Macromol. Symp. ***148****, 241–261 (1999)*

ELEMENT-CONTAINING FIBERS WITH EPOXY BINDERS: STRUCTURES AND PROPERTIES OF HARDENED COMPOSITIONS

Valentina I. Dubkova

Institute of General and Inorganic Chemistry of the National Academy of Sciences of
Belarus, 9 Surganova Street, 220072 Minsk, Belarus

Abstract : New types of composites based on element-containing carbon fibers (ECFs) and an epoxy binder have been developed. The results show that the presence of functional groups within the ECF structure affects significantly the reaction mechanism of the epoxy matrix. Connections between processes occuring in the interphase zone (the boundary layer) and the properties of hardened composites have been revealed. The factors controlling the binder hardening reactions occuring on surfaces of interphases when creating composites with improved physical and mechanical properties as well as with predermined service properties (polishing, anion-exchange, anti-corrosion, flame-resistance, controlled range of electrical resistance etc) are defined.

A potential for using ECFs in a role unusual for them, namely as hardeners for epoxide binders, has been established. Applications of reactive ECFs which may function both as a filler and as a hardener provides longer service life of the composites and minimizes the amount of volatile products released in the process of hardening.

1. INTRODUCTION

Carbon fibers and composites based on them attract considerable attention (1-3). A special place here belongs to element-containing carbon fibers (ECFs). The ECFs contain various elements of the periodic table in their structure in quantities exceeding those usually used for catalysis of thermolysis of polymer fibers. A significant number of the ECFs has been developed in our Institute. Along with the properties characteristic for conventional CFs these materials possess certain special: ion-exchange, magnetic, pyrophorous, catalytic, sorption and other properties (4-6). A microporous film carbon material has been developed (7). The presence of considerable quantities of metals in ECFs has been the prerequisite for obtaining oxide-metallic fibers and hollow microcapillary pipes (8). The results of

CCC 1022-1360/99/$ 17.50+.50/0

investigations on synthesis and properties of ECFs have been reviewed in a monograph of Yermolenko and coworkers (9). Depending on their individual features ECFs may be used as filters for cleaning electroplating baths from organic contaminants, as haemasorbents in medicine, etc.

The ECFs developed in our Institute may be subdivided into four groups: 1) fibers with functional groups on their surface; 2) those containing metal oxides and carbides, with highly dispersed reduced elements in the bulk and on the surface; 3) oxide-metallic fibers and 4) activated fibers with either a solid core and porous external layer, or vice-versa, with a controlled specific surface area (in the range of 200-2000 m^2/g).

As our investigations have revealed, the distinguishing feature of ECFs is their affinity to various oligomer and polymer matrices (10-13). In this paper we analyze interactions of ECFs with functional groups on the fiber surfaces with an epoxy binder and the resulting changes in structures and properties of the three-dimensional reaction products.

2. EXPERIMENTAL

2.1 Materials

We have studied phosphorus-containing carbon fibers (PCFs) on the basis of hydrated cellulose fibers and a cotton fabric. The production of fibers is described by Yermolenko (9). Ion-exchange capacity of PCFs on the functional groups was defined by the method of the straight titration of cationic in hydrogen form with a solution of 0.1 M NaOH in water (14). Unmodified carbon fibers (CFs), obtained on the basis of the same initial raw material and under the same carbonization conditions, were used for comparison. As an oligomeric matrix we have used several commercially available epoxy oligomers of various chemical structures: ED-20 epoxydian and DEG-1 low-molecular weight aliphatic resins (Plastpolymer, St-Petersburg, Russia); alicyclic diepoxides of acetal and ester type (UP-612 and UP-632 respectively), UP-650D alicyclic oligomer with two homogeneous glycide groups and UP-650T alicyclic-aliphatic triepoxide (Pilot-production plant of Ukrainian Institute of Plastic Materials, Donetsk, Ukraine). Also laboratory -made element (phosphorus or chlorine)- containing epoxy oligomers were investigated, particularly those which provide some special features to the final product (15).

2.2 Preparation of Compositions

Two-component fiber+oligomer compositions have been studied for the evaluation of physico-chemical interactions between PCFs and epoxy oligomers. Two methods of preparation were used. In the first method the discrete PCFs (1-2 mm long) and epoxy oligomers with various weight ratios were mixed carefully. The mixtures were heated in an oven under various temperatures and times regimes and were then examined by physico-chemical methods described below. In the second method, weighed pieces of phosphorus-carbon cloth were saturated with an epoxy oligomers in the weight ratio range of 1/1 - 1/4. The oligomers did not contain any hardeners. The pieces of cloth impregnated with the oligomers were placed in an oven and heated under several regimes. After thermal treatment, boiling acetone was used to clean the cloths from the oligomer not connected to the fibers. The amounts of epoxy resins grafted on the fiber surface were determined by a weight of the gel-fraction non-extractable from the PCFs, and are presented in Figure 1. The analogous compositions on the basis of unmodified carbon fibers and the same epoxy oligomers were prepared and heated under the same conditions. The results show that the curing reactions on the surfaces of unmodified CFs have never occurred.

2.3 Determination of Epoxy Groups Content and the Degree of Hardening

Titration was used to determine the concentration of epoxy groups in the oligomers and in their composites, this for PCFs before and after thermal processing. We have followed the well established method described by Kline (16) based on the reaction of hydrochloric acid with epoxy groups in an organic solvent and producing chlorohydrin. For calculating the conversion of epoxy groups during heating, the contents of epoxy groups in the initial oligomer not treated thermally was assumed to be 100 %.

The degree of hardening was assumed to be represented by the gel-fraction, that is by the ratio of the weight of the insoluble binder to the original amount of binder. The extraction of the samples with boiling acetone was being carried out in the Soxhtlet apparatus during 24 hours.

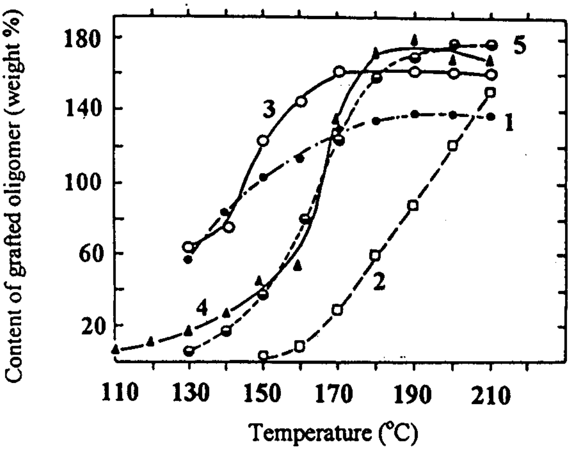


Fig. 1. Dependence of the amount of UP-650D (1), ED-20 (2), UP-650T (3), UP-632 (4) UP-612 (5) oligomers grafted to phosphorus-containing carbon fibers surface at temperature of their joint heat treatment. Phosphorus content in CFs is 11.45 weight %. PCFs-epoxy olygomer ratio is 1:2.

2.4 Differential Thermal Analysis (DTA)

It is well known that liquid-solid transition of epoxy oligomers is accompanied by intensive heat release (17). The PCFs, oligomers and their mixtures before and after the thermal treatment were studied. The samples were prepared according to the method described in an earlier paper (18). We have used a Paulik-Paulik-Erdey derivatograph (MOM, Hungary, Budapest) with the 20-500°C temperature range, in an air stream (20 ml/min) and in the furnace atmosphere, i.e. under the conditions of reduced oxygen supply. These conditions are similar to those in the manufacturing in closed molds. The heating rate was 5 K/min. Aluminium oxide was the reference material.

2.5 Thermomechanical analysis (TMA)

Thermomechanical researches were carried out on the samples of diameter and altitude 10 mm in conditions of continuous effect of a constant effort in 0,6 мПа and speed of heating 3 °C/ minute.Deformations arising at heating and uniaxis compression of samples were registered with the help of Heppler modernized consistometer (VEB MLW Prufgerate-Werk Medingen, Dresden, Germany).

2. 6 IR Spectroscopy and Spectroscopy of Multiple Attenuated Total Internal Reflection (MATIR)

Several methods of preparation of samples were used. The method of liquid film was used for the oligomers and their mixtures with fibers (19). The oligomer or a mixture was deposited on a KBr plate so as to form a thin layer of 10-15 μm and was covered by the other salt plate. The plates with the samples were then placed in a heated cell. The IR spectra were obtained with an UR-20 ("Karl Tseys", UENA, Germany) spectrophotometer at several temperatures. It had been ascertained previously that the components of mixture were not affected by the plates used. The hardened composites were investigated by the immersion method, that is, by pressing them with the KBr powder (20).

MATIR spectroscopy was used to study the surface functional groups of the PCFs and the polymer-fiber interfaces (21). The compositions were prepared as phosphorus-containing carbon fabrics, with gradually increased layers of a grafted epoxide. The MATIR spectra were recorded on the same UR-20 instrument with a MATIR attachment and a KRS-5 crystal with the fascia angle of 45°. KRS-5 crystal is mixed crystal of TlBr and TlI

2.7 Scanning and Transmission Electron Microscopy

We have used scanning electron microscopy(SEM), with the samples coated by a gold /palladium alloy (50nm) and examined in JEOL Model JSM-35 C microscope. Transmission electron microscopy (TEM) was also used. The compositions were prepared as blocks by mixing PCFs with epoxy oligomers and subsequent heat treatment. Fracture surfaces of the hardened composites were prepared in liquid nitrogen (22). One-and two-stage carbon replicas, taken from surfaces of the fractures of the composites and chromium shaded, were used. The observation and photography were performed in the Model UEMV-100 K electron microscope (Plant of electron microscopes, Sumy, Ukraine) at the accelerating voltage of 75 kV and a magnification of 10000-30000.

3. RESULTS AND DISCUSSION

The investigations have shown that the following phenomena take place. On heating two-component PCFs-epoxy oligomer compositions, the epoxy group conversion and the formation of a gel-fraction, non- extractable from the fiber surface, takes place. Effects of temperature on this process are shown in Fig. 1. Irreversible transformations of epoxy oligomers on the PCFs surface are accompanied by intense heat release (Fig. 2, curve 3) and formation of globular structures characteristic of cured epoxy compounds (Fig. 3). We display changes in the PCFs ion-exchange capacity in Fig. 4, effects of phosphorus concentration on the extent of oligomer transformation in Fig. 5, and effects of phosphorus content on thermomechanical behavior linear isobaric expansivity in Fig. 6. We infer from there results that CFs phosphoric-acid groups participate in the oligomer structure transformations. The results of the potentiometric titration of PCFs (Fig. 7, curve 1) confirm the presence of weak- as well as strong-acidic groups in their structures. The content of the latter is significantly reduced after curing the epoxy oligomers on the PCFs surface. The role of the strong acid groups is confirmed by the decrease of the quantity of epoxy oligomer bound to the fiber surface during the substitution of a metal for a mobile hydrogen atom in the CFs phosphoric-acid groups by means of ion-exchange sorption from solutions of the corresponding salts. More specifically, while the insoluble ED-20 oligomer fraction on the PCFs amounts to 96 percent by weight, in the case of a metal-phosphate CFs in the form of salts with nickel, cobalt and chromium, the amount of the non-extractable gel-fraction is 15.7, 18.4 and 14.6 % by weight, respectively. On the other hand, the decrease of the contents of epoxy groups during heat treatment of the PCFs-epoxy oligomer heterophase system, concomitant with the increase of hydroxyl groups, allows us to assume the occurrence of reactions of the epoxy oligomer bound to the PCFs, namely opening of epoxy cycles and formation of new hydroxyl groups. The common character of all oligomeric transformations irrespective of their type implies that the epoxy groups in both in alicyclic and aliphatic fragments participate in reactions of three-dimensional polymer formation on the PCFs surface.

Fig. 8 shows the MATIR spectra before and after heat treatment of PCFs, with various epoxy oligomer contents on its surface. One can observe absorption bands characteristic for

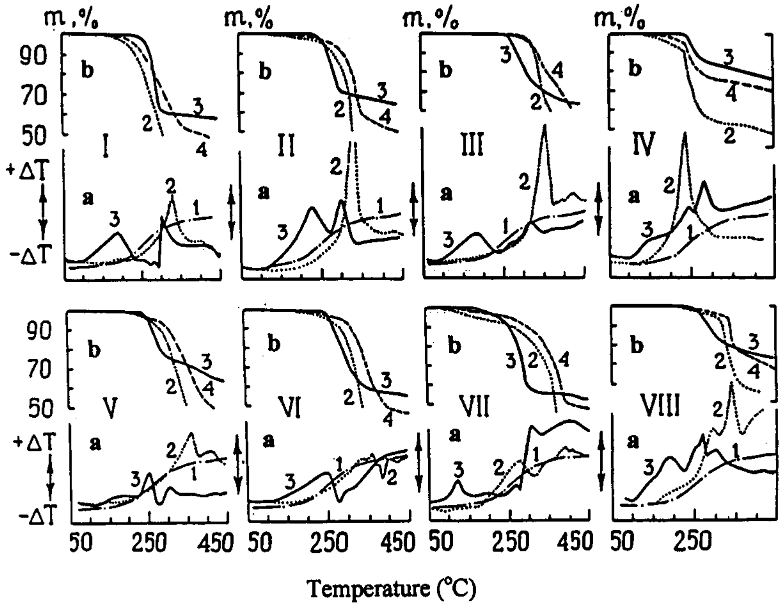


Fig. 2. Curves of DTA (a) and TG (b) of PCFs (1), epoxy oligomers (2), their mixtures (3) and additive (calculated) TG-curves (4) for compositions of PCFs with UP-650D (I), UP-650T (II), ED-20 (III), EOP (IV), UP-612 (V), UP-632 (VI), DEG-1 (VII) and EOC (VIII) oligomers.

both fibers and epoxy oligomers cured on their surface. At the same time, in this specific case, after deposition of the epoxy oligomers up to 300 weight parts on the PCFs, the absorption bands of the PCFs are still observed. With further increase of the oligomer quantity grafted on the PCFs surface, absorption bands of the epoxy coating appear. Thus, by means of a gradual augmentation of the quantity of cured oligomer one can keep traces of changes proceeding on the PCFs surface. The range of 400-600 cm^{-1} proves to be the most sensitive frequency band in the MATIR spectra; one can see here deposition on PCF surface of even small quantities of epoxy oligomers. Moreover one can observe shift of a wide absorption band with a maximum in the 500 cm^{-1} range towards lower frequencies, reaching 460-465 cm^{-1}. Low-intensity narrow absorption bands with maximums at 418, 435, 455, 477, 515 cm^{-1} can be clearly seen; these are not observed in the spectra of initial epoxy oligomers and PCFs. The 450-550 cm^{-1} frequency range is attributed to deformation oscillations of O-P-O for structural elements of polyphosphates (23). The changes revealed in this range are likely to be caused by complex processes, proceeding in the PCF under the influence of the epoxy oligomers deposited on its surface, resulting in a redistribution of functional fiber groups ratio. The appearance of a low-

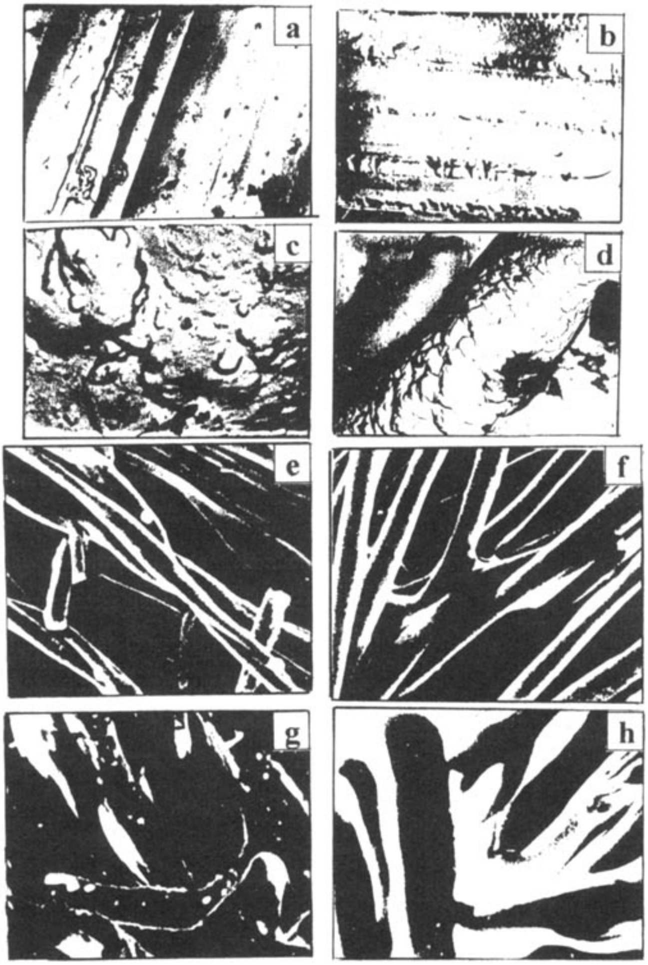


Fig. 3. Electron-micrographs of phosphorus-containing carbon fabric surface before (a,e) and after (b-d, f-h) its treatment by epoxy oligomers. The amount of ED-20 oligomer grafted to the PCFs are 92 weight % (b), 112 weight % (d, g) and 204 weight % (c, h). The amount of UP-632 grafted oligomer is 85 weight % (f). Magnifications are 10000 (a-c), 3500 (d),and 1000 (e-h).

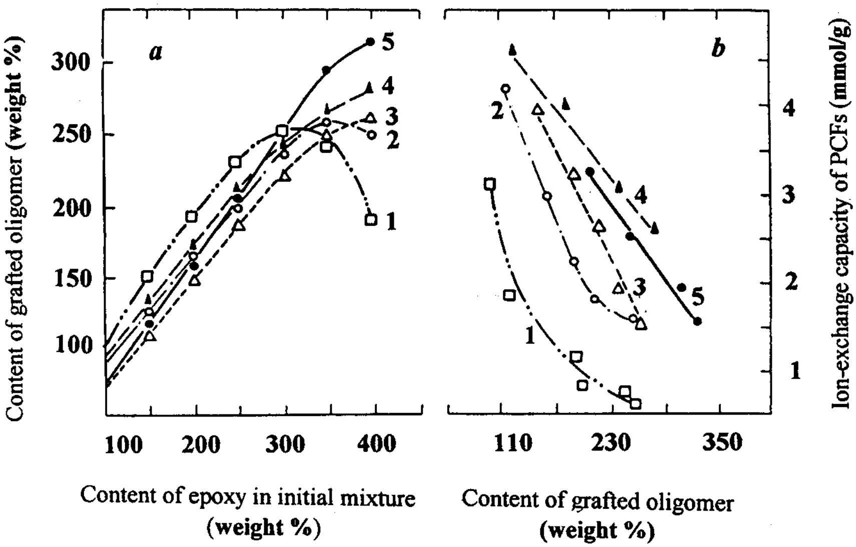


Fig. 4. Dependence of static ion-exchange capacity of PCFs of the amount of ED-20 (1), UP-650D (2), UP-632 (3), UP-612 (4), UP-650T (5) epoxy oligomers grafted to fibers surface.

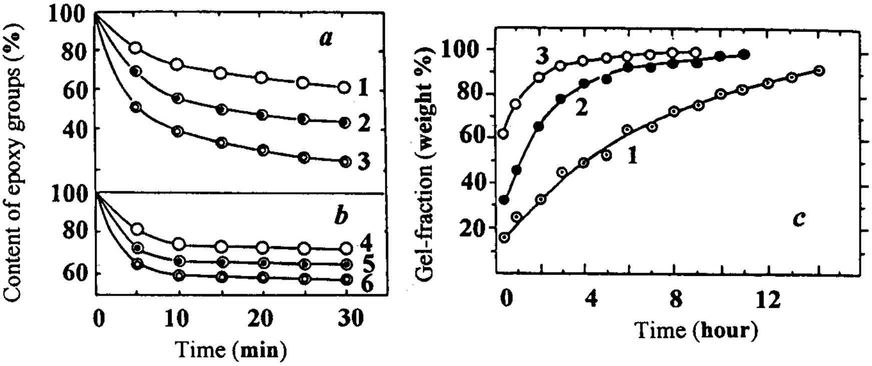


Fig. 5. Change of epoxy groups content (a, b) and of non-extractable from fibers surface gel-fraction yield (c) during the joint heat treatment of UP-632 (a) and ED-20 (b, c) epoxy oligomers and PCFs with phosphorus contents of 3.6 weight % (1, 6), 6.25 (2, 5) and 9,2 weight % (3, 4). The PCFs-epoxy oligomer ratios are 1:1 (c) and 1:2,5 (a, b).

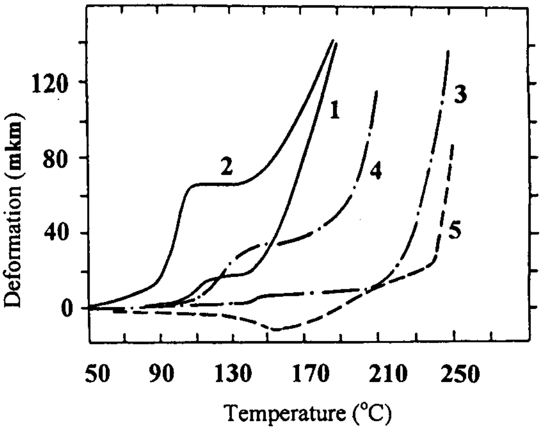


Fig. 6. Thermomechanical curves of the compositions of PCFs with ED-20 (1,2) and UP-632 (3, 4, 5) epoxy oligomers after their joint heat-treatment. The PCFs-oligomer ratios are 1:1 (1, 3, 5), and 1:2 (2, 4). Phosphorus contents in CFs are 4.6 weight % (1-4) and 6.25 weight % (5).

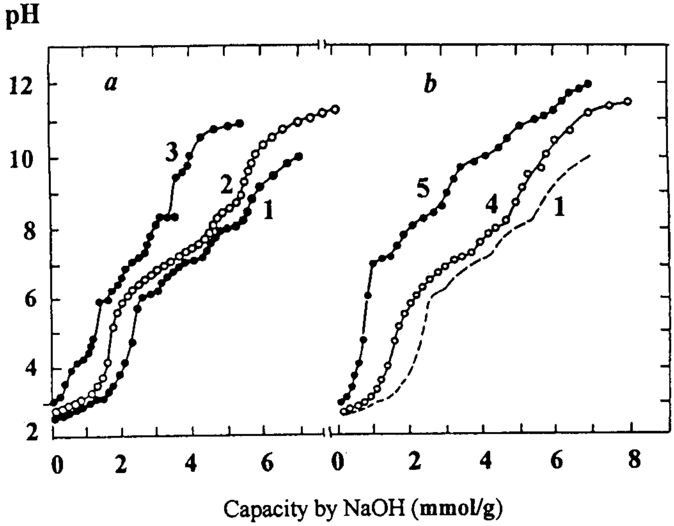


Fig. 7. Curves of the potentiometric titration of initial PCFs untreated by oligomers (1), and with various weignt contents of UP-632 (2,3), ED-20 (4,5) epoxy oligomers grafted to their surface. Phosphorus content in CFs is 6.25 weight %.

intensity narrow absorption band with the maximum at 685 cm^{-1} also testifies to possible transformation of CFs phosphate structures under the influence of its treatment by epoxy oligomers. According to Prodan E.A. and coworkers (24) and also Shagidullin R. R. and coworkers (25), this band along with the absorption band of 660 cm^{-1} range observed for an untreated PCFs may be related to valence symmetrical oscillations of the P-O-P bands. The common pattern of the spectra in the above frequency range for all heat-treated PCFs-epoxy oligomer systems indicates that processes of thermal transformations of PCFs surface groups under the influence of oligomers are similar.

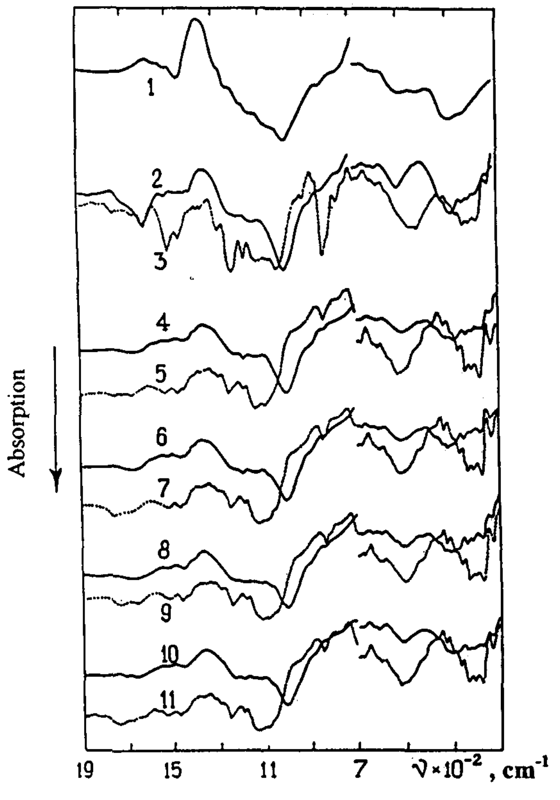


Fig. 8. MATIR spectra of phosphorus-containing carbon fabric before (1) and after their heat treatment with ED-20 (2,3), UP-612 (4,5), UP-632 (6,7), UP-650D (8,9), UP-650T (10,11) oligomers. PCFs-oligomer ratios are: 1:1 (2, 4, 6, 8, 10) and 1:4 (3, 5, 7, 9, 11).

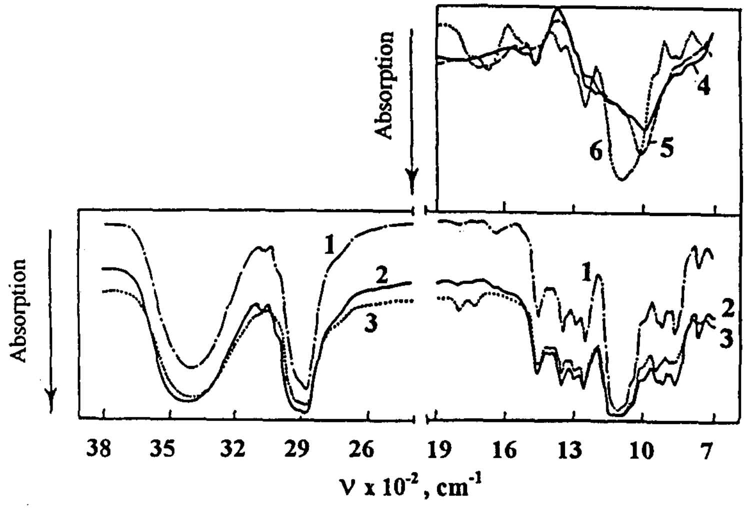
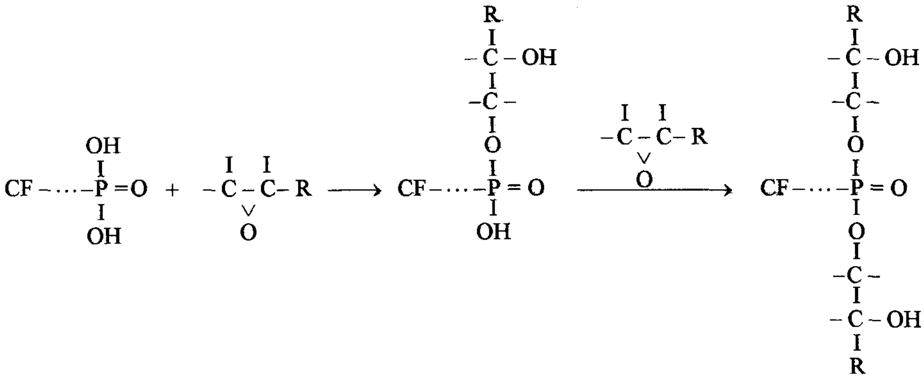


Fig. 9. IR-spectra of DEG-1 oligomer (1) and its mixtures with PCFs before (2) and after (3) heat treatment at 110 °C during 30 min. MATIR spectra of phosphorus-containing carbon fabric untreated by DEG-1 (4) and with the diepoxide gel-fraction, non-extractable from the fibers surface in the amount of 33.1 weight % (5) and 176.2 weight % (6).

Along with the above mentioned changes while increasing the contents of the epoxy oligomer gradually on the PCF surface, changes in the range of 800-1200, 1400-1800 cm^{-1} are observed as well. An absorption band with the maximum at 980 cm^{-1}, representing phosphate-ion absorption (26) shifts towards higher frequencies in the range of 1020-1080 cm^{-1}. At the same time, a new narrow absorption band with a maximum at 1180-1190 cm^{-1} appears. This, in combination with an absorption band in the range of 1030-1050 cm^{-1}, according to Nakanishi (27) represents valency oscillations of alkylphosphates ($P-O-C_{alkyl}$). Such changes can be accounted for by reactions between surface phosphorus-containing groups of CFs and epoxy oligomers. Then, a significant broadening of the integral absorption band observed in the 1020-1150 cm^{-1} range (PCF-DEG aliphatic diepoxide composition, Fig. 9) is due to the superimposition of the absorption band , characteristic of the formed $P-O-C_{alkyl}$ band, on the oscillations of ether groups (1100 cm^{-1} range) characteristic for the initial diepoxide. The appearance of a weak absorption band in the 1330 cm^{-1} range, characteristic of deformation oscillations of CH-group in hydrocarbons with a branched chain (28) also reflects reactions of PCFs with the epoxy oligomers.

Our results imply formation of a chemical bond at the fiber-oligomer interface, probably according to the following scheme:



$$\mathrm{CF{-}\cdots{-}\underset{OH}{\overset{OH}{P}}{=}O} + \mathrm{{-}\underset{\vee\,O}{C{-}C}{-}R} \longrightarrow \mathrm{CF{-}\cdots{-}\underset{OH}{P}(=O){-}O{-}C{-}C(OH){-}R} \xrightarrow{\mathrm{{-}\underset{\vee\,O}{C{-}C}{-}R}} \mathrm{CF{-}\cdots{-}P(=O)(O{-}C{-}C(OH){-}R)_2}$$

where R is the oligomer molecule residue.

Thus, we have demonstrated the possibility of grafting and curing epoxy oligomers directly on the PCF surface, avoiding intermediate compounds commonly used for these purposes. This results in enhancing the PCFs strength by an order of magnitude or more. The grafted polymer is distributed over the entire external surface of monofibers, forming a polymeric "shirt" and isolating the monofibers from each other by a homogeneous film layer. In the case of alicyclic epoxy compounds we have the wetting angle = 0 with the CPF, while for various aromatic structure oligomers the wetting angle is in the range 14.2 - 43.0 °.

The fact that the active role of the PCFs is not limited merely to the interaction at the filler-polymer interface is quite interesting. Electron-microscopic examinations and a chemical analysis show that the increase of additive weight of the non-extractable fraction brings about a gradual filling of the interfiber space with a three-dimensional product (Fig. 3, h). The system is turned into a monolith without introducing standard agents (amines, anhydrides, etc.). In such epoxy compositions the reinforcing filler itself carries out the function of a hardener.

The process of epoxy curing under the influence of a fibrous hardener is complicated; it is determined by the CFs modification. The shape of curves of the epoxy groups conversion without induction periods (Fig. 10) as well as curing rate curves (Fig. 11) show that the process continues with a high initial speed. According to the theory of heterogeneous processes described by Barre P in (29) of such cases correspond to a rapid, possibly instantaneous, seed formation, proceeding with an equal degree of probability at the potential centers, located all over the external surface of the solid phase. Thus, the epoxy oligomer cure

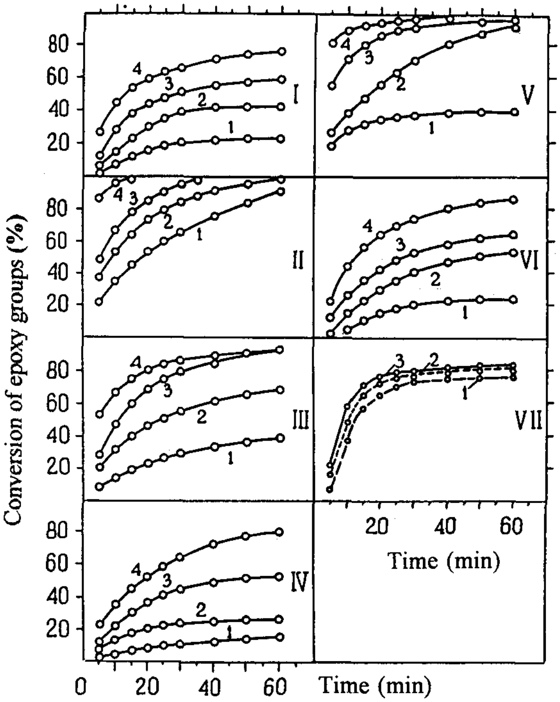


Fig.10. Extent of conversion of epoxy groups while heating at 110 °C (1), 130 (2), 150 (3), 170 °C (4) of ED-20 (I), DEG-1 (II), UP-650D (III), UP-650T (IV), UP-632 (V), EOC (VI) and EOP (VII) epoxy oligomers in the presence of PCFs. Phosphorus content in CFs is 12.1 weight %. PCFs-oligomer ratio is 1:1.

under the influence of PCFs starts from the fiber surface with the direct participation of their reaction-capable groups with a further growth of a kinetic chain in heterophase system bulk.

It is natural to assume that epoxy structure depends on the distance from the PCFs surface. This should be reflected in the morphology of the cured compositions and is indeed confirmed by the SEM results. We also conclude that the surfaces of the initial PCFs are not structurally uniform. Alternative smooth and rough regions are observed; there are granular structures along the same length (Fig. 3, a). A star-like form of the PCFs cross-section is related to the presence of delineated characteristic faces caused by alternating projections and depressions. The oligomer situated in the depression, i.e. in the immediate proximity to the fiber, is subjected to multilateral orientation influence of the fibrous filler surface. As a consequence, the intensity of the structure formation process in the depressions and at the projections may be different. In turn this should result in different supramolecular structures along the fiber perimeter. Such conditions are also

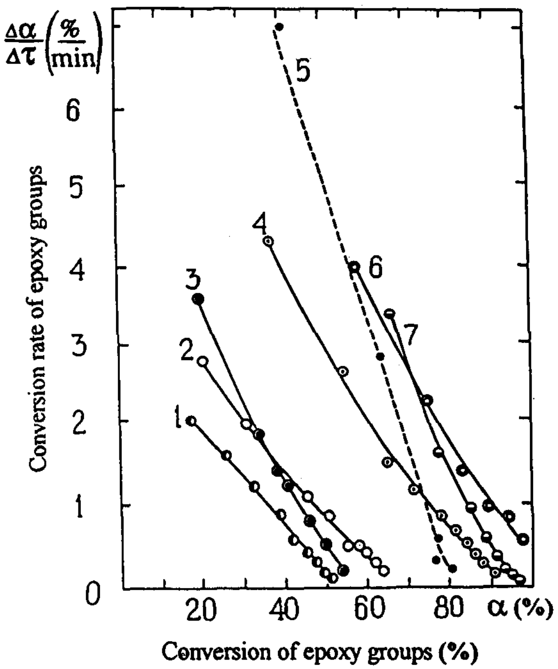


Fig. 11. Conversion rate of epoxy groups while heating at 150 °C UP-650T (1), EOC (2), ED-20 (3), UP-650D (4), EOP (5), DEG-1 (6), UP-632 (7) oligomers with PCFs (1:1 ratio).

supported by our results. Globular formations, characteristic of cured epoxides and structureless fields are seen on the fiber ridges (Fig. 3, b, c, Fig. 12, a - g). An aggregation of regular creases and their orienting across the fiber axis is observed in the depressions. As a consequence, a relief contour of the PCFs faces is observed with an epoxy compound cured on their surface and an alternation of bands with different structures in the ridges and in the depressions.

With the increase of the quantity of the gel-fraction non-extractable from the PCFs surface, one can see aggregated supramolecular formations on the entire external fiber surface; they consist of globules of different sizes (Fig. 3, c) and appear to be the cause of a mosaic surface of the fiber dipped in the polymer (Fig. 3, d). In the interfibrous space, i.e. in the bulk, the structure differs from that in the fiber surface layer. Fibrillar formations with a prevailing directionality are observed (Fig. 12, g, h). In the polymer layers adjacent to the fiber, we see chain structures varying from small globules to of ridges, located at angles close to 90° (Fig. 12, c, d).

Thus, the epoxy compositions cured by PCFs are structurally non-uniform. Due to the intense chemical interaction of active surface fiber groups with the oligomer, there is no distinct

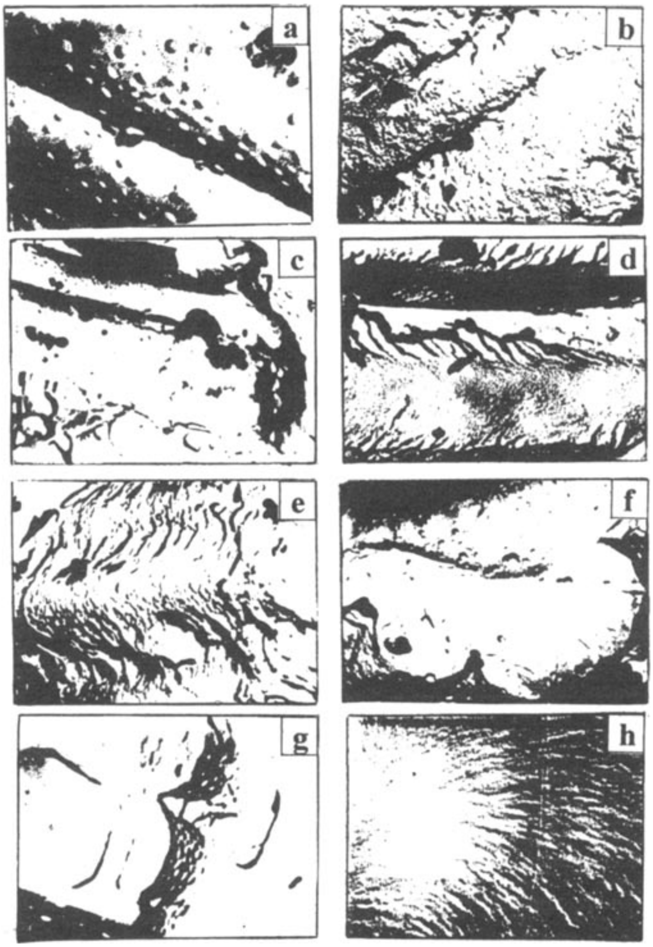


Fig. 12. Electron-micrographs of ED-20 (a, c, e-h) and UP-632 (b, d) epoxy oligomers, hardened by PCFs. Magnification of 10000 (c, e, f), 20000 (f, g, d) and 30000 (b, h).

filler-polymer interface visible in SEM. The strength of the formed bond is higher than the cohesion forces of the cured binder. The fracture character of the composite is confirming all these facts, particularly, at the projected regions of the fibers (Fig. 12, g) and even at its cuts (Fig. 12, f) a cured binder is seen. That is, the destruction occurs not along the interface but inside the binder bulk.

Distinctions in the supramolecular formations sizes are also revealed for the epoxy oligomers of various chemical structures during their curing by the PCF: small globules for alicyclic structure oligomers (Fig 12, b, d) and rather large ones, at a distance from each other, for aromatic series epoxy oligomers (Fig. 2, a, c, e, g). The comparison of the compressive and tensile strength indexes of the epoxy oligomers of different chemical nature in their curing by the PCFs indicates that compositions of the PCFs with alicyclic epoxy compounds have a large compressive strength whereas higher indexes of tensile strength are characteristic for compositions of the PCFs with the aromatic structure epoxy oligomers.

The high degree of hardening of epoxide oligomers of all types under the influence of CFs (88.2-99.9 per cent by weight) (Fig. 13, a) brings us close to solving the problem of forming epoxide composites by excluding standard hardening agents from the binder. By using CFs with a complex function (that of a filler and a hardener) one can obtain composites with useful properties. For example, composites with different level of fire-proof properties have been developed, assuming as a basis the principle of a dominance of chemical interactions of element-containing carbon fibers with a polymer in the boundary zone (30). Non-inflammable and not fuming composites suitable for the application as tool working parts for polishing optical parts have been developed (31). Controlling the processes proceeding at the interface, it was possible to produce composites with oxygen index value significantly exceeding typical values (Fig. 14). In a number of cases the theoretical limit of 100 % was achieved.

Complex physico-chemical interactions of the PCFs with a binder lead to a change in a cured matrix thermal decomposition character. From Fig. 2 it is seen that the rate of thermal degradation changes and decomposition maximum and onset temperature are shifted; the amount of the coke residue increases. Decrease in the amount of solid fume particles released during burning is also observed. For some fire-proof composites thermal decomposition may proceed without fuming altogether while preserving the integrity of the form. This is a significant advantage of our compositions; fatalifies during fires have been caused by considerable fuming and a high toxicity of the decomposition products. It should be emphasized, that the composites produced with the exclusion of the usual curing agents will evolve less toxic products under conditions of thermal decomposition (32).

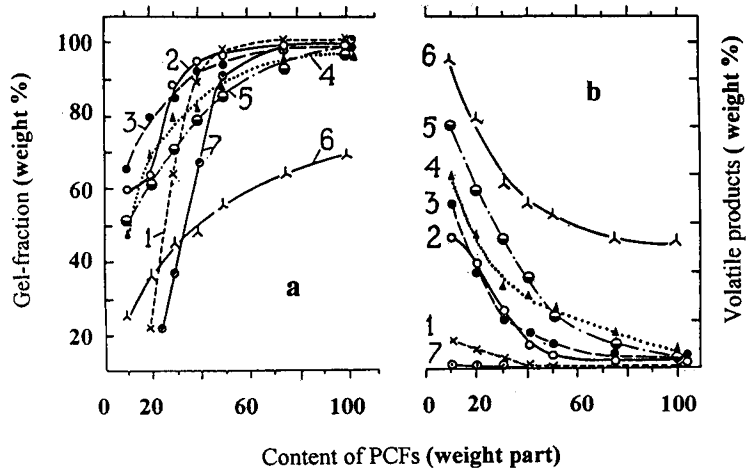


Fig. 13. The gel-fraction yield (a) and the amount of evolved volatile products (b) during the heat treatment of the compositions containing 100 weight parts of ED-20 (1), UP-650T (2), UP-612 (3), UP-650D (4), DEG-1 (6), EOC (7) oligomers and various weight amount of PCFs.

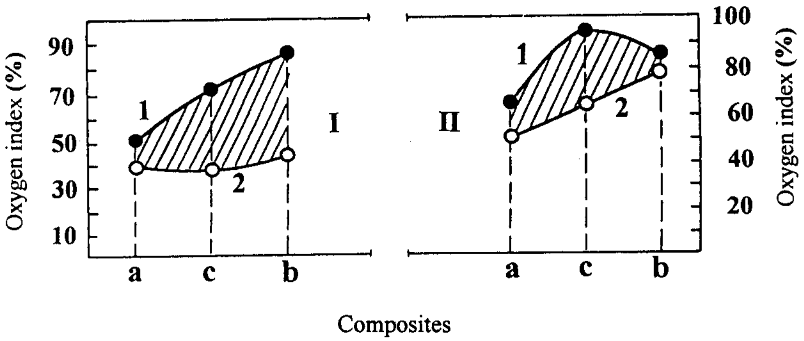


Fig. 14. Experimental (1) and calculated (2) values of oxygen index for epoxy compositions N I and N II hardened by PCFs for different ratios of components (a, b, c).

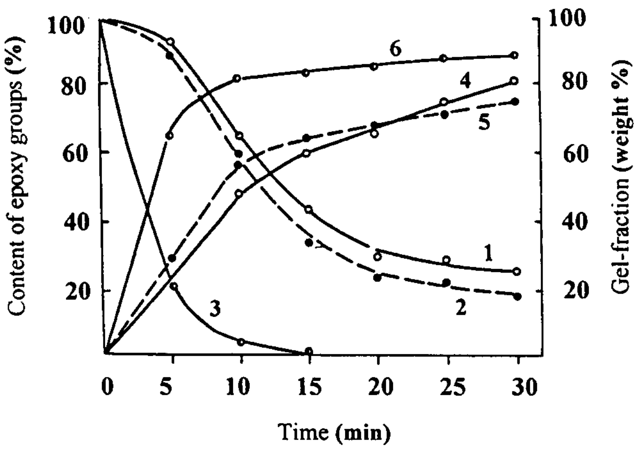


Fig.15. The change of epoxy groups content (1-3) and of the gel-fraction yield (4-6) duringhe heat treatment at 160 °C of the binder on the basis of UP-632 oligomer and anhydride hardener unfilled (1, 4), and filled with non-modified Cfs (2, 5) and with PCFs (3, 6).

An effective use of PCFs is ascertained for forming epoxy compositions highly filled by powders and other fibrous fillers to create materials with defined properties. As it is seen from Figure 15 that by introducing PCFs into an epoxy binder with anhydride hardener the process of curing is intensified; the rate of transformation of epoxy groups and gel-fraction output increase. The compressive strength of compositions containing substantial quantities of powders with use of active PCFs as a hardener or cohardener of an epoxy binder are higher than those for typical compositions (33, 34).

REFERENCES

1. Phitzer, Carbon fibers and carbon composites. Tr. from English, Chemistry, Science, Moscow (1988)
2. Konkin, Carbon and other fire-proof fibrous materials, Chemistry, Moscow (1974)
3. Simamura, Carbon fibers. Tr. from the Japanese, Universe , Moscow (1987)
4. Yermolenko, R.N. Sviridova and Z.I. Kuvaeva, US Patent 3702832, C 01 b 31/08, Pyrolytic carbon fibers
5. Yermolenko, A.M. Saphonova, R.I. Belskaya, et al, Vestsy Akad. Navuk Belarusi Khim. Ser., 5, 17 (1976)

6. Yermolenko, V.I. Savik and V.I. Dubkova,. Vestsy Akad. Navuk Belarusi Khim. Ser., **5**, 22 (1976)

7. Yermolenko and M. Z. Gavrilov, Colloid. Zh., **37**, 156 (1975)

8. Yermolenko, P. I. Sviridova and A.L. Belanovich, USSR authors' certificate, 730585, B 29 C 13/00 (1980)

9. Yermolenko, I. P. Lyubliner and N. V. Gulko, Element-containing carbon fibrous materials, Science and Technology, Minsk (1981)

10. Yermolenko and V.I. Dubkova, Dokl. Akad. Navuk Belarusi, **28**, 239 (1984)

11. Yermolenko, V.I. Dubkova, A. I. Burya and A. G. Levi, Zh. Prikl. Khim., **60**, 2301 (1987)

12. Burya V. I. Dubkova and A. S. Kobets, in Proceedings of International Conference on the Tribilogy of High Friction Materials, Yaroslavl, Russia, 45 (1991)

13. Dubkova, S .A. Gordynets, S. Stancheva, et al, Vestsy Akad. Navuk Belarusi, Khim. Ser., **1**, 39 (1992)

14. Marhol, Ion Exchangers in Analytic Chemistry. Their Properties and Use in Inorganic Chemistry, Academia, Prague (1982)

15. Dubkova, I.N. Yermolenko, A. I. Byria and V. T Dorophеev, Mech. Compos. Mater., **2**, 231 (1987)

16. Kline, Analytical Chemistry of Polymers, Foreign Literature, Moscow, 1 (1963)

17. Chernin, F. M. Smehov and Yo.V. Zherdev, Epoxy polymers and compositions, Chemistry, Moscow (1982)

18. Yermolenko and V.I. Dubkova, J. Thermal Analysis, **34**, 783 (1988)

19. Smit,. Prikladnaya spektroskopia. Osnovy: tekhnika, analiticheskoe primenenie, Universe , Moscow (1982)

20. Mironov, and S. A. Yankovski, Spectroscopy in Oganic Chemistry, Chemistry, Moscow (1985)

21. Xarrik, Spectroscopy of Internal Reflections, Universe , Moscow (1970)

22. Tekhnika Elektronnoi mikroskopii, D. Keyia Editor, Tr. from English, Universe , Moscow (1965)

23. Skorynina, S.S. Gysew, N.K. Vorobeva and I.N. Yermolenko, Vysokomol. Soed., **12 A**, 2452 (1970)

24. Prodan, L.I. Prodan and N.F. Yermolenko, Threepolyphosphates and their applications, Science and Technology, Minsk (1969)

25. Shagidullin, F.S. Muhametov and R.B. Nigmatullina, Atlas of the phosphorus-containing compounds, Science, Moscow. (1977)

26. Bellami, Infra-red spectra and structure of the organic compounds, Foreign Literature, Moscow (1965)

27. Nakanishi, Infra-red spectra and structure of the organic compounds, Universe , Moscow (1965)

28. Kazitsyna and N.B. Kypletskya, Application of UV-, IR- and NMR- spectroscopy in organic chemistry, The Higher Scool, Moscow (1971)

29. Barre. Kinetics of heterogeneous processes, Universe, Moscow, Russia (1976)

30. Dubkova, A.I. Burya and N.I. Rakhmangulova, presented at the 6th Soviet Conference on the Burning of Polymers and Creating Materials with Low Flammability, Suzdal, Russia (1988)

31. Dubkova, V. S. Galkov, N. P. Zybchenkova et al, First International Conference on Polymeric Material of Low Combustibility, Alma-Ata, Kazachstan, **2**, 53 (1990)

32. Burya V.I. and Dubkova, in New materials and Technology in Tribology, Proc. of International Conference on the Tribology, Minsk , 101 (1992)

33. Dubkova and A. I. Burya, in Proceeding. of XV Mendeleev Congress on General and Applied Chemistry, Minsk, **1**, 356 (1993)

34. Dubkova and N. P. Krutko, in New material and technologies, Proc. of Joint India-Belarus Conference : BIMTEX'97, Hyderabad, India, 59 (1997)