduced and in the second it is possible to replace the natural fibres which are still used in technical applications as reinforcing fillers for PCM, for example in the manufacture of blades for looms, textolite, etc.

A polymeric composite material based on nitron, which has effective strength properties, is susceptible to manufacture by modern technology, has a pleasant external appearance, and can be used as a constructional material for the manufacture of various components.

Tests have demonstrated that PCM based on PAN fibre can be usefully employed for the manufacture of bowls for fuel filters. The bowls made from the PCM are light and strong, are oil and petrol resistant, and can successfully replace containers made from metal and AGH-4V material.

References

1. *Osnovnye Napravleniya Ekonomicheskogo i Sotsial'nogo Razvitiya SSSR Na 1986–1990 gody i na Period do 2000 goda: Postanovlenie TsK KPSS* (Principal Directions of the Economic and Social Development of the USSR in 1986–1990 and in the Period up to the Year 2000: Resolution of the Central Committee of Communist Party of the Soviet Union), Politizdat, Moscow, 1986, 96 pp
2. N S Enikolopyan *Zh. Vses. Khim. Obshch. im Mendeleeva,* 1978, (3) 243
3. G P Mashinskaya *Organovoloknity. Plastiki Konstruktsionnogo Naznacheniya* (Organic Fibre-reinforced Plastics. Constructional Plastics), Izd. Khimiya, Moscow, 1974, p. 266
4. V S Smirnov *Khim. Volokena,* 1986, (5) 3
5. Yu S Lipatov *Mezhfaznye Yavleniya v Polimerakh* (Interfacial Phenomena in Polymers), Izd. Naukova Dumka, Kiev, 1980, 259 pp
6. J W S Hearle, R H Peters (Editors) *Fibre Structure* (Translated into Russian), Izd. Khimiya, Moscow, 1969, 308 pp
7. Yu S Lipatov, S E Artemenko, N K Ivchenko et al. *Vysokomol Soedin. B,* 1975, **17**(8) 584
8. Yu S Lipatov, L I Bezruk, S E Artemenko, V V Andreeva *Vysokomol Soedin. B,* 1977, **19**(4) 271
9. Yu S Lipatov, E V Lebedev *Dokl. Akad. Nauk SSSR,* 1976, **230**(6) 1380
10. Yu S Lipatov, E G Moisya, G M Semenovich *Vysokomol. Soedin. Ser. A,* 1973, **19**(1) 125
11. Yu S Lipatov, F G Fabulyak, G P Ovchinnikova *Mekhanika Polimerov,* 1973, (2) 374
12. Yu S Lipatov, F G Fabulyak, G P Ovchinnikova *Fizicheskaya Khimiya Polimernykh Kompozitsii* (Physical Chemistry of Polymeric Compositions), Izd. Naukova Dumka, Kiev, 1974, p. 74
13. Yu S Lipatov, F G Fabulyak, G P Ovchinnikova, S E Artemenko *Sintez i Fiziko-khimiya Polimerov* (The Synthesis and Physical Chemistry of Polymers), Izd. Naukova Dumka, Kiev, 1975, (17) 39
14. Yu S Lipatov, F G Fabulyak, G P Ovchinnikova *Dokl. Akad. Nauk Ukrain SSR, Ser. C,* 1975, (6) 521
15. S E Artemenko *Khim. Volokna,* 1979, (2) 28
16. P I Zubov, L A Sukhareva, M O Kiseleva, et al. *Mekhanika Polimerov,* 1966, (6) 808
17. A V Tokarev, I V Zhmaev *Fiziko-Mekhanicheskie Svoistva Kompozitnykh Materialov na Osnove Organicheskikh Volokon: Obzornaya Informatsiya* (The Physicomechanical Properties of Composite Materials Based on Organic Fibres: Review Information (The Chemical Fibre Industry)], Izd. NIITEKhIM, Moscow, 1981, 35 pp
18. V N Kuz'min, I P Dobrovol'skaya, K E Perepelkin, O S Leninkov *Khim. Volokna,* 1984, (1) 36–37
19. V N Kuz'min, I P Dobrovol'skaya *Khim. Volokna,* 1984, (1) 35–36
20. G P Ovchinnikova *Issledovaniya v Oblasti Fiziko-khimii Polimerov i Elektrokhimii. Sbornik Nauchnykh Trudov Saratovskogo Politekhnicheskogo Instituta* (Studies in the Physical Chemistry of Polymers and Electrochemistry. Collected Works from the Saratov Polytechnic Institute), Saratov, 1975, pp. 53–55
21. K E Perepelkin, A S Andreev, A V Zorin, G I Kudryavtsev *Khim. Volokna,* 1979, (5) 28
22. V N Evdokimov, V A Moskalev, V L Talanov, et al. *Mekhanika Kompozitnykh Materialov,* 1981, (6) 982
23. S N Ul'yanenko, G M Magomedov, G P Mashinskaya et al. *Plast. Massy,* 1987, (1) 39–40
24. L P Nikulina, S E Artemenko, G P Ovchinnikova *Plast. Massy,* 1987, (6) 15–17
25. L P Nikulina, Candidate's Thesis in Technical Sciences, Saratov Polytechnic Institute, Saratov, 1988
26. S N Ul'yanenko, G M Magomedov, L B Lebedev, et al. *Makhanika Kompozitnykh Materialov,* 1987, (3) 414–419
27. S V Startsev, I I Perepechko, L T Startseva, et al. *Dokl. Akad. Nauk SSSR* 1982, **267**(6) 1412
28. Yu S Lipatov, L I Bezruk, V V Andreeva *Vysokomol Soedin. B,* 1977, **19**(3) 166
29. A A Zarin, A S Andreev, A E Vaikhalovskii et al. *Kompozitsionnye Polimernye Materialy* (Composite Polymeric Materials), Izd. Naukova Dumka, Kiev, 1985, p. 7
30. V N Studentsov, S E Artemenko *Izv. Vys. Ucheb. Zaved. Khim. i Khim. Tekhnol.,* 1975, **18**(6) 1603
31. V N Studentsov, S E Artemenko *Vysokomol. Soedin. A,* 1976, **18**(2) 443
32. V N Studentsov, S E Artemenko *Issledovaniya v Oblasti Fiziko-khimii Polimerov i Elektrokhimii. Sbornik Nauchnykh Trudov Saratovskogo Politekhnicheskogo Instituta* (Studies in the Physical Chemistry of Polymers and Electrochemistry. Collected Works from the Saratov Polytechnic Institute), Saratov, 1975, p. 13
33. V N Studentsov S E Artemenko, N M Pchelintseva *Zh. Prikl. Khim.,* 1979, **42**(8) 1974
34. S A Vilkova *Issledovaniya v Oblasti Fiziko-khimii Polimerov i Elektrokhimii. Sbornik Nauchnykh Trudov Saratovskogo Politekhnicheskogo Instituta* (Studies inthe Physical Chemistry of Polymers and Electrochemistry. Collected Works from the Saratov Polytechnic Institute), Saratov, 1975, p. 3
35. S L Kopur, S Rao *J. Sci. Ind. Res.,* 1977, **36**(6) 292
36. M Shimbo, M Ochi, V Shigeta *Polym. Sci.,* 1981, **26**(7) 265
37. N I Prigorovskii (Editor) *Polyarizatsionno-Opticheskii Metod Issledovaniya Napryazhenii* (The Polarisation-Optical Method for the Study of Stresses), Izd. Nauka, Moscow, 1965, 126 pp
38. A B Filipovich, S I Skiba *Plast. Massy.,* 1986, (7) 16
39. I Z Chernin, F M Smekhov, Yu V Zherdev *Epoksidnye Polimery i Kompozitsii* (Epoxide Polymers and Compositions), Izd. Khimiya, Moscow, 1982, 136 pp
40. M Ochi, M Shimbo *Huxon Cattiaky Kekaici I. Adhes. Soc. Ian,* 1986, **22**(5) 255
41. S E Artemenko, L P Nikulina, G P Ovchinnikova, N V Lugovets *Plast. Massy.,* 1980, (10) 34–35

42. P V Kozlov, S P Papkov *Fiziko-khimicheskie Osnovy Plastifikatsii Polimerov* (Physicochemical Principles of the Plasticisation of Polymers), Izd. Khimiya, Moscow, 1982, 223 pp
43. V G Khozin, A G Farrakhov, V A Chistyakov et al. *Vysokomol. Soedin. Ser. A*, 1976, **18**(10) 2293
44. V G Khozin, A G Farrakhov, V A Voskresenskii *Vysokomol. Soedin. Ser. A*, 1979, **21**(8) 1757
45. V G Khozin, R M Sultanov, N S Prokhorova *Mechanika Polimerov*, 1975, (2) 218
46. V G Khozin, A V Murafa, A M Cherevatskii *Plast. Massy.*, 1985, (10) 40
47. S E Artemenko, T P Ustinova, S G Kononenko *Plast. Massy.*, 1978, (12) 27
48. T A Gruznova, M L Kerber, M S Akutin *Plast. Massy.*, 1980, (3) 30
49. G P Kravchenko, N Ya Valetskaya, M S Akutin, et al. *Izv. Vys. Ucheb. Zaved. Khim. i Khim. Tekhnol.*, 1978, **21**(4) 556
50. M S Akutin, N V Afanas'ev, B V Yarlykov *Khimiya i Tekhnologiya Organicheskikh Veshchestv i Vysokomolekulyarnykh Soedinenii: Sbornik Trudov MKhTI im D I Mendeleeva* (The Chemistry and Technology of Organic Substances and Macromolecular Compounds: Collected Reports from the Mendeleev Moscow Institute of Chemical Engineering), Moscow, 1975, p. 112
51. E V Lebedev *Fiziko-khimiya Mnogokomponentnykh Polimernykh Sistem* (The Physical Chemistry of Multicomponent Polymer Systems) (Edited by Yu S Lipatov), Izd. Naukova Dumka, Kiev, 1986, p. 384
52. Yu S Lipatov, E V Lebedev, L I Bezruk *Fiziko-khimicheskie Svoistva i Struktura Polimerov* (Physicochemical Properties and Structure of Polymers), Izd. Naukova Dumka, Kiev, 1977, p. 3
53. A Ya Korolev, S T Garanina, Yu V Zherdev *Plast. Massy.*, 1967, (6) 71
54. S A Vilkova, L G Panova, V A Vilkov, et al. *Zh. Prikl. Khim.*, 1983, **56**(5) 1107
55. I A Gribova, O V Vinogradova *Usp. Khim.*, 1979, (4) 177 [English translation in *Russ. Chem. Rev.*, 1979(4)]
56. L A Glukhova, S E Artemenko *Plast. Massy.*, 1984, (12) 51
57. N V Filichkina *Khimicheskaya Promyshlennost' za Rubezhom* (Chemical Industry Abroad), Izd. NIITEKhIM, Moscow, 1980, (10) 12
58. A A Zabolotskii, V Ya Varshavskii *Kompozitsionnye Materialy* (Itogi Nauk i Tekhniki) [Composite Materials (Advances in Science and Engineering)], Izd. VINITI, Moscow, 1984, Vol. 2, 104 pp
59. S E Artemenko, V A Lyutov, L P Nikulina, V N Markelov *Plast. Massy.*, 1985, 8
60. G S Kats, D V Milevskii (Editors) *Napolniteli dlya Polimernykh Kompozitsionnykh Materialov* (Fillers for Polymeric Composite Materials), Izd. Khimiya, Moscow, 1981, 540 pp
61. G M Gunyaev, Yu N Rabotnov, A F Rumyantsev et al. *Plast Massy.*, 1976, (9) 31
62. V A Kuznetsov, Yu V Vasil'ev, V P Ivanov *Khimiya i Tekhnologiya Vysokomolekulyarnykh Seodinenii* (Itogi Nauki i Tekhniki) [The Chemistry and Technology of Macromolecular Compounds (Advances in Science and Engineering)], Izd. VINITI, Moscow, 1986, Vol. 21, p. 188
63. G P Ovchinnikova, S E Artemenko, L P Nikulina, A A Geller *I Vsesoyuznaya Konferentsiya po Kompozitsionnym Polimernym Materialam i Ikh Primeneniyu v Narodnom Khozyaistve. Tezisy Dokladov* (The 1st All-Union Conference on Polymeric Composite Materials and Their Applications in the National Economy. Abstracts of Reports), Taskhent, 1983, Part 2, p. 28
64. USSR P. 973 574; *Byull. Izobret.*, 1982, (42) 85
65. V E Gul', M S Akutin *Osnovy Pererabotki Plastmass* (Principles of the Processing of Plastics), Izd. Khimiya, Moscow, 1985, 399 pp
66. V E Gul', L Z Shenfil' *Elektroprovodyashchie Polimernye Kompozitsii* (Electrically Conducting Polymer Compositions), Izd. Khimiya, Moscow, 1985, 240 pp
67. D N Akbarov, G F Vlasenko *Khim. Volokna*, 1987, (1) 22
68. A A Geller *Khim. Volokna*, 1979, (3) 10
69. USSR P. 891 721; *Byull. Izobret.*, 1981, (47) 4
70. S E Artemenko, L G Glukhova, M P Bereza *Plast. Massy.*, 1981, (3) 12–13
71. USSR P. 834 027; *Byull. Izobret.*, 1981, (20) 112
72. L G Glukhova *Candidate's Thesis in Technical Sciences, Kiev State University, Kiev, 1982*
73. V G Dedyukhin, V P Stavrov *Tekhnologiya Pressovaniya i Prochnost' Izdelii iz Stekloplastikov* (The Pressing Technology and Strength of Articles Made of Glass Plastics), Izd. Khimiya, Moscow, 1968, 247 pp
74. S E Artemenko, V P Reshetov *Proizvodstvo i Pererabotka Plastmass i Sinteticheskikh Smol: Nauchno-Tekhnicheskii Sbornik* (Saratovskii Politekhnicheskii Institut) [The Manufacture and Processing of Plastics and Synthetic Resins: Scientific-Technical Collection (Saratov Polytechnic Institute)], Izd. NIITEKhIM, Moscow, 1980, p. 3