Chigvintseva O., Dašić P.

The research of polymer composites based on polyarylate polyester

Vrnjačka Banja, Serbia
SaTCIP Publisher Ltd.

2019

UDC 678.7-19.01

For publisher:

Jovan Dašić, Director of the firm SaTCIP Publisher Ltd. –
Vrnjačka Banja

Reviewers:

1. Prof. Dr Anatoly P. Avdeenko, Donbass State Engineering Academy (DSEA), Kramatorsk (Ukraine)
2. Prof. Dr Milutin Milosavljević, Faculty of Technical Sciences, University of Pristina with headquarters in Kosovska Mitrovica, Kosovska Mitrovica (Serbia)
3. Prof. Dr RankoSimonović, University of Prištinawith temporary headquarters at Kosovska Mitrovica, Faculty of Natural Sciences, Kosovska Mitrovica (Serbia)

Chigvintseva O., Dašić P. The research of polymer composites based on polyarylate polyester. Vrnjačka Banja, Serbia: SaTCIP Publisher Ltd., 2019. – 180 pp.

ISBN 978-86-6075-071-8

The scientific monograph reflects scientific research on the study of the nature and content of fibrous and dispersed fillers on the main performance characteristics of composites based on polyester polyarylate

PREFACE

At present the biggest specific gravity in total volume of the polymer production occurs on thermoplastic binders and composite materials on its base [1-3]. They differ from thermosetting polymers with smaller durance engineering cycle and sensibility to damage, ability for secondary recast, raising the destruction adherence, ability to decrease the cost-to-build figure with the perpetual existence. Choosing the thermoplasts with different chemical structure and stated elasticity module and deformability and changing type and filler loading it can greatly expand branded range of the composites materials:

– range of application – deformational-constructional, high endurance, high module, fireproof, chemical and waterproof, electrotechnical, frictionproof, etc.;

– recast – founding under pressure, extrusion, pultrusion, vacuum- and pneumoforming, covering, pressure stamping, melting etc [2, 4-5].

Approximately 60% of volume of the thermoplast production belongs to polymer large-capacity of the general purpose: polyethylene, polyvinilchloride, polysterene. The rest percentage belongs to structural plastic (polypropylene, aliphatic polyamide, polyester, polyuretane, polycarbonate) and polymers with specific physical and special properties [6-9].

Polyarylates belong to a very perspective class of thermoplastical polymers, which applied to complex aromatic polyester. These polymers, composed by rigid macromolecules, saturated aromatic core differ high heat-, thermo- and chemical endurance, impact adherence and good form maintainability after deformation [10].

Polymer materials, received from diacyl chlorides, iso- and terephthalic acids mixing with diphenylolpropane hybrid polyesters "Daron 40", made by DSM (USA), PAE-1, made by "Dynamite Nobel" and "U-polymers", made by "Unitica Ltd" (Japan) and also polyarylates D and DV have the most practical interest.

Amorphous polyarylates based on diphenylolpropane and iso- and terephthalic acids are linear polyesters with high heat resisting under the load and UF resisting, and also have high crash worthiness, ability to self-damping, electric characteristics, high endurance and elongation during the disruption [11].

At the end of this book is also a list of abbreviations and abbreviations, which lists abbreviations and abbreviations for polymers, polymer composites and polymer matrix composites, polyarylate and related polymeric materials, synthesis, characteristics and properties of polymeric materials.

CONTENTS

CHAPTER 1. POLYARYLATE BASED COMPOSITES

1.1. Preparation, properties and application of composites based on polyarylate

Currently, the largest share in the total volume of polymer production falls on thermoplastic binders and composites materials (CM) based on them [12–15]. They differ from thermosetting polymers in the following advantages: shorter technological cycle, the possibility of secondary processing, increased fracture toughness and less sensitivity to damage, the prospect of lowering the cost of manufacturing products, unlimited shelf life.By selecting thermoplastics of different chemical structures with a given modulus of elasticity and deformability, changing the type and content of the filler, it is possible to maximally expand the branded range of composite materials: in terms of application – deformation-structural, high-strength, high-modulus, fireproof, chemically and waterproof, electrical, antifriction, etc., and for processing – injection molding, extrusion, pultrusion, vacuum and pneumatic forming, wrapping, pressure stamping, welding, etc. [14, 16–17].

About 60% of the volume of thermoplastic production falls on large-scale general-purpose polymers: polyethylene, polyvinylchloride, polystyrene, the rest is engineering plastics – polypropylene (PP), aliphatic polyamides (PA), polyesters, polyurethanes (PU), polycarbonates (PC) and polymers with special physical or special properties [27–30]. The upper temperature of long-term operation of large-scale polymers is below 373K, and by modification it is possible to increase this temperature only slightly.

Taking this into account, high-temperature engineering plastics with unique properties are very promising for the development of new polymer composites materials (PCM). These are, first of all, polyarylate (PAR), polyphenylene sulfide (PES), polyimide (PI), polyamidoimide (PAI), polyetherimide (PEI), polysulfone (PS), polyethersulfone (PES), polyetheretherketone (PPEK), liquid-crystalline polymers, and others [17, 18–20]. High temperature resistant polymers with sales of $ 2.5 billion cover 14 polymers produced by 35 companies [21]. The total volume of the world production of such polymers reached 50 thousand tons [21–22]. The total consumption of highly heat-resistant thermoplastics (TP) in Europe amounted to 5.85-7 thousand tons [23], in Japan – 16.7 thousand tons [24].

Along with polyimide and phenylone, complex aromatic polyester PAR, due to the relatively simple processing technology and availability of raw materials, is one of the most thermo-, heat- and chemically resistant polymer binders commercially available in the industry.

It is known that certain types of thermoplastics in some cases of application cannot provide the required properties, and this drawback can be overcome by creating thermoplastic mixtures and polymer alloys [25, 26].

The viscosity of the melts and the high softening points of PAR complicate their processing at 573–673K, which imposes stringent requirements on equipment and tooling [4, 27]. To increase the formability, polymer mixtures of PAR with PA have been developed, which have high chemical and thermal stability, bending stiffness, impact strength, gas tightness, and other properties [28-29].

Improved thermoplastic PAR-PA compositions are obtained using compatibility agents, which are various copolymers (for example, polyester copolymers with simple and ester bonds [30] copolymers of styrene, maleic anhydride, ethylene and glycidyl methacrylate [27], according to -limers with functional epoxy groups [31], ionomers [32], linear hydrocarbon with a molecular weight of 300-10000 [33], which are reactive type.

The introduction of 0.1-15 parts of epoxy resin into the mixture of PAR and PA-6 (per 100 hours of the mixture) leads to the production of compositions for the manufacture of durable, thermo-, light- and fire-resistant transparent products with high rigidity, impact resistance and the action of solvents [34]. Moreover, their properties exceed those of compositions without epoxy resin.

By mixing PA-46 with PAR, a material with increased heat resistance and bending strength is obtained, which is used in the manufacture of automobile parts and electrical devices [35]. Up to 80% of reinforcing agents (glass, carbon, silicon carbide, polyamide fibers, asbestos, graphite, wollastonite, potassium titanates, talc, chalk, mica, clay, granular glass) can be added to these compositions.

When polyoxyesters are added to mixtures of PAR and PA, compositions with significantly improved properties are obtained, for example, elongation at break, tensile strength, notched Izod impact strength, and uniformity of the material obtained by injection molding [36]. A composition with excellent moldability, heat resistance, resistance to heat aging, per 100 hours of a mixture of PAR and PA (PA-6 or 6.6) contains 0.001–1 hours of phosphite [37].

To increase the fire resistance of PAR/PA compositions, Unitika uses aromatic halogen-containing compounds [30] oxides and/or halides of metals of groups IVB, IB, IIB, IIIA, IVA [38], hydrotalcite [39].

Technological impact-resistant compositions are prepared by mixing PAR/PA mixtures with additives that increase the impact strength. First of all, these are polyolefins modified with compo-unds containing anhydrides, ester or epoxy groups [40, 41]; as well as elastomers (ethylene-propylene, butadiene and nitrile rubbers) [42] (Table 1, p. 1–6).

It should be noted that in order to obtain materials processed from the melt into articles with improved surface properties, impact strength, and heat resistance, the company “Kanegafuchi Chem. Ind. Ltd.” (Japan) in a mixture with PA, PARs modified with oxazoline [43] and epoxy compounds [44] are used.

Thermoplastic mixtures of PAR with epoxidized polymers [45], in additionto high thermal stability in dry and humid atmo-

Table 1.1: Properties of polymer mixtures based on polyarylates

№	The composition of the polymer compositions	Viscosity of the melt 10 000 P at temperature, K	Izod impact strength, kJ/m^2	Heat re-sistance under a load of 1.8 MPa	Tensile strenth, MPa	Elastic modulus in tension, MPa	Destruction energy in ension, kg · cm
1.	Polyarylate (p-hydroxybenzoic acid, isophthaleic acid, diphenylolpropane) – 50 parts; PA-6 – 50 parts; epoxy resin (mel. t. 425 K)	543	4,2	–	60,7	2170	–
2.	Tere- and isophthalic acid polyarylate, diphenylolpropane); “U-100”– 50 parst; polyamide – 6 – 50 parts	272	1,6	438	42,0	2110	220
3.	Polyarylate “U-100”– 50 parts; polyamide-6 – 50 parts; epoxy resin (Epichlon 9055) – 5 parts	323	12,5	433	65,9	2280	1740
4.	Polyarylate“U-100”– 50 parts; polyamide-46 – “F5000”– 50 parts	–	–	558*	150**	3000***	–

Notes: ** Heat resistance at a load of 0.45 MPa; ** Flexural strength, MPa; *** Modulus of elasticity in bending, MPa*

Table 1.2: Properties of polymer mixtures based on polyarylates

№	Heat resistance under load 0.45 MPa, K	Heat resistance under load 0.45 MPa, K	Impact strength with overcut, kJ/m^2	Tensile strength, MPa
1	2	3	4	5
1.	Polyarylate (tere- and iso-phthalic acid 7: 3, diphenylolpropane) – 50 parts; polyamide-6 (Amilan CM-1026) – 50 parts; copolymer of ethylene, propylene, maleic anhydride (melt index 1.5g/10 min at 523 K, load 0.22 MPa) – 10 parts; copolymer of styrene – 70 parts, acrylonitrile – 20 parts; and glycidyl methacrylate – 10 parts with a melt index of 10 g/10 min (at 398 K, a load of 0.22 MPa) – 2 parts **	451	37,5	–
2.	Polyarylate (tere- and iso-phthalic acid 3: 7, diphenylolpropane) – 50 parts; polyamide-6 – 50 parts; copo-lymer of styrene – 15 parts, methyl methacrylate – 15 parts, polybutadiene latex – 70 parts	447	63	57,5

Continuation of Table 1.2.

1	2	3	4	5
3.	Polyarylate (tere- and isophthalic acid 4: 1, diphenylolpropane) – 45 parts; polyamide-6 (Amilan CM-1026) – 45 parts; copolymer of ethylene and glycidyl methacrylate (Bondfast E) – 10 parts	439*	40	–
4.	Polyarylate (tere- and iso-phthalic acid 7: 3, diphenylolpropane) – 45 parts; polyamide-6 – 45 parts; copolymer of ethylene and glycidyl methacrylate (Bondfast E) – 4 parts; copolymer of ethylene, ethyl acrylate and maleic anhydride (Bondain AX-8390) – 6 parts; stearic acid – 0.5 parts	442	63	58,1
5.	Polyarylatediphenylolpropane, bis-phenol OH–Ar–CO–Ar–OH, iso- and terephthalic acid 9: 1) – 45 parts; PA-6 – 45 parts; Bondfast E – 3 parts; Bondain AX-8390 – 7 parts	453	54	57,3
6.	Polyarylate (based on diphenylolpropane with glass temp. 573 K) – 50 parts; polyamide-6 – 50 parts; Bondfast E – 5 parts; copolymer of ethylenepropylene rubber with endobicyclo-[2.2.1]-5-heptene-2,3-dicarboxylic acid anhydride grafting – 5 parts	449*	28,4	–

Notes: ** Heat resistance at a load of 1.8 MPa; ** Modulus of elasticity in tension – 2300 MPa* spheres, also have high resistance to cracking in solvents, for example, fats, edible oils,polar solvents. A powder mixture consisting of epoxy-terminated hydantoindiepoxide and DF-based PAR with one side aromatic ring bonded to a central carbon atom with acidic end groups is used to apply heat-resistant electrical insulating coatings.

The mixture is applied to a heated substrate, on which melting and reaction occurs with the formation of a continuous infusible electrical insulating layer [46]. In order to reduce the temperature and time of curing of compositions containing 10-60 hours of PAR per 100 hours of epoxy binder, 0.04 hours of a catalyst are used- asalt of an alkali or alkaline earth metal and a weak acid, for example, benzoates Na, K [47]. Such cured compositions have a glass transition temperature of 333 K and a wide range of highly elastic state with a modulus of elasticity of 0.4 MPa, do not exhibit a viscous flow state up to the decomposition temperature (673 K) and do not dissolve in chloroform.

Heat-resistant compositions of PAR with polyolefins [48], such as PP (10-20 hours per 100 hours of PAR), low-melting (3-30 parts by weight per 100 hours of PAR), and ultra-high molecular weight have been developed, PE, polytetrafluoroethylene (5-80%).

Modification of PAR by the addition of ultra-high molecular weight polyethylene [49] and polytetrafluoroethylene (Teflon 6j and 7j, Daikin, Rublon L-2, L-5 and LD-1, KTL-610) with the addition of graphite [50] or Dyuracon M-90 phosphoropoly-methylene oxide salts [51] allows to obtain materials with increased abrasion resistance and improved antifriction properties.

Compositions based on PAR contain a small amount of fibril-forming fluoropolymer, which gives molded articles from them a predominantly uniform wall thickness [52]. The concentration of the terminal carboxy groups of the PAR resins is reduced by melting the PAR resin with an aromatic carbonate, the amount of which varies from equimolecular to a slight excess in relation to the carboxyl groups. Among aromatic carbonates, diphenyl carbonates, unsubstituted and substituted oligomers or polymers are used as a blocking agent [53]. The mixture reacts upon heating to form a PAR resin having partially blocked carboxy end groups.

Mixtures of PAR with polycarbonate (PC) [54, 55] are single-phase solid solutions of compatible polymers. Compositions from them have high thermal stability, ability, impact resistance, resistance to solvents and good formability (Table 1.3, p. 2).

By mixing 8-80% phosphorus-containing polycarbonate with 20-92% PC [56], compositions with high thermal and fire resistance and the ability to be molded from the melt are obtained.

The introduction of at least 1 part of potassium titanate and 0.1–10% (based on titanate) of carboxylic acid into a mixture of PAR and PC makes it possible to increase the dimensional stability of products, while maintaining high other properties [57]. To obtain materials with improved resistance to yellowing on heating and impact strength at low temperatures, a mixture containing polyphe-

Table 1.3: Properties of polymer mixtures based on polyarylates

№	The composition of the polymer compositions	Viscosity of the melt 10 000 P at temperature, K	Izod impact strength, kJ/m^2	Heat re-sistance under a load of 1.8 MPa	Tensile strenth, MPa	Elastic modulus in tension, MPa	Destruction energy in ension, kg · cm
1	2	3	4	5	6	7	8
1.	Polytetrafluoroethylene – 78 parts; polyarylate “Econol”– 20 parts; graphite – 2 parts*	–	–	66,0	2275	48	–
2.	Polyarylate (diphenylol-propane, tere- and iso-phthaleic acid 1 : 1 – 50 parts; polyester carbonate – 50 parts	435	17,2	66,0	2275	48	435

Continuation of Table 1.3.

1	2	3	4	5	6	7	8
3.	Polyarylate (diphenylolpropane, tere- and isophthalic acids 1: 1-50 parts; polycarbonate (diphenylolpropane, $COCl_2$) – 50 parts; mixture: poly-2,6-dimethyl-1,4-phenylene oxide and styrenebutadiene copolymer TR 1101 (65:35) – 20 parts	428	233K – 10; 243K – 31; 253K – 49; 263K – 60; 273K – 59; 296K – 60**	–	–	–	428
4.	Polyphenylene oxide – 30 parts; polyarylate – 23 parts; polybutylene terephthalate – 14 parts	373	76,4	49,4	–	121	373
5.	Polyarylate – 50 parts; polyketone – 50 parts	420	53,0	83,0	2640	108	420

Notes: ** Static and dynamic coefficients of friction are, respectively, 0.04 and 0.05, wear – 0.001 mg / h at P = 0.25 MPa, v = 0.6 m/s;** Impact strength according to Izod, kJ/m*^{2}.

nylene oxide and copolymer of styrene and butadiene (Tabl.1.3, p.3); is added to the PAR-PC mixture; a grafted acrylate elastomer (not containing an epoxy group) obtained by a two-stage graft copolymerization of an ester of methacrylic acid, styrene or acrylonitrile with a rubber based on an acrylic acid ester previously copolymerized with butadiene [58].

Electrical products are made from polymer compositions that are a mixture of aromatic PAR, PC, polyalkylene terephthalate, glass fiber and an inhibitor of the exchange reaction of complex polyester and aryl [59].

Loop printed circuit boards and other conductive devices are formed from materials consisting of amorphous thermoplastic PAR and crystallizing polymer (polyethylene terephthalate (PETP), polybutylene terephthalate (PBTP),polypropilene (PP), PA, polyphenylene sulfide (PPS), polycyclohexanedimethyleneterephthalate).

Moreover, the most convenient for application to a substrate is a mixture of PAR and PCDMT. Injection molded products from the composition are treated with a solvent (DMF, methyl(ethyl)ketone, (ethyl) butyl acetate, 1,3-dichloroiso-propanol, toluene, γ-butyrolactone, o-dichlorobenzene, cyclohexanone or a mixture thereof until the surface swells slightly, then annealed to obtain the required crystallinity and heat resistance (≥ 503 K) [60].

Polymer mixtures of PAR with polyalkylphenylene ethers [61], in addition to high thermal stability and fluidity during molding, have an increased crystallization rate, are resistant to hot water and steam. Using these components of a certain logarithmic viscosity, transparent compositions are obtained [62]. At reduced pressure and a temperature of 478–493 K, a resin for powder paints can be synthesized from them [63].

An unstretched heat-shrinkable film or sheet used as a packaging material is made from the copolymerization product of PAR and linear polyester resin [64]. It can be subjected to two or more stretching in one or more directions. In the production of frosted film, a charging leader for magnetic tapes, wallpaper, and synthetic paper, films are used from a mixture of PAR, complex linear PEF, styrene, or acrylate resin [65]. The specified film is stretched not less than 1.5 times in at least one direction.

Weatherproof compositions with improved fluidity during molding, good workability and high mechanical, thermal and electrical characteristics are obtained from a mixture of PAR with PSF [66]. Moreover, PSF, mixed with PAR, has a higher impact resistance than one PPS. Improvements in the compatibility of PAR-polyphenylene sulfide mixtures are achieved by adding compatibility agents: SPL of styrene, maleic anhydride, ethylene and glycidyl methacrylate; the specified copolymer is a vinyl polymer [27] and SPL of glycidyl methacrylate, N-phenylmaleimide, 1,6-azobisisobutyronitrile [60]. Homogeneous molded articles made of them have increased impact resistance, thermal and chemical resistance, average surface roughness ≤ 2 mcm.

Solvent-resistant, compatible compounds with various mechanical properties under impact and tension are obtained from compositions of polyphenylene oxide and a mixture of TPP PEF: PAR, PBTF and PC [50, 51] (Table 1.3, p. 4).

Polyindane obtained by polymerization of diisopropenylbenzene containing 95-100% indane units significantly improves the processing of PAR [63]. From mixtures of PAR with polyaryletherketones with good manufacturability during melt processing, plates are made, used as panels in aircraft, with increased fire resistance and strength characteristics [64] (Table 1.3, p. 5). Developed compatible mixtures of PAR with imide-containing polymers [65, 66] used in the production of extruded sheets and profiles, high-temperature resistant couplings, aircraft and cargo vehicle interiors, injection molded and thermoformed products, adhesives, coatings and fiber-reinforced materials.

So, compositions containing: 0.1-0.3 mass % polycarbodiimide, have increased melt flow rates at 623 K and resistance to cracking of products based on them [67]; polyimides or poly-(iso-imides) exhibit improved adhesion to various substrates, resistance to creep and cracking, tensile strength, water absorption < 2% and dielectric constant 5 [68]; polybenzimidazoles – good thermal and moisture resistance, resistance to solvents [69].

Polymer mixtures consisting of PAR and polyorganosiloxane are biologically inert, resistant to hydrolysis, and permeable to oxygen, due to which contact lenses are made from them [70]. Increased resistance to stress cracking, while maintaining high other properties of PAR are characteristic of compositions with polyxylylene [71] and polyoxyphenylene-2-hydroxypropylene [72].

Modification of PAR with oligoarylates [73] makes it possible to control the melt flow rate in a targeted manner by changing the amount and molecular weight of oligoarylates. At the same time, high physical and mechanical parameters are maintained and the thermal stability of the PAR is increased.

New possibilities for creating materials with a high level of properties are provided by the use of liquid crystal PAR. Since the mid-70s, research has been carried out related to the creation of structural materials based on thermotropic PAA, and not fibers, as it was before [74, 75].

To obtain products with increased heat resistance, mechanical strength and resistance to delamination, materials with improved melt flowability are used, containing ≥ 2 liquid crystal fully aromatic PEF [76].

To give polymers various special properties, they are filled with finely dispersed or fibrous NPs. The amount of filler is selected in such a way that the resulting material has the required property, but the level of other useful properties (especially strength) does not decrease [77]. Plastics with high manufactura-bility, stability of physical and mechanical properties and dimensions of products under the influence of temperature, moisture and other factors, good appearance are obtained by introducing inorganic NPs into the PAR: oxides, nitrides, carbides, carbonates, metal silicates, kaolin, alumina, mica, asbestos, talc, graphite [78 – 79].The introduction of small amounts (0.25 – 2%) of filler, such as zirconium, titanium, titanium carbide, makes it possible to regulate the supramolecular structure during processing and to obtain injection molded products with increased specific impact strength (up to 100-200 kJ/m^2) [78], ground silicon oxide – to obtain melts with a viscosity of 4 Pa· s (at 633 K) [80].

Sometimes inorganic fillers are treated with silane dressing agents and organic acids or their derivatives [81, 82], copolymer of acrylate and maleic anhydride [82], increasing the processability of materials during molding. Electrically conductive polymer compositions are prepared from a mixture of PAR with 3–15% conductive carbon black, 1–20% graphite, and 0.1-5% polytetrafluoroethylene fibers [83]. Molding compositions that are not subject to foaming during processing and a decrease in the viscosity of the melt contain 0.5–5% of carbon black [84].Optical elements with an embossed coating of transparent PAR, having in a polymer matrix a three-dimensional framework of inorganic and organically modified inorganic components in the form of nanoscale particles and/or a molecular network, are obtained by mixing PAR with a sol of nanoscale particles (oxides, sulfides, selenides, tellurides, halides, carbides, arsenides, antimonides, nitrides, phosphides, phosphates, silicates, titanates, zirconates, stannates, aluminates) in an organic solvent and a polymerization initiator [85].The mixture, after reaching the appropriate viscosity, is applied to the substrate and the resulting coating, with simultaneous thermal and photochemical curing, is embossed using a special punch. Thus, diffraction gratings, interferometers, splitters, multiplexes, waveguides, optical switches, sensitive and holographic elements are obtained. Molybdenum disulfide and graphite, the particles of which are in the form of flakes, reduce the coefficient of friction; therefore, their introduction into the PAR allows the development of antifriction plastics with increased heat resistance [86-88] (Tabl. 1.4, p. 1-3, Tabl. 1.5, p. 1-2).

Moreover, as binders take PAR, containing at least 3% phosphorus, or based on BSFA, or based on phenolphthalein, as one binder, and in a mixture with other polymers. These materials are distinguished by a low coefficient of friction, which is maintained up to temperatures of 323-573K.The filling of PAR with reinforcing filler leads to the production of compositions for molded articles with improved heat resistance, surface gloss, low degree of warpage, and stability [89–91]. For reinforcement, various fibrous fillers are used: glass fiber [89, 92, 93], carbon fiber [93, 94], polyamide [95, 96], boric, silicon carbide, amorphous metal, silicone-titanium carbon fibers, fibers of aluminum oxide and silicon [95], potassium titanate [93], wollastonite [97]. In order to prevent intensive decomposition of PAR during processing and increase the duration of their operation at high temperatures, stabilizers are used in the compositions [98, 99]: polyphenylene metal sulfide; mixtures of alkyl sulfides withsterically hindered phenols; phosphorus containing organicesters;

Table 1.4: Properties of filled polyarylate compositions

№	Composition of compositions		Density, kg/m³	Maximum operating temperature, K	Thermal conductivity coefficient, W/(m · K)	TCLE, 1/K	Specific impact strength, kJ/m²	Compressive strength, MPa	Hardness according to Brinell, MPa	Coefficient friction	Linear wear intensity
1	2		3	4	5	6	7	8	9	10	11
1	Plastics series “Aman” (polyarylate, molybdenum disulfide and others)	2	3700	–	–	$1{,}2\cdot10^{-5}$	1,5	150	290–310	0,08	10^{-9}
		4	3200	–	0,6	$2{,}0\cdot10^{-5}$	2,0	90	270–290	0,08	10^{-9}
		7	2500	–	0,6	$1{,}5\cdot10^{-5}$	5,0	120	180–200	0,08	$0{,}5\cdot10^{-9}$
		12	3000	–	–	$1{,}6\cdot10^{-5}$	6,0	130	200–230	0,04	–
		13	2000	–	0,5	$2{,}8\cdot10^{-5}$	10,0	130	160–180	0,10	–
		22	3700	–	–	$1{,}2\cdot10^{-5}$	1,5	150	290–310	0,08	10^{-9}
		23	3200	–	–	–	4,5-5,0	100	200–230	0,06	$0{,}3\cdot10^{-9}$
		24	3200	–	0,6	$2{,}0\cdot10^{-5}$	2,0	90	270–290	0,08	10^{-9}
		25	3500		–	–	2,0	100-150	230–250	0,08	10^{-9}

Continuation of Table 1.4.

1	2	3	4	5	6	7	8	9	10	11
2	“Delan” (polyarylate, MoS_2, additives) ***	1250	443	–	–	8–15*	90-93	–	0,10-0,15	$5 \cdot 10^{-9}$
3	Polyarylate based on bisphenol A – 19 parts, polyarylate based on phenolphthalein – 65.5 parts, polycarbonate – 9 parts, molybdenum disulfide – 5 parts	–	473	–	–	50	–	–	0,14-0,16	$4{,}8 \cdot 10^{-3}$ **

Notes: ** Notched specific impact strength, kJ/m*^{2}*; ** Depreciation for 5 hours, g; Vicat heat resistance – 478 K.*

oxygen-, sulfur- or fluorine-containing organic compounds or their mixtures. And for protection against ignition, fire retardants are used (Tabl. 1.4, p. 3). Most often these are halogen-containing compounds [100, 101], for example, decabromodiphenyl ether, halogenated phthalamides, aromatic halogen-containing polymers. In addition, incom-bustibility promoters are sometimes introduced: Sb_2O_3, Sb_2O_5, sodium pyroantimonite, SnO_2, barium metaphosphate, zinc borate, $Al(OH)_3$, ZrO_2, MoO_2 [93], as well as specially developed flame retardants prepared with subsequent introduction into the treated pore. shock of salts of fatty acids and metals (Mg, Zn or Ca) [102]. Polyester oil, liquid at 298 K, imparts high chemical, oil and radiation resistance to the compositions [103]. The most widespread are compositions with CB, which are characterized by high values of strength, impact and heat resistance (Tabl.1.5, p. 4, 5). Compo-sitions with carbon fiber, in particular, phosphorus-containing, in addition to good strength properties, have increased resistance to ignition: their oxygen index is 46–48% [94]. The use of high-strength, high-modulus organic fibers in PAR composites makes it possible to obtain thermo- and moisture-resistant electrical insu-lating paper [96], antifriction materials [104] and structural mate-rials with resistance to high-energy impulse impact [105] (Tabl. 1.4, p. 7-9). It is interesting to note that, due to their high thermal stability, PARs themselves are used as an organic polymer filler in the form of a fine powder, fibers or films [106], as well as for impregnation of fibrous materials [107].

Table 1.5: Properties of filled polyarylate compositions

№	Composition of compositions	Heat resistant bone by Vika, K	Specific impact strength, kJ / m^2	Compression strength, MPa	Friction coefficient / Linear wear rate
1	2	3	4	5	6
1	Bisphenol A polyarylate – 20 parts; phenolphthalein based polyarylate – 60 parts; polyamide – parts; molybdenum disulfide – 15 parts	473*	50	–	$\frac{0,15\text{-}0,16}{3,5\cdot10^{-3}}$
2	Polyarylate based on bisphenol A – 10 parts; polycarbonate – 10 parts; low pressure polyethylene – 5 parts; molybdenum disulfide – 70 parts, cadmium oxide – 5 parts	473*	45	–	$\frac{0,05\text{-}0,06}{2,5\cdot10^{-3}}$
3	Polyarylate DV-101 – 100 parts;; polyphenylene metal sulfide – 0.5 parts	–	20 (notched)	74** 56***	–

Continuation of Table 1.5

1	2	3	4	5	6
4	Polyarylate-1 (hydroquinone, isophthalic and hydroxybenzoic acid) – 55 parts; polyarylate-2 (4,4'-diphenol, isophthalic, hydroxybenzoic acid) – 15 parts; fiber glass – 30 parts	524	15	199,3***	–
5	Polyarylate – 50 parts; glass fiber – 10 parts; glass particles – 30 parts; TiO_2 – 10 parts	541	15	91**	–
6	Polyarylate – 65-90 parts; phosphorus-containing carbon fiber – 10-35 parts	481-490	16,6-34,5	78,7***-105,7	–
7	Polyarylate DV-105 – 30 parts; fiber phenylone + arimide C (1: 2) – 70 parts; functional additive – 0.02 parts	608$^{\bullet}$	125	190	–

Continuation of Table 1.5

1	2	3	4	5	6
8	Polyarylate DV-105 – 60 parts; fibers SVM + arimide C (1: 0.05) – 40 parts; functional additive – 0.05 parts	648•	does not collapse	310	–
9	Polyarylate DV-105 – 70 parts; fiber phenylone + arimide C (1: 1) – 30 parts; functional additive – 0.1 parts	628•	321	295••	–

Notes: ** – maximum operating temperature, K; ** – tensile strength, MPa; *** – ultimate bending strength, MPa; • –temperature of the beginning of thermal oxidative destruction, K; •• – breaking stress in compression, MPa*

1.2. Processing of polyarylates and compositions based on them

In view of the high melting points of PAR, methods of their processing based on the use of solutions are used [108]. As noted earlier, PARs are very poorly soluble, but the problem has been solved by the development of mixed PARs, by introducing various groups into the macromolecule chain. This method is used to make films, fibers, and also apply film coatings to various products using solutions.

Polyarylates are thermoplastic polymers and, therefore, can be subjected to various methods of forming in the viscous flow state [109-110]. In this case, durable products are obtained both from the PAR themselves and using various NPs, which greatly facilitates the process of processing the PAR. Difficulties arose in the proces-sing of PAR by such high-performance methods as injection mol-ding and extrusion: the presence of rigid-chain macromolecules, transition to a viscous-flow state in a narrow temperature range bordering on the polymer degradation temperatures.

However, the creation of complex fully aromatic polyesters, which are capable of forming liquid crystals when the temperature in the melt rises, helped to solve this problem. Sheaths for wires and cables, threads and films are obtained by extrusion of amorphous PAR by orientation of the initial material followed by cooling [111] or quenching and heat treatment [112]. They have high strength and elongation at break. A polyester foam sheet is produced as follows: a) is fed into an extruder and a melt is obtained of a mixture containing amorphous copolyester (or its mixture with thermoplastics) and compounds such as glass, talc, Al_2O_3, mica, which will serve as centers of foam formation; b) inert gas is introduced into the mixture melt, c) the mixture is extruded [113].

Isaryl 15 (PAR 15) and Isaryl 25 (PAR 25) polyesters are processed into products by sintering: first, at room temperature in a mold under a pressure of about 50 MPa, a workpiece of the required configuration and dimensions is formed from a powder material, and then the workpiece is removed from the mold and, in a free state, is subjected to heat treatment at a certain temperature, after which it is allowed to refine the parts by turning, drilling and milling [114].

Productive production of powdered copolyarylate is proposed in [115]: a polymer is obtained in a melt with PCS, then it is introduced in a molten state into a drum cooling device, where, under the action of a pressure roll and an adjacent belt, it is rolled into a sheet on the surface of the cooling drum and cooled, after which the polymer is pulverized in a paint mill.

Polyrylates are also suitable for the production of surface films on glass, metal, and ceramics by plasma spraying [116] or vacuum sublimation with further polymerization under the action of temperature, plasma, UV-, ionizing radiation, or an electron beam [117].

Such films are distinguished by increased moisture and weather resistance. Molded products made of PAR are sometimes coated with varnishes and metalli-zed. In order to improve their adhesion, the surface of products is specially treated with chemical reagents [118, 119] or short-wave UV- radiation, the sources of which are low, high and ultrahigh pressure mercury lamps, a xenon lamp, and an ultrahigh pressure mercury-xenon lamp [120].

And antistatic properties are imparted to products by treating them with an ion flow with an accelerating voltage of 0.2-50 MeV and an irradiation dose of $1{\cdot}10^{14} – 1{\cdot}10^{18}$ cm^{-2} [121].

1.3. Applications of polyarylates

On the basis of PAR, as noted above, materials with a very wide range of performance properties and, therefore, with very wide fields of application can be created.

Polyarylates are used in instrument making, radio, electrical engineering, and electronics [114, 120, 122, 123]. They are used for making housings of electronic devices, small-sized resistors, switching devices, switches, plug connectors, thin-bone frames of high-voltage transformers, chokes, sockets, soldering pads, printed circuits, diode and transistor housings, lining of electrical and telephone wires and power cables, coil cores, precision parts for office equipment, sealants for electronic devices, electrical insulating paper, films and many other products. They are known to be used as materials for electrophotography [124], photodetector matrices [125], as well as for supporting fins of photovoltaic devices [126].

Due to its high transparency, low birefringence coefficient, optical lenses and disks, optical elements (diffraction gratings, interferometers, splitters, waveguides, optical switches, sensitive and holographic elements) are manufactured from PAR and are used as an optical medium in optical fibers [120, 127–129].

As plastics for structural purposes for parts subjected to significant mechanical loads at elevated temperatures, PAR are used in aerospace engineering [114, 130], automobile construction [114, 119, 129, 131]. Airbus portholes, high-emitting coatings and light guides, car parts (panels, bumpers, casings and pump rotor blades, impellers), antifriction parts – this is not a complete list of uses in these areas.

Polymer bearings, bushings, seals from antifriction compositions [51, 77, 122, 132-134] well resist the action of various contaminants, bearings are valuable materials in industry, withstand shock loads and vibrations due to elastic properties, can work for a long time in conditions of high temperatures, vacuum and high velocity gradients between rubbing surfaces. PAR is a promising raw material for the production of heat-resistant and high-strength fibers [87, 135, 136]. They have a strong intermolecular interaction, a tendency to order due to increased chain rigidity. PAR fibers are used in the production of cords, conveyor belts, sleeves, cables, synthetic paper, fibrous filter materials used for cleaning gases, liquids and capturing aerosols. Diffusion membranes, characterized by high permeability and selectivity [77, 137, 138], were obtained from PAR films, and they are especially effective in the separation of air to obtain oxygen and nitrogen, in water desalination and biotechnology.

In medicine and pharmaceuticals, PARs are used to manufacture drug vessels, ampoules, controlled drug delivery systems [139], spectacle frames, dentures [140], contact lenses and packaging materials that can withstand sterilization conditions [141]. Packaging materials for food products [142, 143] and blown multilayer bottles and bottles for drinks [142] from PAR are not inferior to polyethylene terephthalate in barrier properties, chemical resistance, attractive appearance, but also surpass them in resistance to UV- to rays, heat resistance, impact resistance.

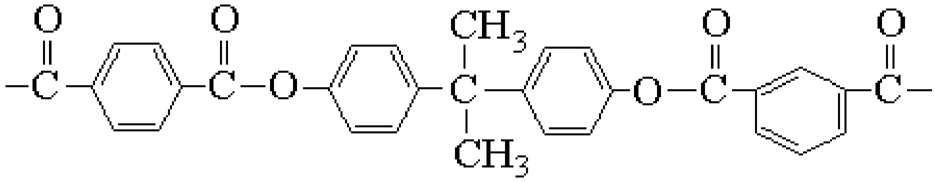
Developed and put on the market PAR compositions intended for equipping HF and electric ovens, as well as contamination-resistant kitchen utensils [144, 145], possessing high thermal stability, mechanical strength, good appearance. It has also been repor-ted about the use of PAR as adhesives [68], powder paints, foams [113], watch parts [129].

Thus, PARs represent a very broad class of polymers that can be used in many areas of technology and in everyday life. From the point of view of creating polymeric materials with a complex of valuable properties, they are promising for the development of compositions with an increased level of mechanical properties and improved manufacturability, which will ensure the fulfillment of fairly stringent requirements for structural materials.

Chapter 2. Composites based on polyarylate, reinforced by discontinuous fibers

2.1. Subject of research

In an effort to receive new composite polymer material for construction purpose it is used polyarylate DV-102 which is a complex aromatic polyester received by emulsion polycondensation diphenylolpropane with acid chloride of iso- and terephthalic acids in a ratio 1:1, and which has following structure formula [146,147]:

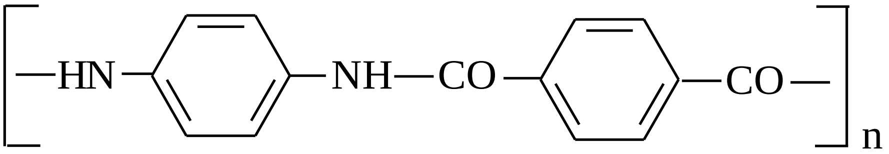


At present times, one of the most effective methods of increasing exploitation characteristics of polymer binders is reinforcing them by discontinuous fibers such as carbonic, organic and glass ones.

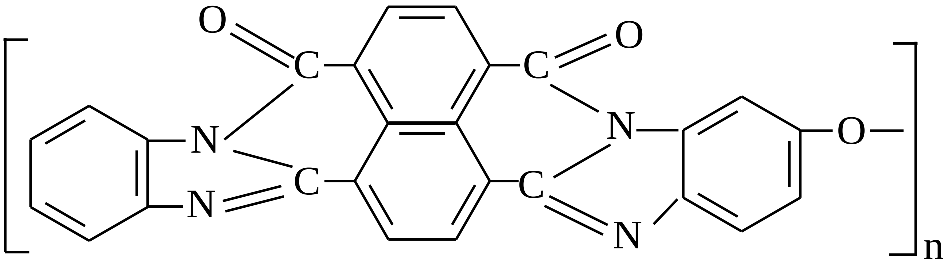
During the selection it is needed to get into account that mass using of high module carbonic fibers are limited by its price, rather low outcome, low capacity of used equipment and partially immense cost of raw materials of fibers [148]. That’s why during polyarylate reinforcing to use hydrate-cellulose carbon fiber uglen-9 (TU 6-06-i-87-81) line, which is belonged to coal fiber [148-151].

Highly perspective reinforcing fillers of polymer binders are high-modulus heat-resistant organic fibers vniivlon and terlon [152, 153].

Organic fiber terlon can be used in 23-548K temperature interval and has high specific tenancy on the disruption, stability to frequent deformation, chemical resistance, low heat set and electrical transport. Chemically, terlon is a polyphenilenterephtalamid:



Organic fiber vniivlon, received from rigid chain polygeteroarylen has following formula:



Vniivlon is not the most competent, but it refers to heat and chemical resistant fibers. It does not melt up to decomposing temperature, at 673K it keeps 50 % of initial durability and this characterristic is higher than many heat resistant polymers have (including nomex and arimid); it also hasn't shrinkage either after boiling dwell or at heating up to 573K. It has high chemical resistance to big amount of known reactive chemicals.

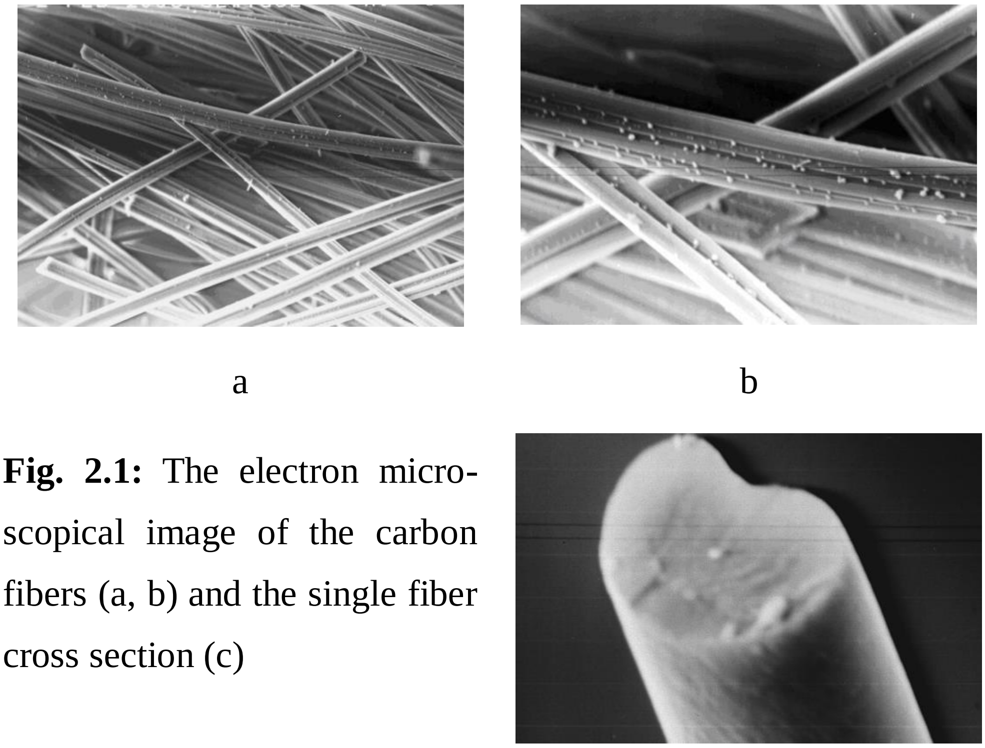
To estimate the influence of fibrous filler nature on the composites states based on polyarylate were also chosen highmodule beryllium-calcium-solicate glass fiber alkali-free M-5 line [154].

The content of chosen fibrous fibers in polyether binders were changing from 5 to 35 mass %. Manufacturing of blend compounds was made by dry blending in a rotating electromagnetic field with the use of unequlaxial ferromagnetic particles, and recast block wears by compression pressing.

2.2. Structure research of composite materials

At the beginning of complex research it was interesting to study the state of a surface and crystal morphology of reinforcing fibers uglen, terlon, vniivlon and glass fiber, microstructure of polymers composites samples destroyed fracture surface and made a result analysis by following characteristics: mode (homogeneity) of fibers allocating; condition of fiber linking surfaces – polymeric matrix; features of fiber destruction and scale of the element of polymeric matrix micro structure in fracture. The structure research of composites, which contained 15-25 mass % of pointed fibers, was made with the use of raster electronic microscopy combined with electron probe microanalysis (Careca – SX50). The materials X-ray diffraction technique was made on DRON-2 in copper monochromatised ejaculation, IR spectroscopic analysis on spectro-photometry UR-20.

The typical electron microscopical image of studied fibers is shown on the figure 2.1-2.5 [155].



a

b

c

Fig. 2.1: The electron microscopical image of the carbon fibers (a, b) and the single fiber cross section (c)

The results of the electron microscopical research show that the carbon fiber has a “lenticular” cross section (fig. 2.1). The dimensions of the single carbon fiber cross section (fig. 2.1 c) are 5-7 micrometers, however its major part is clumped, and each group consists of 2-5 single fibers (fig. 2.1b). It is established that the surface of this filler is smooth and has no prominences, but dregs like pimple (dimensions of the particles < 0.3 micrometers) which are enriched by the silicon and contain of the oxygen spotting (fig. 2.1b, pointed by arrow) are found on the surface of each fiber.

The terlon cross section also had “lenticular” type (fig. 2.2a) and was changing within 15-20 micrometers. The formation of the fiber bundle is established on the base of single fibers groups. The surface of terlon is smooth, and it has sulfur, sodium and bromine spotting (basis points).

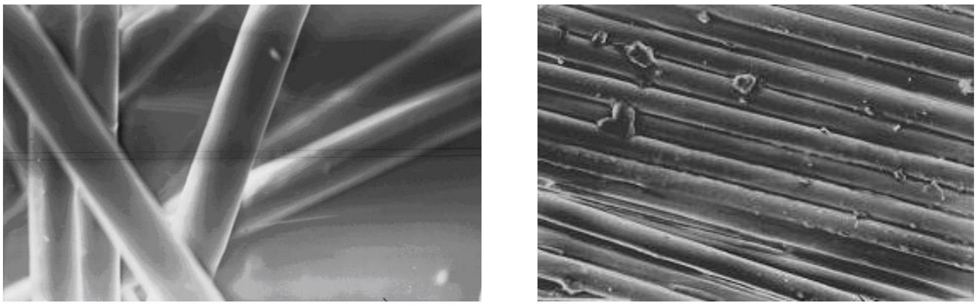

a b

Fig. 2.2: The electron microscopical image of terlon (a) and glass (b) fibers

As distinct from another two sorts, glass fibers have prominent surface. Dregs in the form of amorphous (shapeless) particles, which dimensions are from 1 till 10 micrometers can be observed on the surface of the glass fiber (fig. 2.2 b). The elemental compo-sition of these particles are: calcium, silicium (basic components), aluminum, magnesium and oxygen. The cross section of the glass fiber is 10-15 micrometers.

The fraction microstructure of the polyarylate binder mono-phase sample is mainly consisted of the anisometric shaped elements with the dimensions of 15-20 micrometers on the long side, which are separated with clearly visible limits.

That sort of structure elements contain the disconnected pores with dimensions of 0.5-1.0 micrometers, and also extended parts of such micro structure fraction elements are separated by porous layer. The distinctive feature of the fraction is availability of the micro structure elements in a form of regular four-sided prism with dimensions of section quadrangle from 5 × 7 till 7 × 10 micrometers. According to the X-ray spectrometry analysis these are crystals of sodium chloridum (fig. 2.3 pointed by arrow).

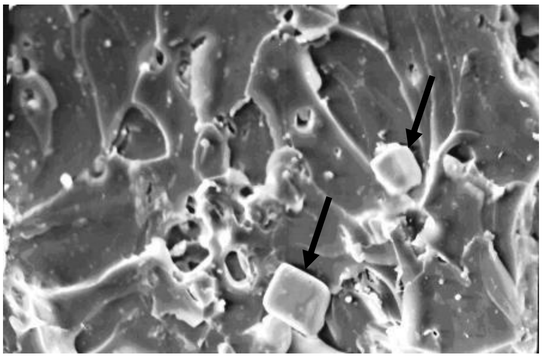
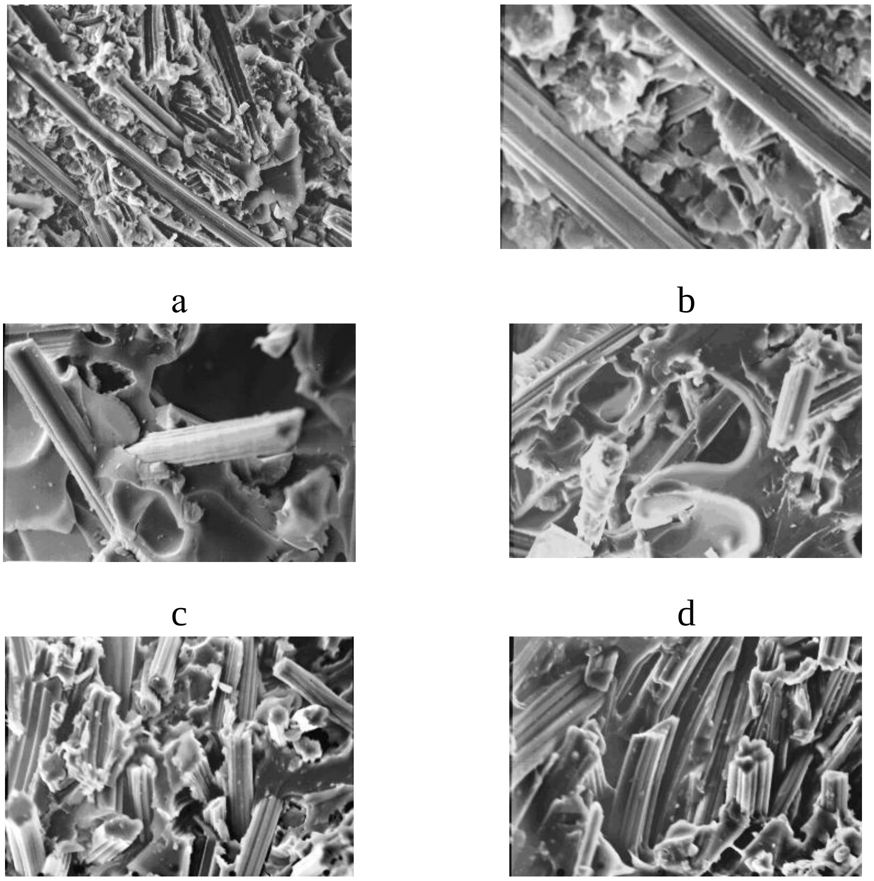


Fig. 2.3: Typical fracture structure of polyarylate monophasic sample

The microstructure of the destruction (fracture) surface of the carbon plastics on the base of the polyarylate shown on the fig. 2.4. has some pecularities. During the samples destruction the following processes can be seen: the carbon fiber drawing off the polymer matrix (fig. 2.4 c, e, f,); destruction of the carbon fiber by detrusion as during the cross section as along the length (fig. 2.4 c, d); changing of the fibers form with saving their entire structure, and this effect appears most with the increasing carbon fiber content in the composite (fig. 2.4 e, f). Such a low adhesive ability of the carbon fiber



a b

c d

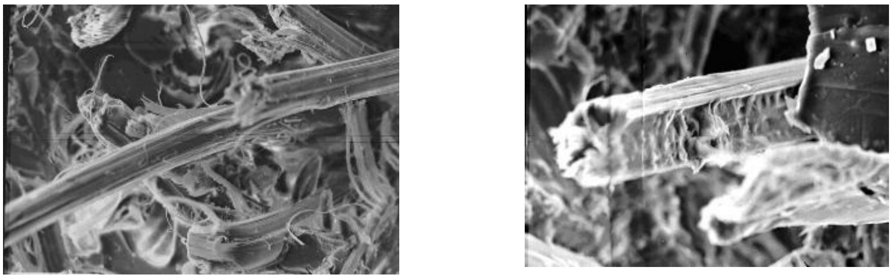
e f

Fig. 2.4: The microstructure of the fraction surface of the polymer composites samples based on polyarylate reinforced by the carbon fiber

to the binder surface can influence on changing some physical and mechanical values of the composite especially it can reduce their impact adherence. The confirmation of this conclusion is the results of the research about the influence of the carbon fiber percentage content on carbon plastics impact adherence: it is established that the enhance of this filler amount from 5 to 15-25 mass % can reduce carbon plastics impact adherence from 45 to 22-12 кJ/m^2 [156, 157].

It takes notice the fact that the carbon fiber admission in the polyarylate binder there is a great fragmenting of the polymer matrix (fig. 2.4 a, b). The last one is confirmed by the X-ray diffraction analysis, according to which there is a character changes of the carbon plastics diffraction curves. It appears that it can be connected to the fact that the admission of the carbon plastic fibers induce local, liquid crystalline, system ordering [158]. On the assumption of this we should expect the enhance of the material endurance character-ristics. The confirmation to the last one is the results of the physical and mechanical composites research: in comparison to the polyarylate the tensile strength during the compression increased at almost 30% and it was 182-231 MPa, and modulus of elasticity increased from 900 (for polyester) till 1163-1263 MPa – for carbon plastics.

Fragmenting of the matrix components in case of reinforcing them by terlon is going in a less degree as by carbon plastics. For the composites, reinforced by terlon there are also some areas with fiber exhaustion during the fracture forming. However there is a great fiber shattering up to its division on a separate threads (fig. 2.5a).



a b

Fig. 2.5: The micro structure of the fraction surface of the polymer composites samples on the base of the polyarylate, reinforced by terlon

Interaction between fiber and polymer matrix with great surface deformation of fibers is found during the organoplastics research (fig. 2.5b). Made conclusions are confirmed by X-ray diffraction analysis data, according to which there is an intermole-cular hydrogen binding between composition components [158]. In addition to this the organoplastic crystalline structure increases. So, the calculation of the crystalline volume rating by the Metew's approach [159] shows that it increases in more than 4 times [160].

Glass fibers based on the polyarylate characterize by very heterogeneous microstructure of the fraction surface. The main components of the micro structure are the parts which contain particles destroyed by interacting with glass fiber matrix and fiber splitting by length with the element formation like "shell". In such a case these sections contain highly porosity matrix components (fig.

2.6 b). In addition to pointed sections fibers which could save initial surface were found very rarely (fig. 2.6a).

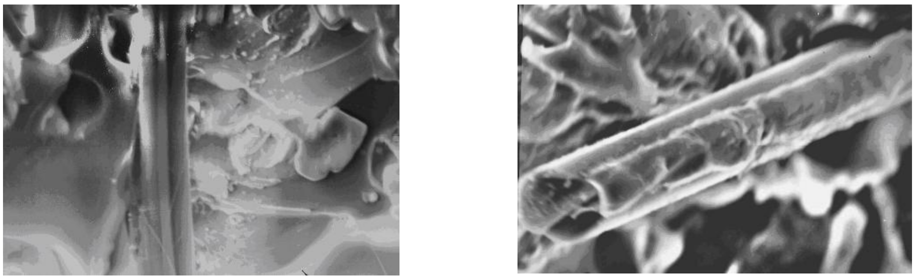


Fig. 2.6: The microstructure of the disruption surface of the polymer composites samples based on polyarylate, reinforced by glass fiber

Received in a structural research data can be explained in a such way. It is known [160] that glass fibers are very sensitive to mechanic damages, that's why during the combining of the composition components the glass fiber destroyed slowly. It shattered in a small particles in a result of which besides dispergating of this fiber, there was a reduction of its diameter into a minimum value 12 micrometers [161]. In a case of carbon fibers, glass fibers adding in the polyarylate don't allow to get materials which can have high impact adherence: for glass fibers with the increasing amount of filler this characteristic is down from 21 to 10 кJ/m^2 square meters. However, the mechanic characteristics of glass fibers had rather high values: its tensile strength during the compression in comparison with the binders increased in one and half and was 235-245 MPa, but modulus of elasticity increased from 900 (for binders) to 1200-2000 MPa – for glass fibers.

Therefore it is possible to conclude that mechanical characterristics in a substantial way depend on changing in the composites structure caused by physical and chemical processes of the polymer binder and fiber filler. The polyarylate reinforcing by discontinuous fibers let us to attain the increasing of the endurance index of the research composites. Studying the levelness of fiber distribution in composites shows that under unequlaxial ferromagnetic particles discontinuous fibers divide homogeneous in the polymer matrix with fiber preferred orientation to the cross direction of compression.

Thanks for using discontinuous fibers and also their distribution levelness in binder structure received composites characterize by isotropic structure. In the polymer matrix of the fiber, set in a random way, in a result of contacting with each other the heating ducts are formed, and it provided the improvement of their thermophysical and as a consequence tribological characteristics [162].

The determination of crystallinity degree of researched composites, and determinate variations of binder structure in dependence on nature and filler contain was made with the help of the X-ray diffraction technique.

General view of the diffraction curves of the binder and carbon fiber on its base is shown on the fig. 2.7. The analysis of the binder diffraction curves let us conclude that its structure is amorphous, what is shown by the existence of well-defined diffusion halo in the area Wulf-Bragg's angles 2θ = 18 radian and the second sloping maximum at 2θ = 45 radian, characteristic for the substances possessing amorphous structure.

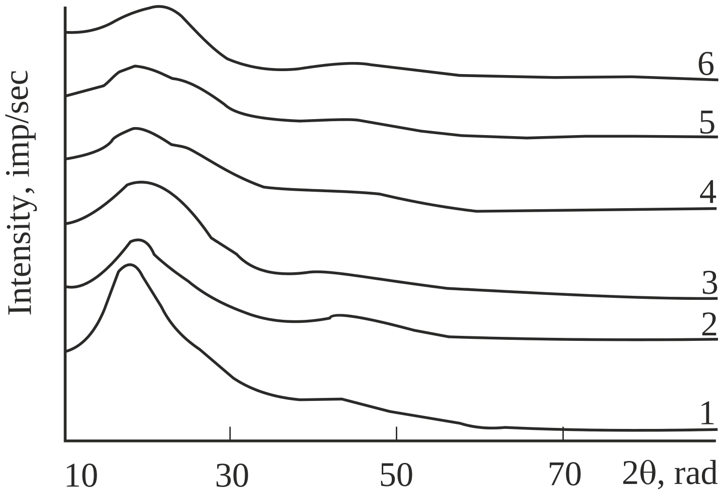


Fig. 2.7: Diffraction curves of polyarylate (1), uglen (6) and carbon plastic on the polyarylate base, reinforced 5 (2), 15 (3); 25 (4) and 35 (5) mass % uglen

Compare the diffraction curves of the base polymer, carbon fiber and carbon plastics, it ought to be noted that with the increasing of filler amount the amorphous ring occurred for polyester in Bragg's angles area 18 radian moved in the area of higher angles (20-22 radian), and its intensity decreased. At all carbon plastic diffraction curves we can see the second flat maximum at 2θ = 45 radian, distinctive for the base cohesive, intensity of which declines with the increasing of the carbon fiber content.

Somewhat different view has diffraction curves when we use them as the filler of the base polymer terlon fiber (fig. 2.8b). The diffraction pattern of terlon is characterized by the existence of the three lobes with the Wulf-Bragg's angles 2θ = 20 (first); 22 (second) and 45 radian (third), which can characterized by the crystal organic fiber and the diffraction rind in the area of 2θ = 29 radian. In the area of the same Wulf-Bragg's angles the three lobes and the diffraction rind for organoplastic are appeared. The intensity of all three lobes with the increasing of the organoplastic amount also increase. And it shows us the filler influence on the organoplastics structure. From the other side, the influence of the binder structure appears, and it shows the flat diffraction rind for composites in the area 20-45 radian, distinctive for polyarylate. With the enhance of the terlon content the intensity of this rind in decreased, and its minimum intensity is distinctive for organoplastic, with the 35 mass % of terlon [158].

Volume percent of the crystalline phase (Table 2.1) was estimated by Metews approach [159] by approximation profile of the amorphous dispertion in the area of crystal lobes in a ratio 1:1:

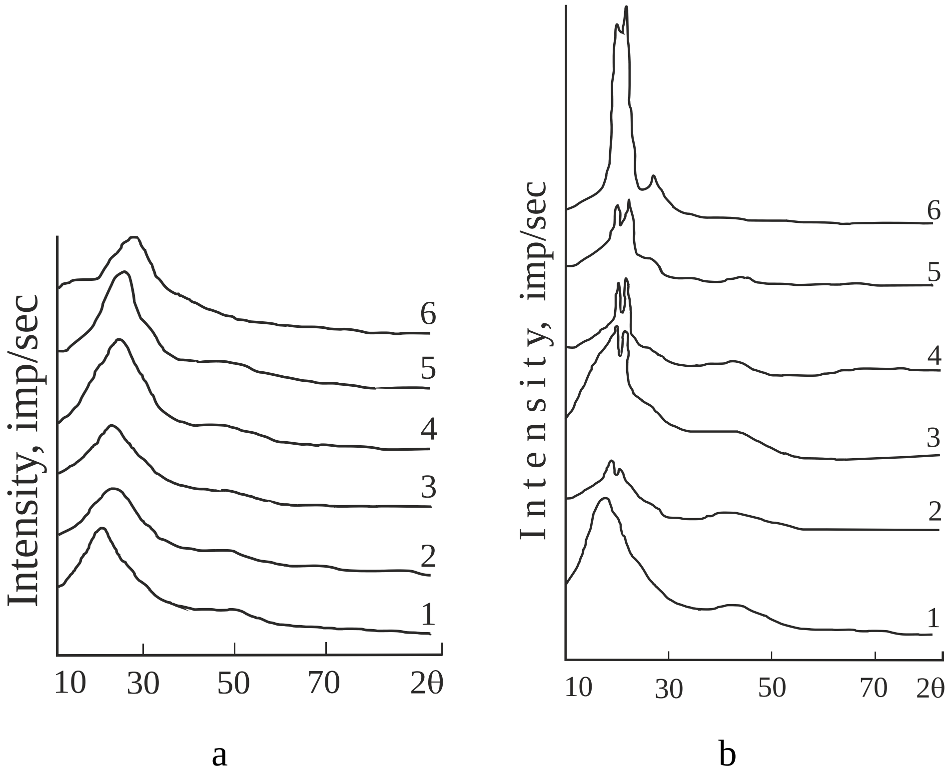


Fig. 2.8: Diffraction curves of the polyarylate (1) and organoplastics on its base, with the content 5 (2), 15 (3); 25 (4) and 35 (5) mass % of vniivlon (a) and terlon (b)

$$x_{cr.} = \frac{Q_{cr.}}{Q_{cr.} + Q_{am.}} \tag{2.1}$$

where: $x_{cr.}$ – degree of crystallinity; $Q_{cr.}$ – square under crystal reflex; $Q_{cr.} + Q_{am.}$ – general square under the curve of the coherent scattering; $Q_{am.}$ – square of the amorphous ring.

Table 2.1: Dependence between the crystallinity degree of the organoplastic structure and terlon content

Terlon content, mass %			
5	15	25	35
0.05	0.16	0.21	0.18

The enhance of the binder filler degree from 5 to 25 mass % increase the degree of organoplastic crystalline, and it indicates about more implicit process of the composites structure in a short-range order. The estimated data also indicate that for the composite with 35 mass % terlon content, the intensity of the amorphous halo increased a little with rather high lobes savings, characterized crystalline phase structure.

General view of the diffraction curves of binders and composite on its base, reinforced by vniivlon, is shown on the fig. 2.8a. There are two clearly shown areas on the diffraction curve: with lower ordering of the structure at $2\theta = 13$ radian and higher one at $2\theta = 26$ radian, in comparison with the organoplastics. With enhancing of the organic fiber content, the diffuse halo moved in the area of the bigger Wulf-Bragg's angles (2θ = 20 radian) in comparison with polyarylate. It indicates about the organic fiber influence on the processes development of the short-range order of the amorphous composite structure that in its turn allows to increase their physical and mechanical characteristics. On the diffraction curves of the base polymer and organoplastics in the area of Wulf-Bragg's angles

2θ = 45 radian, the second slope lobe, intensity of which decline in 1.1 – 1.2 times with the increasing of organic fiber amount (Table 2.2).

Table 2.2: Dependence between intensity of the diffraction radiation organoplastics and fiber content at the Wulf-Bragg's angle 2θ = 45 radiation

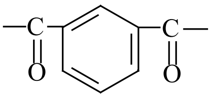
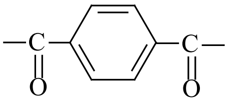
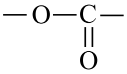
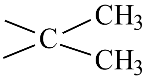
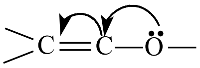
Viivlon content, mass %				
–	5	15	25	35
50	40	37	35	33

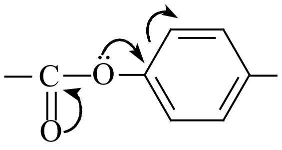
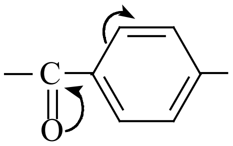
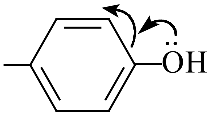
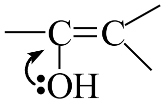
It takes notice the fact that the slope lobe at 2θ =12 radian on the filler difraction curve is not shown on the composites diffracttion curves. It indicates about physical and chemical interaction of the vniivlon with the binder macromolecules.

Taking into account the fact that the intermolecular interacting on the border of the phase interface of the polymer – fibrous filler refers to the main factors which determine their basic composites performance figures [163], the research of structural material transformations by infra-red spectroscopy has a great scientific interest.

During the comparison of the polyarylate infra-red spectrum (fig. 2.9), carbon fiber (fig. 2.10) and carbon plastic (fig. 2.11) some conclusions can be made. According to the results of the infrared spectroscopy the research for polyester there were two kinds of linking, shown in the Table 2.3.

Table 2.3: The application of the characteristic bands in the infra-red spectrum

Range, cm^{-1}	Spectral information	
1	2	3
735	1,3-substitution	
820, 885	1,4-substitution	
1030	Stretch symmetrical vibrations	$>C-O-C<$
1075	Deformation oscillations	 $-O-\underset{\underset{O}{\parallel}}{C}-$
1255, 1275, 1305	Stretch asymmetrical vibrations of the triplet	$>C-O-C<$
1735	Stretch vibrations	$>C=O$
1370, 1390, 1400	Deformation oscillations of the triplet	 $>C<^{CH_3}_{CH_3}$
1510, 1605	Stretch vibrations	
1305, 1255	Deformation oscillations	$>C=O\ -O-H$
1275	Stretch vibrations	$>C=O$
1180, 1215	Stretch vibrations	$>C=C<$
2885, 2945	Stretch vibrations	$(C-H)_{CH_3}$
2980	Stretch vibrations	$(C-H)_{Ar}$
2390	Stretch vibrations	(O—H ...Î)

1	2	3
3300-3600	Stretch vibrations of π-linking and hydrogen bindings	 
	Phenolic and enol	 

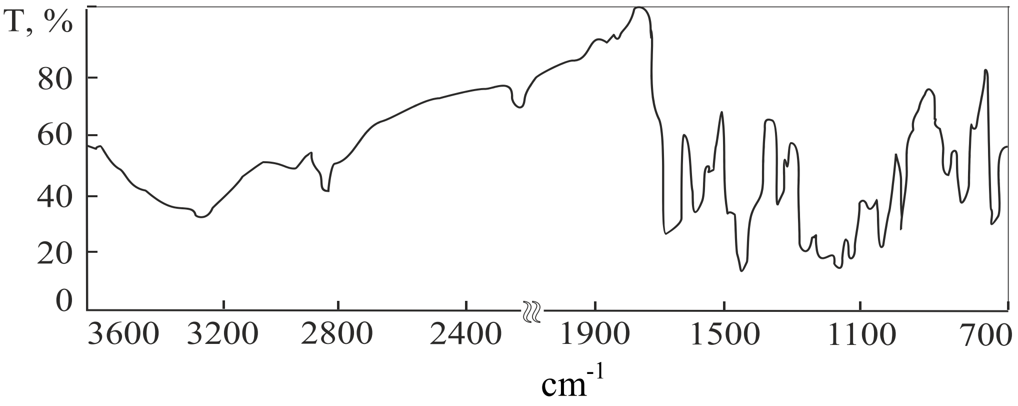


Fig. 2.9: Infra-red spectrum of the polyarylate

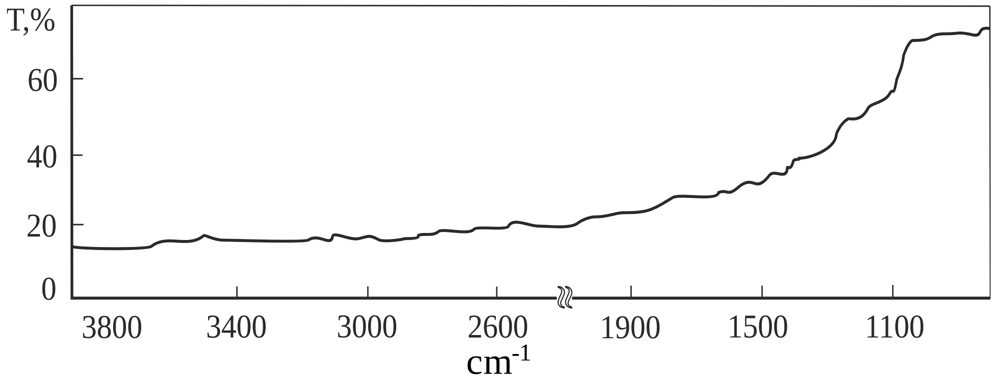


Fig. 2.10: Infra-red spectrum of the uglen fiber

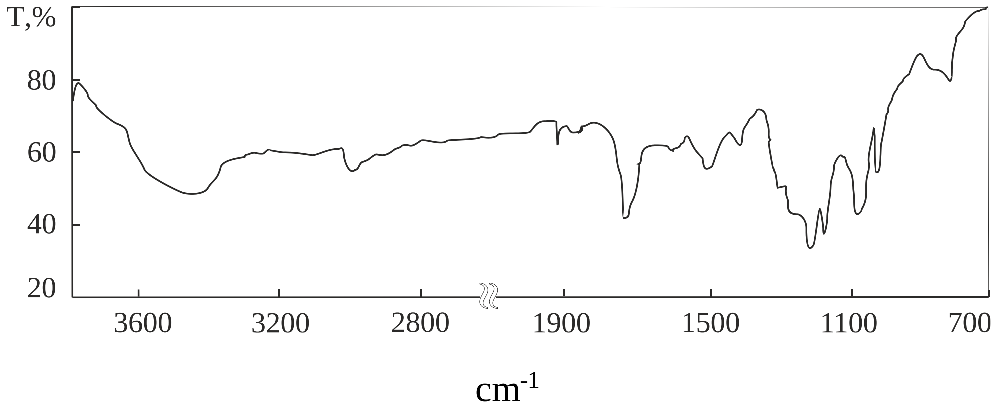


Fig. 2.11: Infra-red spectrum of the carbon fiber,
reinforced by 35 mass % uglen

It was broken in the composites because of 1,4 not 1.3-linking. On the infra-red spectrum of the carbon fiber hydrogen binder because of the carboxyl and hydroxy groups of the filler and binder is noted:

–COO–, – OH … OH –

and the hydrogen binder in the carbon plastics is made by carbonyl and nitrile groups: $C = O \ldots H - C \equiv$.

On the base of received data we can concluded that the formation of the intermolecular linking in the carbon plastics the methyl and diphenylolpropane groups are involved.

Comparative analysis of the binder infra-red spectrum (fig. 2.9), terlon (fig. 2.12) and organoplastic on its base (fig. 2.13) help us to conclude that there is a chemical interaction between polyarylate and terlon, specified:

1. Making the hydrogen binders between

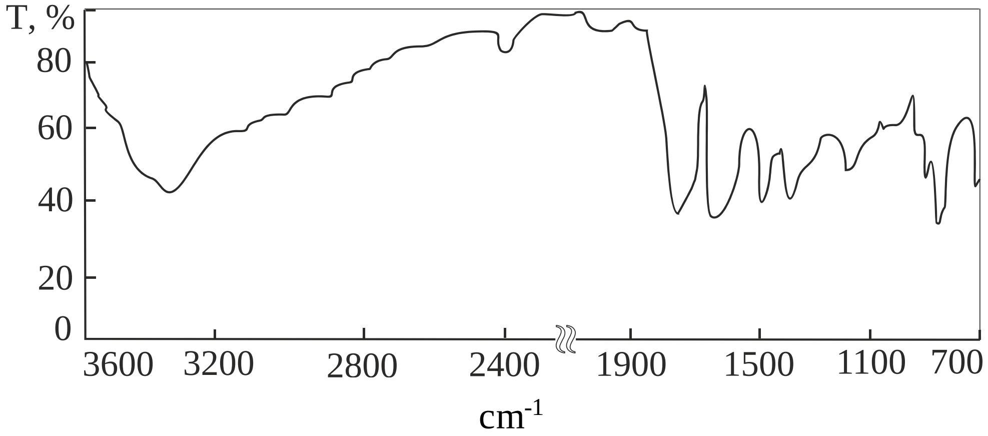


Fig. 2.12: Infra-red spectrum of terlon

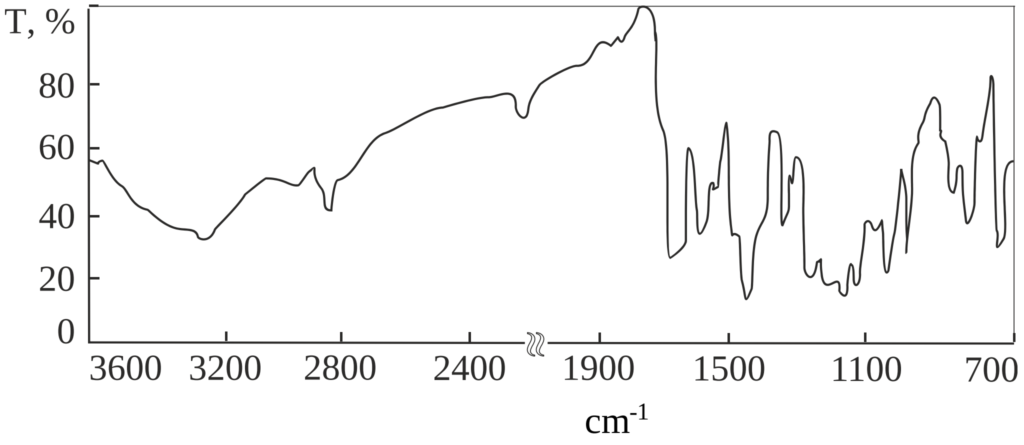
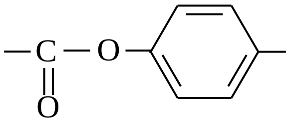


Fig. 2.13: Infra-red spectrum of the carbon plastic, reinforced by 35 mass % terlon



and –CO – NH – .

2. Making imide structures by the type: C=N–

3. Intermolecular hydrogen binders between – OH…O=C–

4. Participation of the methyl groups of the diphenylolpropane in formation of the intermolecular hydrogen binder and transformation of the last one in groups: $H_2C=C=$.

Comparative analysis of the binder infra-red spectrum (fig. 2.9), vniivlon (fig. 2.14) and organoplastic on its base (fig. 2.15) shows that there is a chemical interaction between composite components, provided:

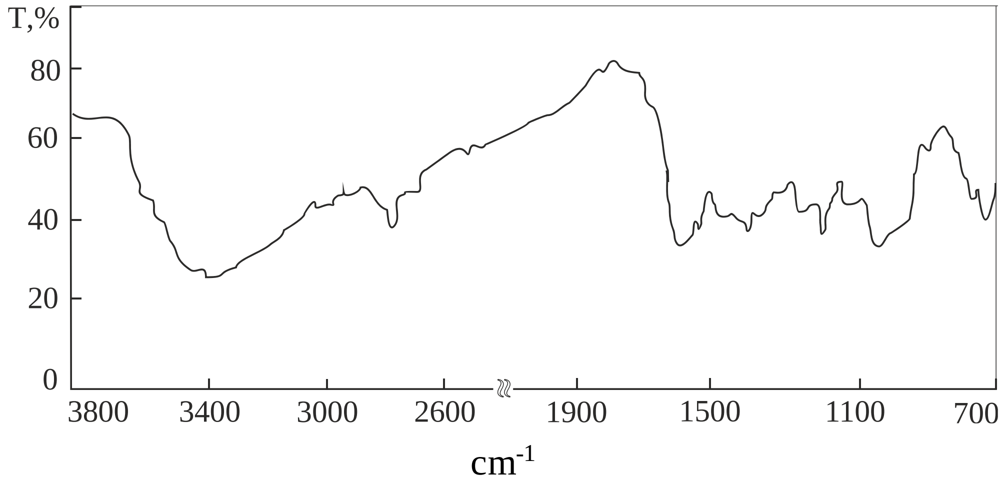


Fig. 2.14: Infra-red spectrum of vniivlon

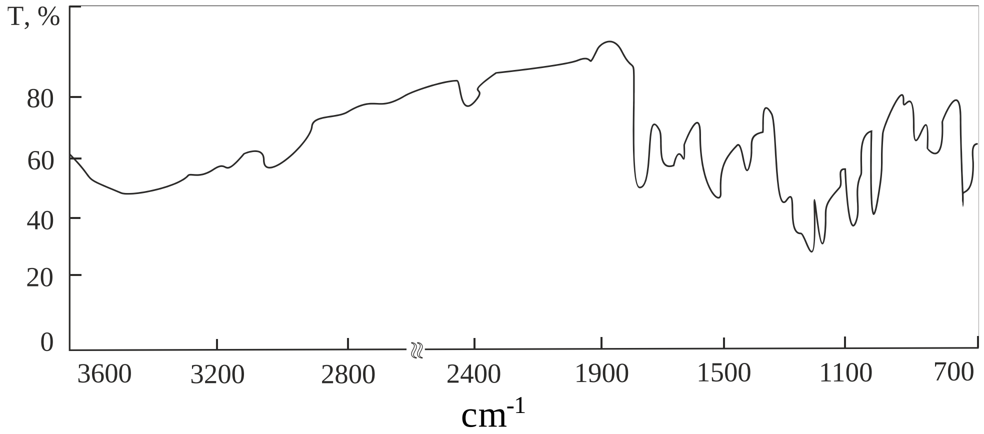


Fig. 2.15: Infra-red spectrum of the organoplastic, reinforced by 35 mass % of vniivlon

1. There is a destruction of the hydrogen binder between fibrous filler molecules and formation of the new intermolecular hydrogen binder for account of the amido groups of vniivlon, about

which indicates the extinction of absorption bands at 1645 and 1660 cm^{-1}, characterized by stretch vibrations of this functional group, and methyl groups of diphenylolpropane.

2. The absorption band of the stretch vibrations of the vniivlon amido groups at 1470 and 2945 cm^{-1} on the organoplastic infra-red spectrum vanish completely, and the absorption band of the imine group appears.

3. The deformation oscillations of the binder methyl groups at 1370 and 1390 cm^{-1} vanish, the absorption band of the asymmetric stretch vibrations of the polyarylate methyl groups move from 2980 till 2990 cm^{-1} and intensify that shows us in a somewhat different view of their interacting with the filler, than in a previous composites consideration.

4. On the vniivlon infra-red spectrum at 1125-1130 cm^{-1} wide and weak absorption band, typical for –C=N– groups, was found. On the organoplastic infra-red spectrum the narrow and strong signal appears in the area of 1100 cm^{-1}. The last one could be explained by the fact that the –C=N– group of vniivlon was in linking, and as for organoplastic, it became isolated.

5. We can see a narrowing of the absorption band at 3400-3470 cm^{-1}, characterized intermolecular hydrogen binder.

6. In contrast to the carbon plastics and organoplastics, reinforced by terlon, in this case the binder carbonyl groups are not involved in the intermolecular interacting of the composites components.

Based on the previous information, we can conclude, that there is a chemical interaction between researched composite components, which is mainly in formation of the intermolecular hydrogen binder for the account of breaking off the quaternary atom of the carbon of the diphenylolpropane binder of methyl groups and formation of imide groups.

2.3. Thermal properties of the composites

As a result of a hard domain structure, narrow interval of the polyarylate transition in viscous-flow condition, border on the decomposition temperature, some definite difficulties at its recast by the extrusion techniques and injection moulding appear. Taking it into account, the compression moulding approach was chosen for the recast of polyester and composites on its base.

To determine the comfort temperature of the polymer recast in the products the research of the binder main exploitation characteristics, without heat treatment and pressed at different temperatures – 503, 523, 528, 533, 543 and 553K was made. At the initial stage of the research the influence of the pressing temperature on polymer thermal resistance was studied. Data of the activation energy of the polyarylate's thermal decomposition process, pressed at different temperatures is shown in a Table 2.4.

Table data show us the growth of the polymer activation energy during the pressing temperature increasing up to 543K. The last one is determined by the fact that the polyarylate structuring processes dominate in the temperature interval of 423-523K at the thermal and thermal oxidative breakdowns. In this case, in addition to cross-linking, the binder molecules in the recast process is exposed to the breakdown [10]. At the temperature exceeding 523K this process is dominated that's why there is a decrease of binder activation energy at further growth of the pressing temperature (fig. 1.16).Confirmation of the last one is the presence of the exothermic peak on the DTA at the temperature of 698K (fig. 1.16, curve 3).

Table 2.4: Polyarylate thermal decomposition process of the activation energy dependence on the recast temperature

Pressing temperature, K					
–	503	523	528	543	553
122.83	125.31	154.26	145.76	131.24	120.68

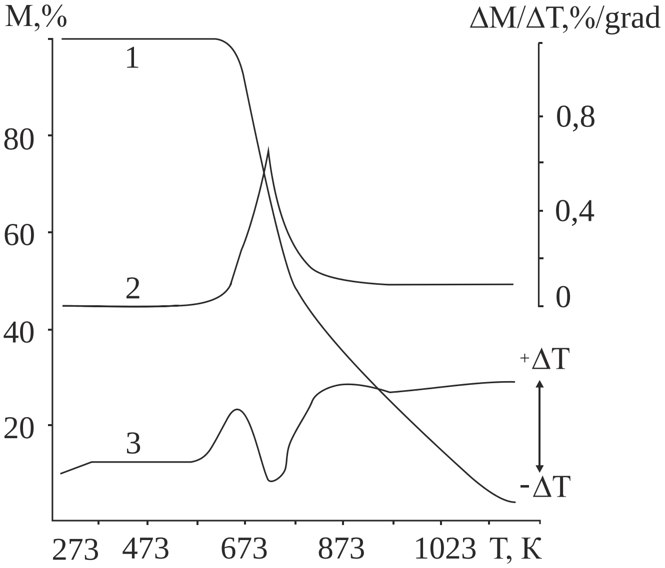


Fig. 2.16: Curves of the thermal gravitational (1); differential thermo-gravimetric (2) and thermal differential (3) analysis of the polyarylate

The optimum regime for the polyarylate recast was chosen in a result of the research: the highest activation energy of the thermal decomposition is distinctive for the polymer, processed at the tempe-rature of 523K.

Studying of the polyarylate pressing temperature influence on one of the most sensible physical and mechanical parameters – the impact resistance (fig. 2.17) confirms the correctness of the comfort temperature of the binder recast choice: the polyester samples, pressed at 523K have maximum impact resistance. So, we can see full correlation between activation energy temperature dependence and impact resistance.

At present a big amount of the kinetic equations is known [164-167], and it makes difficult to choose the optimal model for the thermal destruction of the definite polymer matrix process describing. There is no clarity in the criteria of the mathematics model choosing for the thermal decomposition of the polymer matrix process describing. So, to research the opportunity of the determination of the optimal kinetic parameters of the binder thermal decomposition process at the experimental thermogravimetric analysis data processing with the involvement of the mathematical models of the different heterogeneous processes have a great interest.

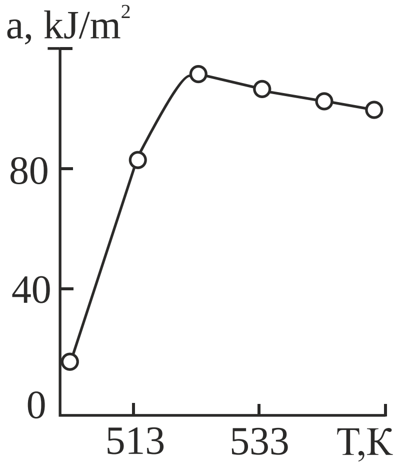


Fig. 2.17: Influence of the pressing temperature on the polyarylate impact resistance

Kinetic analysis of the thermo-gravimetric data of the composites, based on polyarylate was made on the assumption of the speed of the heterogeneous reactions is determined by the equation 2.2:

$$\frac{d\alpha}{d\tau} = kf\left(\alpha\right), \tag{2.2}$$

where: α – fractional conversion; k – specific reaction rate; t – time; $f(\alpha)$ – algebraical function, describing the process mechanism.

Kinetic constant dependence of temperature describes by the Arrhenius equation:

$$k = Ze^{\frac{E}{RT}} \tag{2.3}$$

where: Z – pre-exponential factor; E – apparent activation energy; T – temperature; R – absolute gas constant.

For the reactions, the order of which is unknown, the equation (2.2) can be presented in the integral form [167].

$$lg\,\frac{g(\alpha(}{T^2} = lg\,\frac{ZR}{\beta E}\cdot\left(1-\frac{2RT}{E}\right)-\left(\frac{E}{2{,}3RT}\right) \qquad (2.4.)$$

where: β – heat speed; n – apparent reaction order, if $g(\alpha)=\frac{(1-\alpha)^{1-n}-1}{n-1}$ $n \neq 1$ and $g(\alpha)=-ln(1-\alpha)$, if $n = 1$.

Dependence of the value $lgg(\alpha)$ on $1/T$ at the right choice, n has a shape of a straight line with tangent angle of the slope of line, equal $E/2{,}3R$.

Value $lg\frac{ZR}{\beta E}\cdot\left(1-\frac{2RT}{E}\right)$ is considered to be constant for the majority of meaning E and temperature interval, in hichheterogeneous processes is taking place. Values E and Z polyarylate thermal destruction processes determined at the n with 0.01 step changing up to linearization.

As a maximum coefficient of the correlation corresponds to the n and E range values, for more accurate determination of the kinetic parameters the minimum function is used:

$$f\left\{\alpha(\tau),T(\tau(\tau n,E,Z\right\} = S \qquad (2.5)$$

$$S = \sqrt{\sum_{i-1}^{m}\frac{\left(\alpha_{exp.} - \alpha_{cal.}\right)}{m}} \qquad (2.6)$$

where: $\alpha_{exp.}$, $\alpha_{cal.}$ – experimental and calculated values of the fractional conversion; *m* – experiment data amount.

One minimum at which the solution $\{n, E, Z\}$ with the lowest inaccuracy satisfy the input data is distinctive for the concerned function (α, T) (Table 2.5).

Table 2.5: Kinetic performance of the thermal destruction process of the polyarylate on mathematical models of the main heterogeneous solid-phase processes

Temperature of the finishing, K	r	n	E, kJ/mol	$lg\ Z$	$S \cdot 10^{-2}$
–	0.997	0.99	122.82	8.49	1.40
503	0.997	0.99	125.31	8.23	1.69
523	0.993	0.85	154.26	10.59	2.17
528	0.994	0.90	145.76	9.90	2.17
543	0.997	0.74	131.24	8.71	2.03
553	0.998	0.89	120.68	7.73	1.04

Determination of the possible process mechanism and calculation of the kinetic parameters of the polyarylate thermal decompo-sition was made with the usage of kinetic integral equations of the different heterogeneous mechanisms processes, in particular reac-tions of the speeding type N_1, N_2, reactions on the separation phase border R_2, R_3, incident nucleation F_1, $A_2 – A_4$ and diffusion $D_1 – D_4$, D_2, D_3 [167].

N_1
$$k\tau = \alpha \tag{2.7}$$

N_2
$$k\tau = 2\alpha^{\frac{1}{2}} \tag{2.8}$$

R_2
$$k\tau = 2\left[1\text{-}\left(1\text{-}\alpha\right)^{\frac{1}{2}}\right] \tag{2.9}$$

R_3
$$k\tau = 3\left[1\text{-}\left(1\text{-}\alpha\right)^{\frac{1}{3}}\right] \tag{2.10}$$

F_1
$$k\tau = \text{-}\ln\left(1\text{-}\alpha\right) \tag{2.11}$$

A_2
$$k\tau = 2\left[\text{-}\ln\left(1\text{-}\alpha\right)\right]^{\frac{1}{2}} \tag{2.12}$$

A_3
$$k\tau = 3\left[\text{-}\ln\left(1\text{-}\alpha\right)\right]^{\frac{1}{3}} \tag{2.13}$$

A_4
$$k\tau = 4\left[\text{-}\ln\left(1\text{-}\alpha\right)\right]^{\frac{1}{4}} \tag{2.14}$$

D_1
$$k\tau = \frac{1}{2}\alpha^2 \tag{2.15}$$

D_2
$$k\tau = \left(1\text{-}\alpha\right)\ln\left(1-\alpha\right) + \alpha \tag{2.16}$$

D_3
$$k\tau = \frac{3}{2}\left[1-\left(1-\alpha\right)^{\frac{1}{3}}\right]^2 \tag{2.17}$$

D_4
$$k\tau = \frac{3}{2}\left[\left(1-\frac{2}{3}\right)-\left(1-\alpha\right)\right] \tag{2.18}$$

Calculation was made according to the computer programme with Coats-Redfern approach [168]. Mean square deviation S, r, E and Z is used as an output data for each mechanism. Check of the function linearity $lg\ g(\alpha) - 1/T$ was the main for the algorithm calculation, and also for the function minimum determination (2.4) for the mathematical models of the main heterogeneous mechanism processes (2.7 – 2.18).

Calculation results of the kinetic performance of the polyarylate thermal destruction process, refined at the temperature 523K according to the mathematical models of the main solid-phase processes (Table 2.6) shows us that the best straight linearization in the coordinates $lgg(\alpha) - 1/T$ and minimum value S corresponds to the first order reaction (1.11) with the following kinetic performance: $r = 0.993$; $S = 2.22 \cdot 10^{-2}$; $E = 168.51$ kJ/mol; $lgZ = 8.64$.

Calculation of the kinetic parameters of the composites thermal oxidative breakdown process (Table 2.7) shows that it as is binder describes the equation of the first order (2.11) [33].

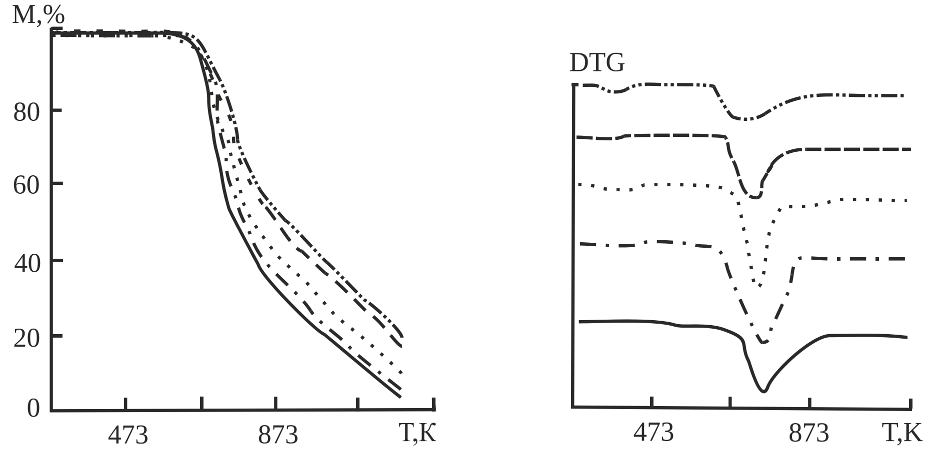
Curves analysis of the thermo-gravimatic analysis (fig. 2.18a) show us that there is some composites structural changes at the temperature of 623-673 K (mass loss is 2.5-5 %). According to the received data, the carbon plastic heat resistance is higher than polyarylate’s one and increases with the growth of reinforcing

Table 2.6: Kinetic performances of the thermal destruction process of the polyarylate on mathematics models of the main solid-phase processes

Mathematics model of the process	*r*	$S \cdot 10^{-2}$	*E*, kJ/mol	*lg Z*
N_1	0.982	5.63	10.60	3.92
N_2	0.978	5.61	47.97	0.19
R_2	0.991	2.57	133.46	6.00
R_3	0.993	2.26	144.27	6.81
F_1	**0.993**	**2.22**	**168.51**	**8.64**
A_2	0,992	28.83	79.25	2.54
A_3	0.991	42.08	494.95	0.59
A_4	0.990	47.54	346.17	-0.34
D_1	0.983	5.72	221.93	11.69
D_2	0.989	9.64	254.62	14.16
D_3	0.993	29.69	298.54	16.98
D_4	0.991	18.41	268.97	14.76

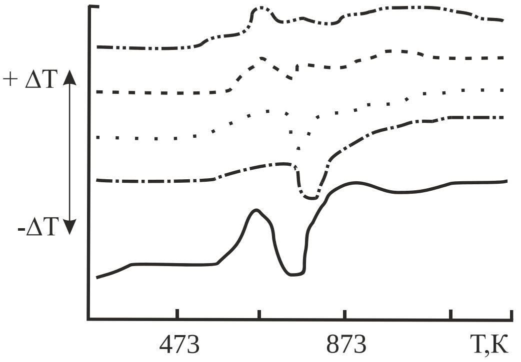
Table 2.7: Calculated kinetic parameters of the thermal destruction process of the polyarylate and composites on its base

Reinforcing fiber		Coefficient of correlation *r*	Energy of activation *E*, kJ/mol	Preexponential factor *Z*, 1/c	Mean-squared departure $S(\alpha)$
Type	Content				
uglen	5	0.996	122.08	$0.11 \cdot 10^{9}$	$0.15 \cdot 10^{-1}$
	15	0.985	109.28	$0.27 \cdot 10^{8}$	$0.34 \cdot 10^{-1}$
	25	0.993	116.37	$0.27 \cdot 10^{9}$	$0.25 \cdot 10^{-1}$
	35	0.981	104.53	$0.30 \cdot 10^{8}$	$0.37 \cdot 10^{-1}$
terlon	5	0.999	153.16	$0.73 \cdot 10^{11}$	$0.15 \cdot 10^{-1}$
	15	0.998	145.37	$0.36 \cdot 10^{11}$	$0.13 \cdot 10^{-1}$
	25	0.867	137.50	$0.64 \cdot 10^{4}$	$0.81 \cdot 10^{-1}$
	35	0.725	194.20	$0.24 \cdot 10^{5}$	0.15
vniivlon	5	0.990	118.20	$0.13 \cdot 10^{9}$	$0.14 \cdot 10^{-1}$
	15	0.998	115.74	$0.65 \cdot 10^{8}$	$0.11 \cdot 10^{-1}$
	25	0.998	106.65	$0.23 \cdot 10^{8}$	$0.78 \cdot 10^{-2}$
	35	1.000	85.13	$0.42 \cdot 10^{6}$	$0.23 \cdot 10^{-2}$



a b

Fig. 2.18: Curves of the thermogravimetric (a), differen-tial thermogravimetric (b) and differential thermal (c) analysis of the polyarylate (—) and carbon plastics on its base, contented 5 (–·–); 15 (·····) ; 25 (– –) and 35 (–··–) mass % of terlon



c

degree. In particular, the mass loss in amount of 10, 20 and 30 mass % for the carbon plastics, reinforced by 35 mass % of the filler obtains at 25, 55 and 60 degrees higher than for the binder (Table 2.8) [169].

Table 2.8.: Thermal properties of polyarylate and composites

Reinforced fiber		T_{10}		T_{20}	
Type	Content	Additive	Experi-mental	Additive	Experi-mental
uglen	5	680	693	702	713
	15	693	698	720	718
	25	707	703	738	723
	35	720	708	756	728
terlon	5	665	693	687	713
	15	650	698	676	718
	25	635	703	665	723
	35	620	703	653	728
viivlon	5	669	688	690	703
	15	661	690	684	708
	25	653	691	677	710
	35	644	693	671	713

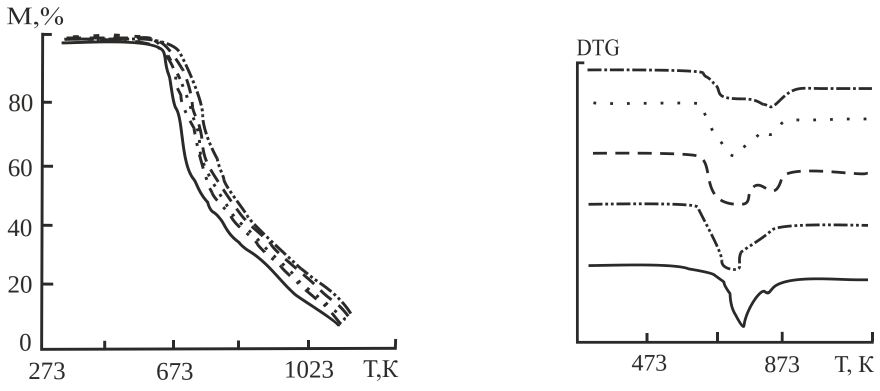
Note: *T_{10} and T_{20} – temperature 10 and 20-percent loss of the materials mass accordingly.*

Character of the thermo-gravimetric analysis curve changes of the binder and carbon plastics is the same. Exothermic maximum, corresponding to the oxidative transformation development is observed on the binder thermograph in the temperature area of 623-723K. Studying of the carbon plastic content influence of the composites thermal resistance shows that oxidative processes for them are going in the high temperature area (673-733K): as for the carbon plastics with filler content of 5 mass % – at 693-763K.

It takes notice the fact that the endoenergic effect at the 723K, clearly seen on the curves for carbon plastics with the 5-25 mass % of the carbon content shift in the higher temperature side. For example, for the carbon plastics with filler content of 15 and 25 mass % it is at the temperatures 743 and 728K accordingly.

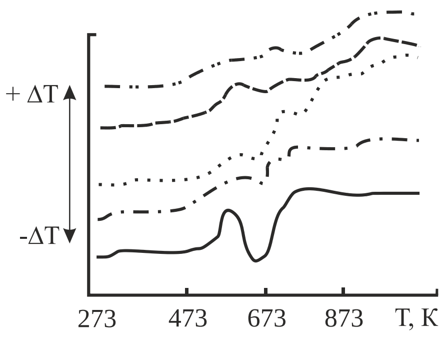
Analysing the general view of the organoplastics DTA curves, terlon fiber content we should mention the following. The oxidative processes, prevailing in a thermal destruction processes at the binder reinforcing for the organoplastic start developing at higher temperatures: for the organic plastics, contented 5 mass % of the fiber – at 673K, for composites, reinforced by 15, 25 and 35 mass % of terlon – at 693K (fig. 2.19). In contrast to the binder, organoplastics have the second exothermic maximum, which shifted in the area of high temperatures with the filler amount growth, on the curves of thermal analysis.

TG analysis data (Table 2.8) shows us that the heat resistant terlon fiber provides increasing of the material's heat resistance. DTA curves of the organoplastics, reinforced by vniivlon, have somewhat different character (fig. 2.20). In contrast to the binder, for the organoplastics with the increasing of the organic fiber content, the oxidative transformations don't have clear-cut character, the decreasing of the exothermic peak intensity proclaims about it.



a b

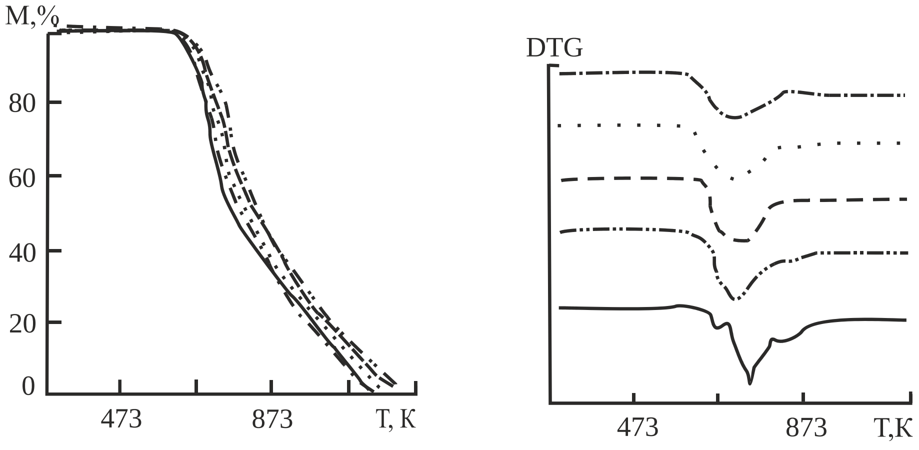
Fig. 2.19: Curves of the thermogravimetric (a), differential thermogravimetric (b) and differential thermal (c) analysis of the polyarylate (—) and organoplastics on its base, contented contented 5 (–·–); 15 (·····) ; 25 (– –) and 35 (–··–) mass % of terlon fiber



c

Besides that, this peak is at the higher temperatures for the composites, especially for organoplastic with 5 mass % of vniivlon. Maximum increasing of the composites heat resistance is found for the composites, contented 5 and 15 mass % of vniivlon (Table 2.8).

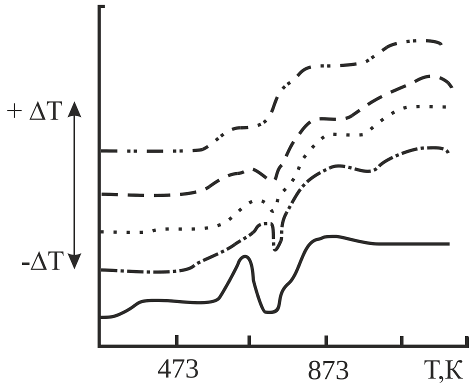
In whole, it ought to be noted, that the base polymer reinforcing by chemical fibers provides the increasing on 10% (in average) of heat resistance of the composites on its base.



a

b

Fig. 2.20: Curves of the thermogravimetric (a), differential thermogravimetric (b) and differential thermal (c) analysis of the polyarylate (—) and organoplastics on its base, contented 5 (–·–); 15 (·····) ; 25 (– –) and 35 (–··–) mass % of vniivlon fiber



c

Comparing the calculation and experimental data of the Table 2.8 we can conclude that the additive contribution of the heat resistant organic fibers in enhance of the organoplastics heat resistance is not significant. Apparently, composites heat resistance enhance is caused by the developing of the chemical and physical interactions between composition components, about which proclaim the higher temperatures increasing on 10%, at which we can see 10 and 20% loss of the organoplastics mass in comparison with the calculation data.

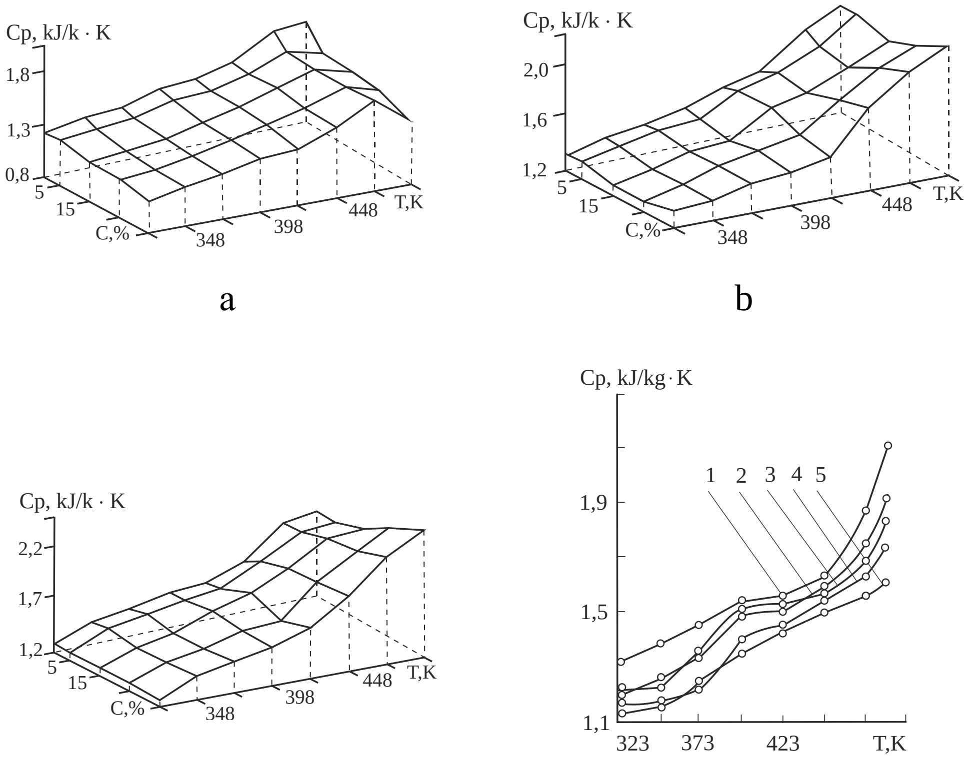
2.4. Thermo-physical properties of the composites

Among the construction materials, polymers possess rather low heat conduction coefficient and the highest specific heat capacity and the coefficient of the heat shrinkage. These polymer properties make some difficulties in the technology of parts production. Particularities of the polymer heat widening in the area of its softening depend on temperature speed changing, that's why possibility of thermo-physical properties research is rather important.

The research of the heat capacity of the polymer materials in a wide temperature interval lets us to determine its glass melting temperature, which is one of the main characteristics, linked with the mobility as structural elements of the macromolecular chains, as elements of the supermolecular structures.

Adding the filler in the polymer matrix goes to the great change of the pointed structural elements mobility, and the degree of this change depends on as the nature of the polymer binder and reinforced filler, as the character of the interaction between them.

Study of the temperature dependence of the specific heat capacity of the binder and composites on their base (fig. 2.21a, b, c, d) has shown its linear increase at the temperature range of 323-423K. As we have already known [170], at the temperature below the glass transition temperature, the stress relaxation tempe-



a b

c d

Fig. 2.21: The heat capacity temperature dependence of the composites based on the polyarylate, reinforced by uglen (a), terlon (b), vniivlon (c) and glass fiber (d)

rature connected to the regrouping of the big macromole-cule's parts was so great that regrouping was almost inhibited and captured from outside heat spent completely on enhance of the separate atoms oscillation energy in macromolecules. At the temperature higher than 423K in the area of the polyarylate transition and composites from glassy condition into the highly elastic one, we observe the intensive growth of this thermophysical indicator. Such character of the curves is explained by the segmental mobility and it can be defined as a potential barrier of glass melting which characterize two conditions of the energetic difference – glassy and highly elastic [171, 172]. Further, at the polymer transition in viscous-flow condition (at the temperature more than 498K) we can see a sharp decrease of heat capacity, which is proper for polymers with amorphous structure. It takes notice the fact, that the intensity of the binder heat capacity decrease in the pointed temperature range is rather low than in carbon plastics on its base.

Among the data about filler influence on thermo-physical characteristics of the polymers, the important place is taken by the analysis of a temperature leap ΔCp in the area of the composites' phase transitions, while its value can be referred to as the half-quantity measure of the comparative contents of the boundary layers in a filled system [173].

It must be mentioned that with the increase of filler percentage, ΔCp the value decreases (Table 2.9) in comparison with the linking element and it is the most intensive for the glass plastics.

Table 2.9: The heat capacity leap of the composites on the base of polyarylate [174]

Reinforced filler	Fiber content, mass %			
	5	15	25	35
uglen	0.27	0.26	0.27	0.35
terlon	0.24	0.20	0.42	0.58
vniivlon	0.45	0.43	0.58	0.88
glass fiber	0.24	0.19	0.13	0.10

Note: *the heat capacity leap of the polyarylate – 0.49 kJ/kg · К*

ΔC_p index decreasing at the glass melting shows us the elimination of some macromolecule's part in the amorphous areas from the glass melting process and explains it by coming the filler in the system of the border part of the polymer, macromolecule's mobility of which is rather low [175].

Such assumption lets us calculate the polymer fraction, situated in a boundary areas, and the thickness of the boundary layer in a rough (Table 2.10) according to the ratio [176]:

$$\left(\frac{\Delta r + r}{r} - 1\right)^3 = \nu \cdot \frac{V}{1 - V} \,, \tag{2.19}$$

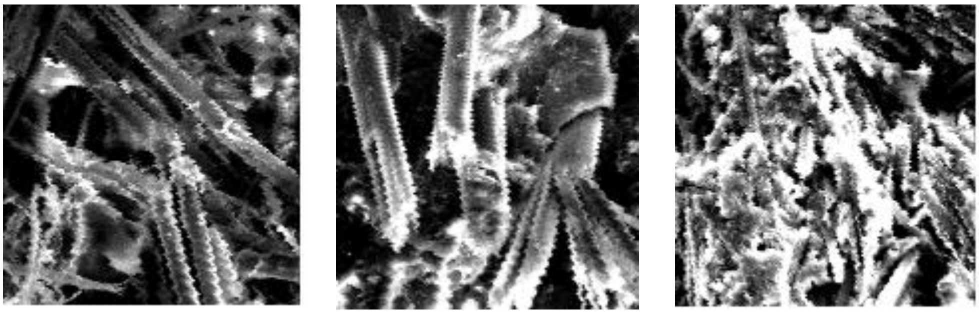
where: $\nu = 1 - \Delta C_{p.f.} / \Delta C_p$ – polymer fraction of macromolecules, moved in a boundary layers; $\Delta C_{p.f.}$ – heat capacity leap of the filled polymer; ΔC_p – heat capacity leap of the unfilled polymer; V – volume filler content.

As you can see in the Table 2.10 with the enhance of the filler quantity from 5 till 15 mass % the thickness of the composites boundary layers increase, and the values become as high, as the fiber is closer to binder by their chemical nature. At the same time, at the increase of filler content up to 35 mass % $\Delta C_{p.f.}$ becomes a little bit higher (except glass plastics), and it can be explained by developing the shattering process in a composites structure.

Table 2.10: Thickness of the boundary layer of composite based on polyarylate, Å

Content of filler, mass %	Reinforced filler			
	uglen	terlon	vniivlon	glass fiber
5	319	1260	120	25
15	994	5570	828	102

The last conclusion is confirmed by the researched data of the microstructure of the fragile fracture samples with the pointed filler content (fig. 2.22).



a b c

Fig. 2.22: Microstructure of the fracture surface in the liquid nitrogen of the polyarylate, reinforced 25 mass % of fillers: vniivlon (a); terlon (b) and uglen (c). Enhance: × 300.

The encrathy calculation C_p/T – of the temperature coefficient, which makes the mobility of the macromolecular structural elements more visible [177], shows us that there is a decrease of this index on 14-67 % during the addition of carbon fiber in the polymer matrix in researched temperature interval (Table 2.11).

The analysis of the temperature dependences of the organo-plastics heat capacity, contented terlon and vniivlon (fig. 2.21b, c) tells us about small temperature decrease with increasing of the organic fiber contain at the temperatures about 323-423K.

Table 2.11: The dependence of the carbon plastic encrathy on the base of the polyarylate from the temperature

Temperature, K	Carbon fiber content, mass %				
	–	5	15	25	35
323	4.20	3.99	3.80	3.79	3.78
348	4.19	3.99	3.88	3.78	3.68
373	3.92	3.83	3.76	3.64	3.46
398	3.84	3.82	3.70	3.67	3.31
423	3.99	3.88	3.70	3.70	3.32
448	4.68	4.24	4.23	3.92	3.82
473	5.02	4.39	4.32	4.17	4.09
498	4.98	4.15	4.14	4.11	4.08

In the areas of high temperatures (more than 448K) for composites, contented 25 and 35 mass % of the filler the heat capacity increases, and the most visible character this dependence has at the temperature 498K (temperature of the polyarylate's most intensive structuring). Probably, it can be caused by the polymer molecular organization fracturing in the boundary layers, in a result of which part of the polymer functional groups work off the inter-molecular bonds, it becomes more movable, and also the quantity of the conformational transformations increases and it leads to the heat capacity increase [178].

The declination of the glass plastics heat capacity temperature dependences of linear ones in the form of a slow drifts (398K) and leaps (448-473K) can be explained by the presence of the relaxation processes, which appears in the process of the phase transitions, and also during another slow heat processes, which takes place in a composites structure at the temperature increasing [179]. Analysing concentration dependences of the glass plastics heat capacity, we can mark that during the increasing of the glass fiber contain from 5 to 35 mass % in the temperature interval 323-498K this index decrease on 13-23%.

The temperature dependence of the heat conduction coefficient of the composites, based on polyester is characterised by the presence of the fracture at the glass transition temperature, and it can be explained according to the model concept of the heat transfer in the amorphous compound, linked to the atom oscillative motion. Lower than the glass melting temperature, the heat conduction increases linear with the temperature enhance, and with higher one, it decreases, and it caused by sharp increase in the free volume and thermal resistance (the value opposite to heat conduc-tion) at the glass melting temperature [180].

Composites products can be used for a long time at the estimated temperatures, and then they should cool naturally, as a rule, in other words with a small speed.

Indicated working regime of the polymer composites products is basically a multiple annealing.

That's why before you start goods producing from the polymer composites, you should study the influence upon its conditions of the annealing properties. Whereas the heat processing influence greatly upon molecular mobility, polymer structure on the different levels of its organization, and it means that it influences on the complex of the physical properties, and this method of modification is one of the most effective tool for the improvement of the composites characteristics exploitation.

Taking into account the fact that the burnt specimen obtained directly in the ampoule of the measuring cell of the instrument at spontaneous cooling from 498K is rather interesting. The studying of the temperature dependence of the "sewed" samples (fig. 2.23) and the influence upon its content of the carbon fiber shows the following: heat conduction coefficient of the annealing samples of the all compositions, except polyarylate, contented 35 mass % of the filler, increases on 10-20% in average.

The most intensive growth of the heat conduction coefficient is observed in the temperature area upper than 473K.

Probably, at this temperature the energy of polymer macromolecules' movement reaches the value which is sufficient for the chemical structuring beginning [10]. In a result of the sewing the flexibility reduces, the dimensions of the macromolecules segment increase, and this fact leads to increasing of the elementary wave guide and as a consequence carbon plastics heat conduction [177].

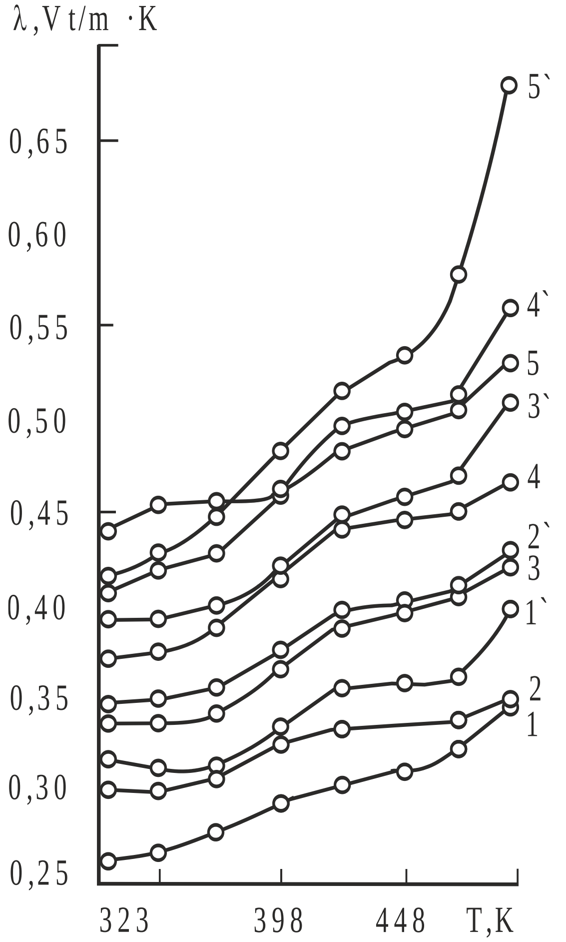


Fig. 2.23: Temperature dependence of the polyarylate heat capacity (1), annealed polyarylate (1') and carbon plastics on its base, containing 5 (2,2'), 15 (3,3'); 25 (4,4') and 35 (5,5') mass % uglen

In general, it is established that the using polyester of carbon fiber as a reinforced element increases this index on 10-70%, and on average values of the heat conduction coefficient, researched materials surpasses ones, based on the same wider used thermoplastic binders (Table 2.12).

Table 2.12: The coefficient of the carbon plastics heat capacity on the base of polyarylate [182-184]

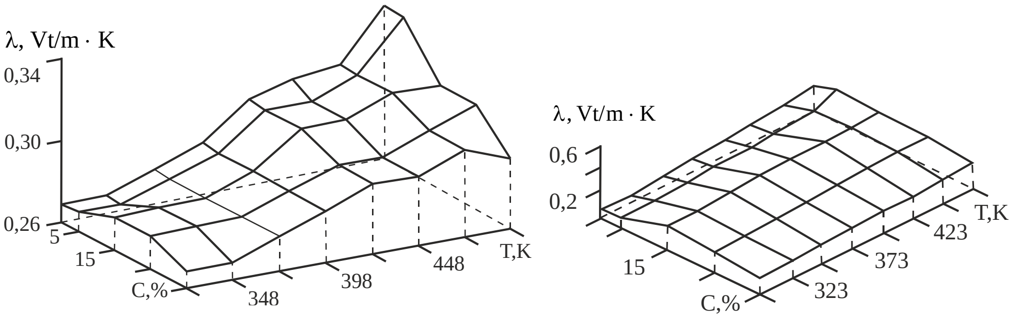
Polyarylate	0.40-0.70
Polyvinilchloride	0.28-0.62
Dneprolon	0.32-0.35
Phenylon	0.27-0.55
Block copolymer-7	0.33-0.52
Polyphenylquinoxaline	0.24-0.36
Polyethyleneterephtalate	0.29-0.54

Adding the organic fiber in the binder increase slightly the heat conduction coefficient. It can be explained that the organic fiber and polyarylate have a very close values of the heat conduction. During the polyester filling by terlon (Table 2.13) till 25 mass % heat conduction coefficient increases and then it slightly decreases. Decreasing of the heat conduction coefficient for the composites with the filler content 35 mass % explains by fracturing of the polymer molecular organization in the boundary layers.

Table 2.13: The coefficient of the composites heat capacity based on polyarylate, reinforced by terlon

Temperature, K	Polyarylate	Terlon content, mass %			
		5	15	25	35
323	0.269	0.273	0.274	0.278	0.271
373	0.280	0.283	0.287	0.288	0.284
398	0.289	0.297	0.304	0.306	0.289
423	0.312	0.317	0.324	0.326	0.317
448	0.315	0.319	0.328	0.331	0.311
473	0.321	0.325	0.330	0.333	0.313
498	0.346	0.354	0.357	0.355	0.335

More notable growth of the heat-conduction we can see for the composites, reinforced by vniivlon (fig. 2.24). This parameter rises



a b

Fig. 2.24: Temperature dependence of the heat conduction coefficient of the polyarylate and composites on its base, reinforced by vniivlon (a) and glass fiber (b)

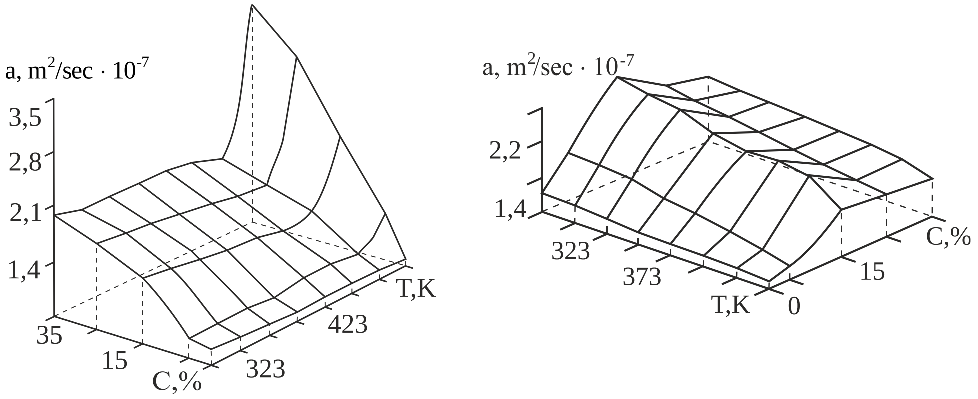
to the greatest degree (in 1.1-1.2 times) for composites which have vniivlon content 25 mass % with increasing of the filler content, further filling of the matrix provides its lowering. Notably, when the temperature (498K) is high the character of the changing heat conduction is strongly pronounced.

Heat conduction has antibate changes to specific heat: it monotonically increases on 12–27 % with adding glass fiber into the binder up to 15 mass %, then it rather decreases exceeding in absolute values the original polymer. It might be supposed, that fiber additive contribution in increasing of this index is inappreciable because of the low [0.035–0.09 Wt/(m · K)] thermal conductivity of the glass fiber. Therefore the cause for increasing of this parameter for the composites, which content 5 and 15 mass % of glass fiber, is coursing of physical-chemical processes on the boundary polymer filler: the increasing of the regularity structures of the binder is occurred with the specified fiber content and accompanied by increasing of the heat conduction.

The reduction of the glass fibers heat conduction, which content 25 and 35 mass % of the filler can be explained with the advent of emptiness on the phase boundary because of poor imbibitions glass fiber by polymer binder.

Heat diffusivity is a measure of the “effective” rate equalization of the temperature fields in the body. Temperature dependence of the composites heat conduction is a typical for the amorphous polymers: it decreases with increasing temperature up to the glass transition temperature in the area of the glassy state. The abrupt increase of the heat conductivity is observed for carbon plastics at the glass transition temperature, that is the consequence of a sharp increase in the heat capacity at the glass transition and weak change of the heat conduction in this area [168]. The study of the concentration dependence of the carbon plastics heat conduction on the base of the polyarylate is showed that in all explored temperature interval it increases with rising filler content, that is caused by increasing of the composites heat capacity. The increase was on average 30–40% in the temperature area 323–398K, and at the temperature of 498K the heat diffusivity was strongly increased, that can be observe on the graph (fig. 2.25a). Analysis of this thermal indicator temperature dependence shows its lowering with temperature increasing to the point of the carbon plastics glassy state area. The decrease of the heat diffusivity in this area can be a characteristic of the glass transition, but its sharpest lowering is typical for the glass transition temperature (473K).

The character of the heat diffusivity concentration dependence for organic plastics is more complicated as well as the changing of heat capacity ΔCp, and it is combined with the processes which proceed in the structure of composites. Slight lowering of the heat capacity, ΔCp, and heat diffusivity are occurred when the filler content is till 25 mass %, and when there is the process of ordering in the structure due to the transition of polymer macromolecules in the boundary layer.

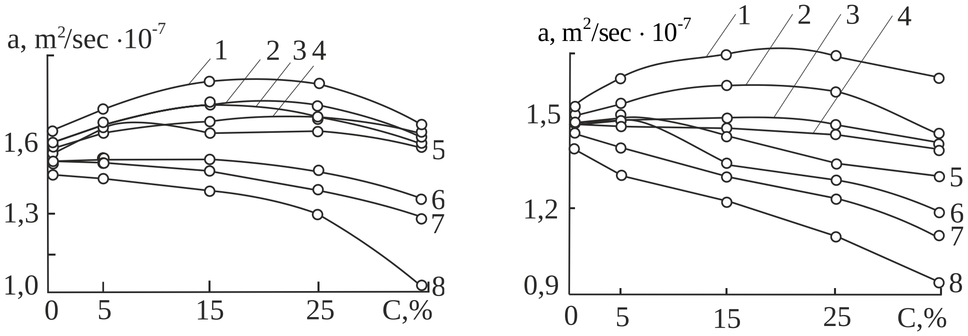


a b

Fig. 2.25: Temperature dependence of the heat diffusivity of the polyarylate and composites on its base, reinforced by uglen (a) and glass fiber (b)

For the composites, reinforced by vniivlon and terlon this increasing takes place at the temperature 323–398 K and has 2–12 and 2–4% accordingly. At the further increasing of the binder filling degree, when the fracturing process in the composites structure is the main, heat capacity and ΔC_p increase, but heat diffusivity, which is an opposite value, decreases. Draws attention to the fact that the most intensive lowering of this index is observed when the temperature is 498K (fig. 2.26 a, b, curves 8) – in 1.5 and 1.3 times accordingly for the composites, reinforced by terlon and vniivlon.

Heat diffusivity concentration dependence of the glass fiber is similar to the heat capacity (fig. 2.25b). However, as distinct from heat conduction that in the whole researched range of concentration was increasing with temperature rising, heat diffusivity was decreasing. The highest values of this parameter has glass fiber, reinforced by 15 mass % of the filler.

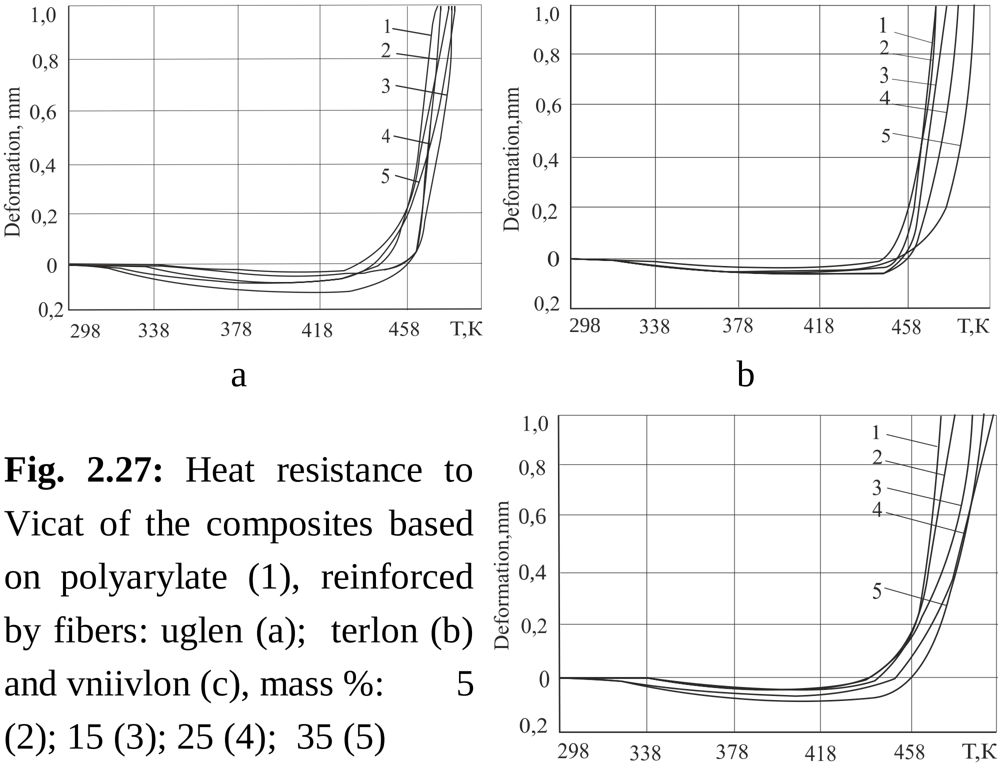


a b

Fig. 2.26: Dependence of the heat diffusivity of the composites, based on the polyarylate from the terlon (a) and vniivlon (b) content and temperature: 1 – 323; 2 – 348; 3 – 373; 4 – 398; 5 – 423; 6 – 448; 7 – 473; 8 – 498К

Taking into account the fact that polyarylate belongs to the most heatproof and termoplastic binders, studying the content influence on the filler nature on composites heatproof according to Vicat (T_V) has a great scientific interest.

General view analysis of the curves deformation – the polyester temperature and composites (fig. 2.27 a, b, c) we should notice that they has the same character: materials deformation increases with the temperature. However, the thermo-mechanical curves of the organo-plastics, reinforced by vniivlon, have more flat slope in comparison with polyarylate, apparently, it caused by the fact that there is a short range order processes (it approved by the X-ray diffraction analysis of the organoplastics (fig. 2.15) in the composites structure. It takes notice the fact that the deformation on the curves of all researched materials have negative sign, and it shows that the indicator doesn't collapsed into the sample at the temperature increase, and it behaves on the contrary, enhance a little. It caused by the fact that there is some residual stress, relaxation of which we can see in the process of the thermomechanical testing, in the composites, which consist of the binder and filler with different heat conduction and heat diffusivity.



a

b

Fig. 2.27: Heat resistance to Vicat of the composites based on polyarylate (1), reinforced by fibers: uglen (a); terlon (b) and vniivlon (c), mass %: 5 (2); 15 (3); 25 (4); 35 (5)

c

The research about the influence of the fiber nature on heat conduction according to Vicat of the composites shows us that this parameter increases directly proportional to the filler content (for organoplastics), at the same time polyarylate reinforcing by terlon and vniivlon leads to the heat conduction enhance according to T_V with the growth of the organic fiber content compatible with 2–17 and 6–25 degrees in comparison to the binder (fig. 2.28).

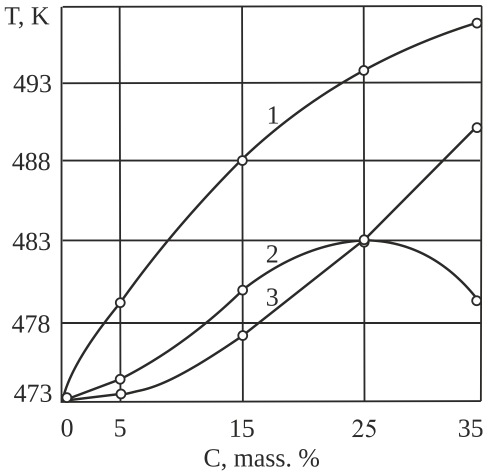


Fig. 2.28: Dependence of the heat conduction according to Vicat on the content in the polyarylate of the fibers: vniivlon (1); uglen (2); terlon (3)

Heat conduction of the organic plastics according to Vicat goes through the maximum at the uglen content 25 mass %, and then reduces. As we can see from the received data, the filler nature has significant influence on this thermophysical index: reinforcing of the polyester by heatproof and heat resistant organic fiber leads to more intensive growth according to Vicat.

In general, it ought to be noted that the composites, based on the polyarylate, especially organoplastics, reinforced by vniivlon, is more heatproof according to Vicat composites, based on polypropylene, polysulfone, polyamyde-12, block copolymer-7 accordant with: 78–79; 67; 51–54; 36–51 degrees [183, 184] (Table. 2.13).

Table 2.13: Heatproof according to Vicat composites based on thermoplasts

Polyarylate	474–498
Polyamide-12	423–444
Block copolymer-7	459–462
Polysulfone	431
Polypropylene	395–420

Thermal expansion or wider heat deformation connected to the dissymmetry of the heat atom’s oscillations, thanks to which interatomic spacing increase with the temperature enhance.

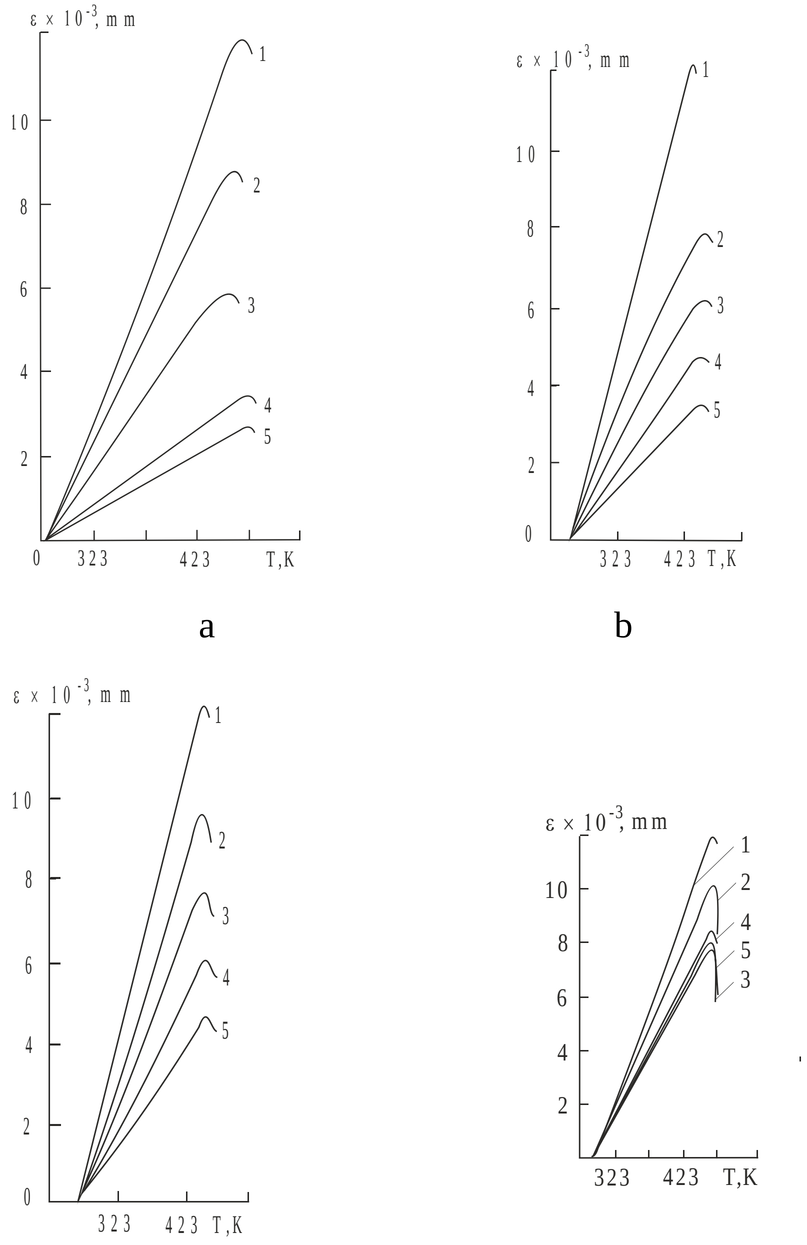
In addition to the heat capacity and heat conduction, the heat thermal expansion reflects forces between particles especially heat oscillations linked between particles [180].

We can understand the processes of the molecular structure regrouping, crystallization, polymerisation of the structural glass melting from the linear dilatation of the temperature coefficient changes and its temperature dependence. From the other side the linear dilatation of the temperature coefficient is characterized by the anisotropy degree of the material, the magnitude of thermal stress and deformation in the construction elements at the temperature changes [181].

Calculation of the temperature coefficient of the linear expansion is important for a few reasons. At first, its decrease reduces to a minimal shrinkage of the plastics at the temperature changes during the process of their manufacture. Secondly, unequal expansion or compression of the components of the composition can reduce to the occurrence of the residual stresses, which have a material effect on the mechanical properties of the material.

In our case, curves specific deformation – binders and composites temperature, which are obtained by dilatometer DKV (fig. 2.29) have an identical character: when the temperature is lower than the glass transition temperature the composites are expending, because of amorphous areas, which state is glassy, and when the temperature is higher than the glass transition temperature they are benting under the weight of the rod as the result of emolliating. Deformation of the analysed materials is significantly reduced all over the entire searched temperature interval when the content of filler is rising, and the maximum in the area of the glass transition temperature is moving to higher temperatures for composites, reinforced by 35 mass % of filler.

At the calculation according to the curves "tension temperature" the linear dilatation of the temperature coefficient of the composites (Table 2.14) this parameter decreases more intensive (in 7.3 times) for carbon plastics with increasing the filler content in the polymer matrix For the organoplastics reinforced by vniivlon, the temperature coefficient of linear expansion is decreasing all over the entire



a b

c d

Fig. 2.29: Curves of the deformation dependance of the polyarylate and polymer composites samples on its base, reinforced: 5 (2), 15 (3); 25 (4) and 35 (5) mass % uglen (a), trlon (b), vniivlon (c) and glass fiber (d) from temperature

Table 2.14: Temperature coefficient of the linear dilatation of the composites based on polyarylate, $\alpha \cdot 10^{-6}$, К$^{-1}$ [169]

Reinforced filler		Temperature interval, K				Temperature of the glass melting
Type	Content	298–323	323–373	373–423	423–463	
–	–	78.5	73.1	72.4	73.8	468
uglen	5	57.5	56.7	61.7	56.8	453
	15	50.8	49.5	50.6	36.0	458
	25	22.9	42.3	48.8	44.8	463
	35	10.7	24.5	37.4	44.6	473
terlon	5	54,9	55,7	59,1	46,8	463
	15	33,5	40,8	43,5	34,1	463
	25	25,3	30,9	31,9	14,8	473
	35	18,4	22,5	23.9	14.6	488
vniivlon	5	41.8	58.8	63.1	51.5	459
	15	26.5	34.0	43.2	26.9	461
	25	22.9	29.4	34.8	23.7	463
	35	21.6	25.3	27.3	19.2	473
glass fiber	5	64.5	86.5	15.7	25.9	470
	15	55.1	79.1	19.3	24.8	466
	25	57.1	84.1	19.3	27.3	466
	35	53.3	81.3	13.1	20.6	463

searched temperature interval, and to the greatest degree (by 63 %) – at heightened temperatures (423–463K). The temperature coefficient of the linear expansion of the organic plastics reinforced by terlon has lower values and decreases for 69 % with the increasing in the amount of filler in the above temperature interval [167].

Glass fiber insertion in the polyarylate reduces the tempera-ture coefficient of linear expansion in 1.5–3.6 times (Table 2.15), this parameter decreasing the most intensively when the quantity of glass fiber in composites is rising from 5 to 15 mass %.

The calculation of the additive values of the temperature coefficient linear dilatation for the organoplastics shows us that for the binder, filled by 5, 15 and 25 mass % glass fiber, the additive values are higher than experimental ones, but in a contrary for the glass plastics with 35 mass % – we can see rather different situation: the experimental linear dilatation of the temperature coefficient is higher than additive. Besides, the results of calculation show that for the binder this parameter has a little dependence of temperature, but for glass fibers, especially in the high temperature areas (373–463K) decreasing extensively (in 3.6–5.5 times).

As for the effect of the filler content on the glass transition temperature of the plastics, that its most significant growth is observed when the content of terlon fiber, vniivlon fiber and carbon fiber is 35 mass % (on 20, 5 and 5 degrees according) What about

Table 2.15: The average temperature coefficient of the lin ear dilatation of the glass plastics, based on polyarylate in the temperature interval 298–323 K, $\alpha \times 10^{-7}$, K^{-1}

Content glass fiber, mass %	Additive	Experi-mental	Inclination percentage of the additive values from experimental ones
5	7.48	6.45	13.8
15	6.42	5.51	14.2
25	5.97	5.71	4.4
35	5.21	5.33	2.3

the glass fiber, they slightly reduce the glass transition temperature of the composites compared to polyarylate.

2.5. Physical and mechanical properties

Comparative analysis of the calculation density and composites samples density, determined by the hydrostatic weighing method (Table 2.16) shows that the character of their changes determined by the processes of the physical and chemical interactions of the components take place into a material structure.

The results of the research shows us that the density of the carbon plastics increases a little (on 2% in average). For the composites contented 15 mass % of the carbon fiber the experimental density is higher than the calculated one (additive). The last one is caused by the fact that under filler influence in a structure of

Table 2.16: Density of the polymer composites based on polyarylate

Filler		Additive density, kg/m^3	Density determined by hydrostatic weighing, kg/m^3	Coefficient of the correlation
Type	Content			
uglen	5	1261	1263	0,99942
	15	1302	1305	
	25	1343	1352	
	35	1384	1391	
terlon	5	1251	1252	0,96664
	15	1273	1286	
	25	1295	1298	
	35	1317	1312	
vniivlon	5	1252	1260	0,96728
	15	1269	1280	
	25	1288	1290	
	35	1307	1330	
glass fiber	5	1313	1267	0,99957
	15	1459	1334	
	25	1605	1412	
	35	1751	1486	

Note: *Polyarylate density – 1240 kg/m*^{3}.

carbon plastics the ordering processes is developing. Made conclusion is confirmed by the data of the X-ray diffraction analysis of the composites: there is some changes of the organoplastics diffraction curves character, bespoken by the dislocation in the area of more higher Bragg's angles and reducing of the amorphous halo intensity.

Organoplastics, contented 5–25 mass % of terlon, have experimental density, exceeding additive. However, for the composites with filler degree of 35 mass % the feed back appears: additive density exceeds experimental, and it explains by the developing the organoplastics fracturing process in its structure and confirmed by the X-ray diffraction analysis data. The crystallinity degree calculation of the organoplastics, reinforced by terlon shows that it decreases for the pointed composite. Organoplastics, contented vniivlon, independent on the filler degree, have higher experimental density than the calculated one, that explicitly show us that there is a tendency to increasing structure ordering degree with increasing the quantity of this organic fiber.

From all researched composites the maximum density have organoplastics samples, and it explains by the high density of the filler (the density of the glass fibers is 2700 kg/m^3).

Polyester reinforcing by discontinuous fibers decreases the composites impact resistance: the bigger amount of the filler, the bigger degree. At the binder reinforcing by vniivlon, terlon, uglen and glass fiber decreases at the increasing of the fiber quantity from 2 till 35 mass % it is 36–44; 49–84; 36–90 and 46–86% accordingly (fig. 2.30). Apparently, it can be explained by insufficient high adhesion bond between binder and filler.

It is known [150] that the peculiarities of the carbon fiber surface construction after its high temperature finishing don’t allow to get the optimised strength connection between fiber and binder. Crispness and shortness of the carbon and glass fiber, and the significant damage them in a combining process with the base polymer makes some difficulties for the developing of the carbon and glass plastics with high impact resistance. However, despite rather low values, this physical and mechanical index is higher at the absolute value, than impact resistance of the carbon plastics, based on PA-6.10 and polypropylene (Table 2.17).

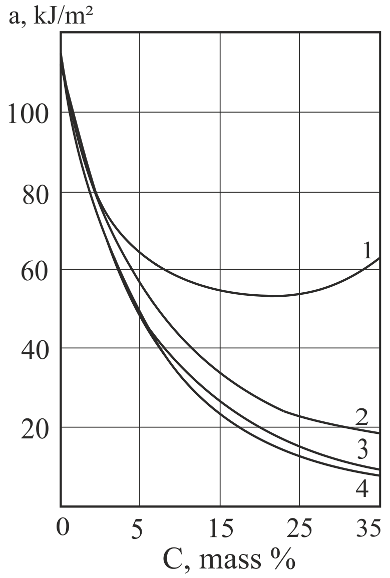


Fig. 2.30: Dependence of the composites impact resistance on vniivlon (1); terlon (2); uglen (3) and glass fiber (4)

Rather low values of the organoplastics impact resistance, reinforced by terlon, explains by the fact that this fiber was covered by the finishing oil. The highest impact resistance has the composites samples, reinforced by vniivlon; the experimental values of this index for carbon and glass plastics have close values.

Table 2.17: Influence of the carbon fiber content on the impact resistance of the composites based on polyarylate, PA-6.10 and polypropylene [183, 184]

Binder – polyarylate				Binder – PA-6.10				Binder – polypropylene			
5	15	25	35	5	10	15	20	5	10	15	20
71	28	15	12	8	7	4	10	35	20	11	10

Flintiness of the composites according to Brinell (Table 2.18) in comparison with the binder increases on 12-28% in average attains maximum value for the samples with the 35 mass % of the fiber content.

Table 2.18: Dependence of composites flintiness on the nature and fiber content according to Brinell

Fiber	Fiber content, mass %			
	5	15	25	35
uglen	82.4	88.7	96.5	98.9
terlon	81.2	87.4	94.1	97.5

***Note:** Polyarylate flintiness according to Brinell – 71.5 MPa.*

Flintiness of the carbon fiber, based on polyarylate, which is within 82-99 MPa, concedes a little at average flintiness values of organoplastics, based on oxetane resin (102 MPa), PA-12 (116 MPa) according to Brinell and exceed carbon plastics, based on polyprepylene [186].

Carbon plastics have maximum micro flintiness, and organoplastics, vniivlon contented have the minimum one (fig. 2.31).

Received data correlate with the research results on the determination of the impact resistance of the carbon and organoplastics rather good. Considering the fact that increasing material flintiness, as a rule, is accompanied by the growth of its crispness, rather regular is the fact that organoplastics have the lowest impact resistance values and organoplastics, reinforced by vniivlon have the maximum ones in comparison with other fillers.

Compression test is one of the widely used experimental methods for materials mechanical properties determination [185]. To understand the whole variety of the mechanical behaviour of the composites, based on polyarylate the main regularities between actual stress and setting up deformation were considered at the compression pressure.

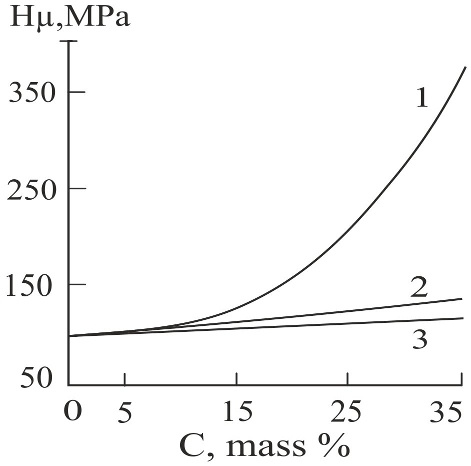


Fig. 2.31: Dependence of the microflintiness of the composite materials based on polyarylate on the fiber content: uglen (1); terlon (2) and vniivlon (3)

The curves of the tensile strength dependence at compression from carbon and glass plastics, according to the Herzberg classification belongs to the 2nd type of curves as the results of the mechanical research shows. Stiffening and deformation is proportional to each other (describing by the Hooke's law) and characterized material's spring deformation at the first straight-line segment at small deformation values. Parabolic segment of the curve, describing homogeneous plastic deformation follows next [187, 188]. Based upon curves character (fig. 2.32 a, b, c), carbon plastics modulus of elasticity depends on filler content. The modulus of elasticity calculation confirmed the correctness of the visual estimation (Table 2.19). So, organoplastic, glass plastics and carbon plastics with the fiber content of 35 mass % have higher modulus of elasticity at the compression, than the binder in 2.3, 3 and 1.5 accordingly.

Research of the material destruction character at the compression (fig. 2.32) shows us that binder samples destruct plastically: they have barrel shaped form and don't perish till the deformation moment. Carbon plastics perish delicately: on the composite samples, contented 5 and 15 mass % of carbon fiber, there are incline (approximately 45° to the samples pad) cracks, directed parallel to the squares, in which there is big shearing strength. It is an indirect proof that these carbon plastics have high resistance to the shift. For the composites with 25 and 35 mass % of carbon fiber at the same deformations material decompose on the pieces. Horizontal cracks on the samples from the organoplastics shows us the low adhesion of the glass fiber to the binder.

Curves character stiffening – deformation of the organo-plastics (fig. 2.32a) depends on filler content: so, at the polyarylate reinforcing by 5 and 15 mass % of vniivlon (curves 1, 2 – II type), samples have delicate character of destruction, and at the increasing of the polyester reinforcing degree – organoplastics destruct springily under the compression pressure, and sharp change of the curve character shows that (curves 3, 4, 5, – I type).

Table 2.19: Influence of the content and fiber nature on strength capacities of the composites during the compression

Fiber filler		Tensile strength, MPa	Elasticity modulus, MPa	Destruction work, kJ
–	–	168	900	2888
uglen	5	182	1138	3531
	15	231	1163	4931
	25	165	1263	2300
	35	155	1375	2332
vniivlon	5	210	800	3348
	15	231	1000	2933
	25	242	1600	2413
	35	253	2670	2535
glass fiber	5	217	750	2760
	15	235	1200	3115
	25	245	2000	4020
	35	260	2100	4636

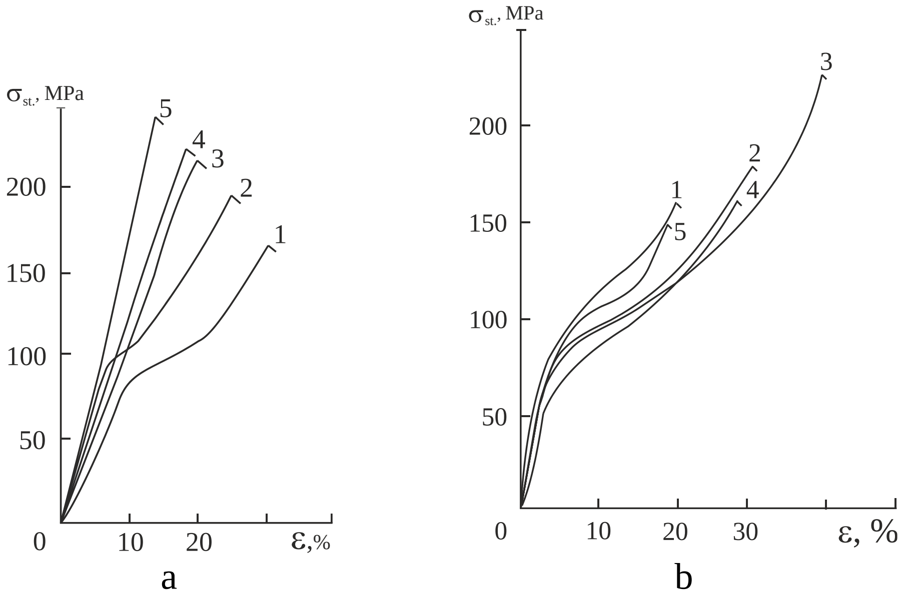


Fig. 2.32: Stiffening curves – polyarylate deformation (1) and polymer composites on its base, reinforced by vniivlon (a) and uglen (b) in an amount of 5 (2); 15 (3); 25 (4) and 35 (5) mass %

The researched data shows us that the filler nature influences a lot on the composites strength capacity: more stiffness glass and organic fibers provides the bigger increasing of the tensile strength at the compression in comparison with carbon plastics (on 92 and 85 MPa higher than the binder accordingly). In general reinforcing of the base polymer by discontinuous fibers provides the exceeding of its strength capacities on the 24–35% established according to the results of the research.

Composites dynamic characteristics research is rather important at the choosing materials for the parts, working in an intensive dynamic loads conditions, so the last causes polymer mechanical degradation, as a results of which their structure and physical and mechanical properties are changing.

High vibration-absorbing capacity of the plastic make a favourable effect on construction dynamic work, suppressing its resonance oscillation and reducing stiffening maximum from the impact shock. Thanks for the high value of the mechanical losses coefficient the resonance condition doesn't cause sharp exceed of the amplitude of oscillations in the plastic details. It could lead to the destruction in the case of metallic details at the same conditions, despite of the higher metal fatigue strength.

Taking into consideration the above, the influence of the reinforcing fillers on the composites dynamic characteristics, based on polyarylate – dynamic modulus.of elasticity ($E_{dyn.}$) and mechanical losses coefficient (η) (Table. 2.20, fig. 2.33) is studied.

The researched data show us that the dynamic modulus of elasticity increases in all cases, but it depends on the fiber nature. The most important contribution in this organic fiber parameter increases: for the composites, reinforced by vniivlon and terlon, the dynamic elasticity modulus is higher than polyarylate's in 2.4 and 3 times accordingly. We can mention that the mechanical losses coefficient increa-

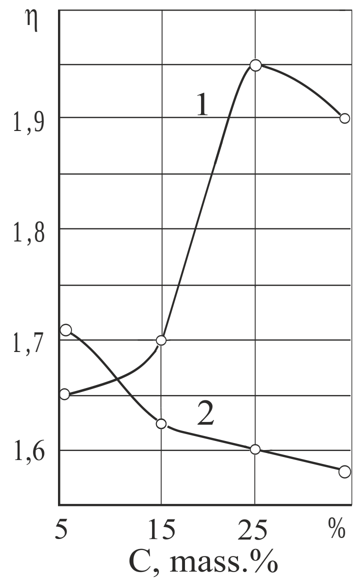


Fig. 2.33: Fiber content influence on the mechanical losses coefficient of the composites, based on polyarylate, reinforced by terlon (1) and carbon fibre (2)

ses ith the enhance of the filler quantity for the organoplastics, reinforced by terlon. It increases coming through the maximum at the fiber content of 25 mass %.

The mechanical losses coefficient of the carbon fibers changes antibate: with the carbon fiber quantity increase in the composites, it reduces in 1.1 times.

Table 2.20: Nature and fiber content influence on polyarylate dynamic elasticity modulus

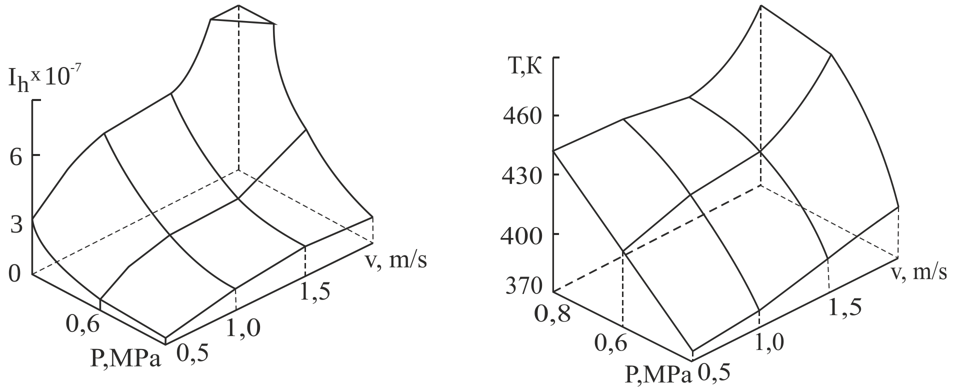
Fiber	Fiber content, mass %			
	5	15	25	35
uglen	2290	2870	3510	4910
terlon	2560	2690	3850	5930
vniivlon	2900	3850	4170	4880

Note: *Polyarylate dynamic modulus of elasticity – 2000 MPa*

We can place fibers according to the nature influence of the fiiler on the changes of the dynamic modulus of elasticity in a following order: terlon (on 57 %) > uglen (on 53 %) > vniivlon (on 41 %) [189].

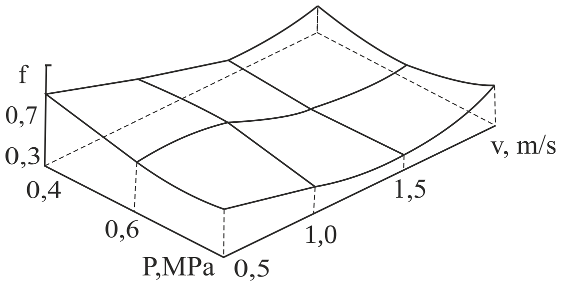
2.6. Tribological properties

Tribological properties of materials are estimated by the friction coefficient (*f*), intensity of the linear outwearing (I_h), temperature in a contact zone of the polymer sample – counterbody (*T*), and also stability of these characteristics in time at the sliding speed changing (*v*) and specific load. The main characteristics, determined the boundary condition of the dry rubbing bearing exploitations, are *PV* factor (specific load and sliding speed set) [190]. The results of the research at exploitation regimes influence on friction and polyarylate wear-out are presented on the fig. 2.34.



a b

Fig. 2.34: Dependence of the linear outwearing intensity (a), temperature in a contact zone polymer – counter-body (b), and friction coefficient (c) on specific load and sliding speed

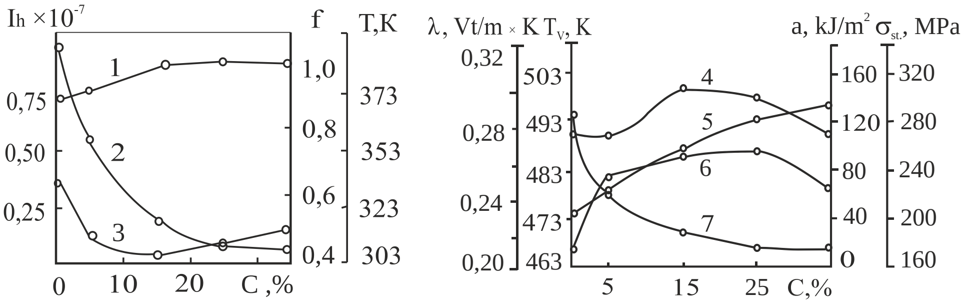


c

Binder has high friction coefficient (0.64) and applied as friction material is specified according to the data of the tribological tests. In the area of low sliding speeds (0.5–1 m/s) this index changes in modest degree and is in a range of 0.52 – 0.64. At the load enhance and sliding speed in researched range, the friction coefficient decreases in 1.5–1.9 times in average. Intensity of the linear outwearing changing and temperature in a contact zone polymer sample – counterbody with exploitation regimes stiffening have opposite character. In particular, at the enhance of the sliding speed from 0.5 to 2 m/s and specific load from 0.4 to 0.8 MPa polyarylate samples outwearing increase from 14 to 88 mg, tempe-rature in a contact zone increases on 33–47 degrees [191].

Base polymer can work at the *PV* criteria value no more than 1.2 MPa m/s was specified in research results. Friction coefficient and catastrophic wear-out of the binder can be seen at the further enhance of the *PV* criteria. The last one, obviously, can be explained by the fact that the temperature, close to the emolliating temperature of the polymer develops at these conditions in a friction zone. It leads to the polymer material seizing with the counterbody and as a consequence to enhance of the friction coefficient and intensification process of plastics outwearing.

Studying the exploitation regimes influence on friction and polyarylate outwearing shows that the most stable values of the intensity of the linear outwearing, friction coefficient and temperature in a contact zone polymer – counterbody have samples of the polyester, tested at the 0.4 MPa load and sliding speed of 1 m/s. That’s why studying the content of the organic fiber influence on organoplastics tribological characteristics makes at this regime exactly. As the research results show, the friction coefficient decreases in 1.4 times (fig. 2.35a) in average at the enhance of the filler amount, at that the most intensive decrease (on 34%) is distinctive for organoplastic with 15 mass % of vniivlon content. For composites, contented 25 and 35 mass % of filler, friction coefficient is 0.46 and 0.52 accordingly.



a b

Fig. 2.35: Temperature dependence in a contact zone (1); intensity of the linear outwearing (2); friction coefficient (3) and heat conduction coefficient (4); heat resistance according to Vicat (5); tensile strength at compression (6) and organoplastics impact resistance (7) on vniivlon content

Polyester reinforced by vniivlon provides significant wearing property enhance of organoplastics (fig. 2.35, curve 2). So, if for the base polymer the intensity of the linear outwearing value is $0.96 \cdot 10^{-7}$, then for the organoplastics, contented 5, 15, 25 and 35 mass. % of vniivlon, it takes following values: $0.55 \cdot 10^{-7}$; $0.19 \cdot 10^{-7}$; $0.078 \cdot 10^{-7}$ and $0.069 \cdot 10^{-7}$.

As for the temperature in a contact zone polymer – counterbody, so with the growth of filler amount up to 15 mass % it increases on 9%, after which it is practically unchanged (fig. 2.35, curve 1).

Received data correlate good with the thermophysical and physical and mechanical researches. As you can see from the figure 2.35b, organoplastics, reinforced by 15 mass % of vniivlon have the most optimal complex of properties.

The research of the friction surface microstructure of the composites shows that during the process we can see pilling (fig. 2.36a, b).

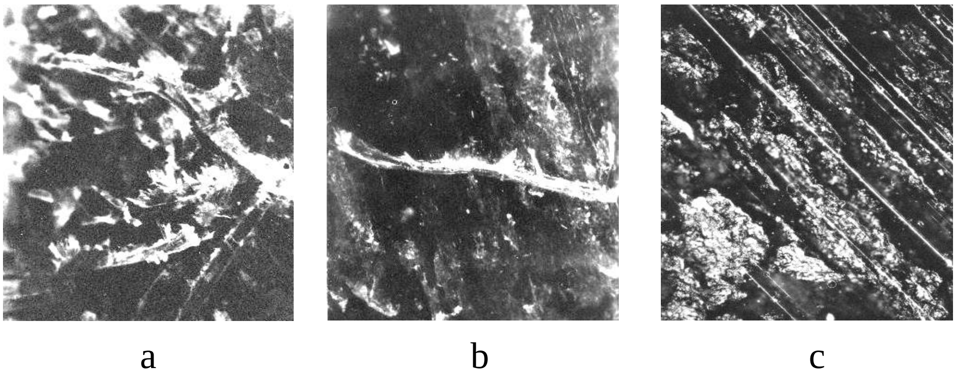


Fig. 2.36: Friction surface microstructure of the organoplastics, reinforced by 5 mass % of vniivlon after outwearing at the 0.4 MPa load and sliding speed of 1 m/s. Enhance: × 250.

As we can see from the fig. 2.36c, the shearing-off the polymer surface coat and plastering on the counterbody is happened at organoplastics friction.

It is known, that the direct destruction of the surface coat by shearing-off or breaking away is happened during the friction of the grits on the part's surface in stated conditions. Material resistance to grit destructive effect is the most important factor, determined wear resistance. Taking this into consideration, organic fiber content influence on organoplastics comparative wear resistance is studied.

Research results show, that polyarylate reinforcing by terlon and vniivlon provides the enhance of the abrasive wear resistance in 1.4 and 1.7 times accordingly (Table 2.21).

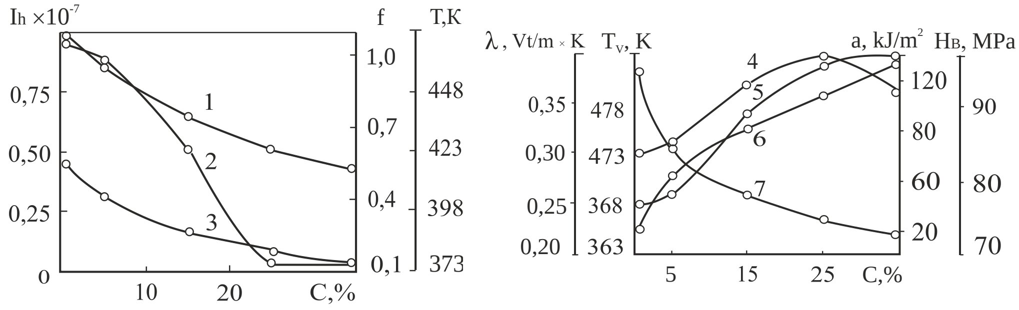
Table 2.21: Comparative wear resistance of the polymer composites based on polyarylate

Material	Weigh detrition, mg	Comparative wear resistance
Polyarylate	89.2	0.11
Polyarylate + 5% vniivlon	87.7	0.13
Polyarylate + 15% vniivlon	78.2	0.14
Polyarylate + 25% vniivlon	83.8	0.15
Polyarylate + 35% vniivlon	71.9	0.15
Polyarylate + 5% terlon	44.4	0.14
Polyarylate + 15% terlon	50.7	0.16
Polyarylate + 25% terlon	57.1	0.18
Polyarylate + 35% terlon	60.2	0.19

At present time carbon fiber, as a filler of the thermoplastics for antifrictional purpose displaces traditional glass fiber despite the fact that the cost of the first one is higher. It explains by the fact that carbon fiber has less friction coefficient than glass fiber (for the carbon fiber this index on steel is about 0.25, and as for the glass fiber it is 0.8) [190]. Physical and mechanical properties of the carbon fiber is determined mostly by its structure, presence of alloying modifiers, defect presence.

Oeolotropic carbon fibers obtain from highly-oriented chemical fibers with developed system of fibrillae. Fibrillae, which are had in a base fiber, in a changed view are saved in carbon fibers, keeping oriented along fiber axis. Watt said rather original thought: Fibrillae impart a property to oeolotropic carbon fiber, preventing extension and growing of raptures, and so it leads to the fiber self-reinforcement. Except this, such fiber is more resistant to friction in comparison to glass fiber and isotropic fibrous forms of the carbon [151]. Considering that, the composites speciation must satisfy the construction requirements and necessary abrasive resistance, to determine optimal filler content in carbon plastics is of some interest.

Studying the influence of the binder reinforcing by carbon plastics degree shows us the maximum decrease if the friction coefficient and intensity of the carbon plastics linear outwearing attain at the binder filling by the fiber in amount of 25 mass % (fig. 2.37a). So, the comparative analysis of the tribological research data of the unfilled polyarylate and composite with the uglen content in amount of 25 mass % shows that the friction coefficient and intensity of the linear outwearing is decreased in 4.7 and more than 20 times accordingly [194, 195]. Increased abrasive resistance of the composites with carbon fiber in concordance with the fatigue abrasion theory achieved by the means of the polymer conductivity factor, prevented heat localization in a friction zone [190], that we actually see (fig. 2.37b, curve 5). Temperature decreasing in the contact zone polymer – counterbody (on 63 degrees) is happened with the increasing of the polyarylate reinforcing degree. It is very important because of decreasing of the binder thermal destruction, as a result of which load capacity of the friction unit increases.

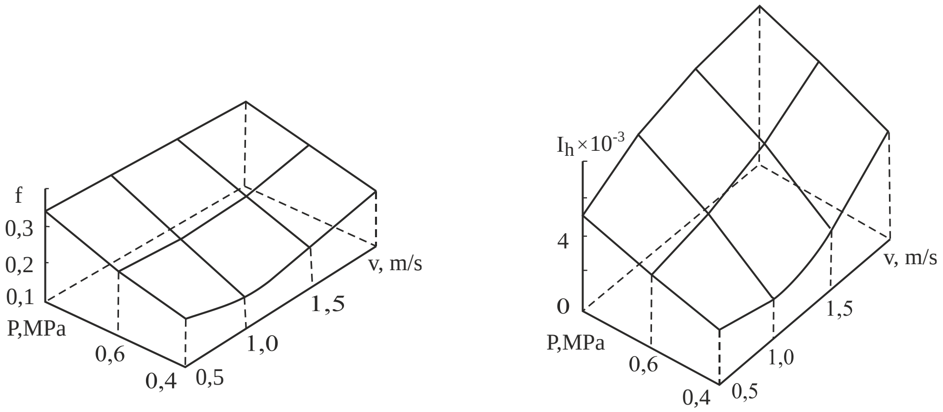


a b

Fig. 2.37: Temperature dependence in a contact zone (1); in-tensity of the linear outwearing (2); friction coefficient (3) and heat conduction coefficient (5); heat resistance according to Vicat (4); tensile strength according to Brinell (6) and carbon plastics impact resistance (7) on uglen percentage content

Based on the above, we can conclude that the most optimal carbon fiber content in polyester, allowing to receive material with complex of the improved thermophysical, physical and mechanical and triboligical characteristics is 25 mass %.

Studying the exploitation regimes influence on friction and carbon plastic wear-out (fig. 2.38) shows that at the specific load enhance from 0.4 to 0.8 MPa in all researched speed diapason (0.5–2 m/s) friction coefficient increases on 16–25%. At the load of 0.8 MPa the friction coefficient is stabilized, taking average values of 0.31–0.32. Stabilization effect of the friction coefficient can be explained by the fact that the web of finely-divided wearing particles affords during long tests. Because of it, samples friction is made not on steel bowl, but on polymer web.



a b

Fig. 2.38: Dependence of the friction coefficient (a) and intensity of the linear outwearing (b) carbon plastics, reinforced by 25 mass % of uglen on sliding speed

Product's outwearing analysis shows us that during the wear-out, carbon fibers shattered along fibrillous floor (fig 2.39).

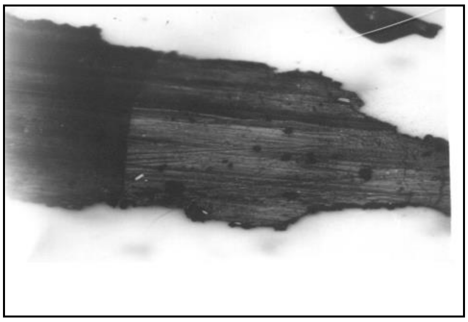
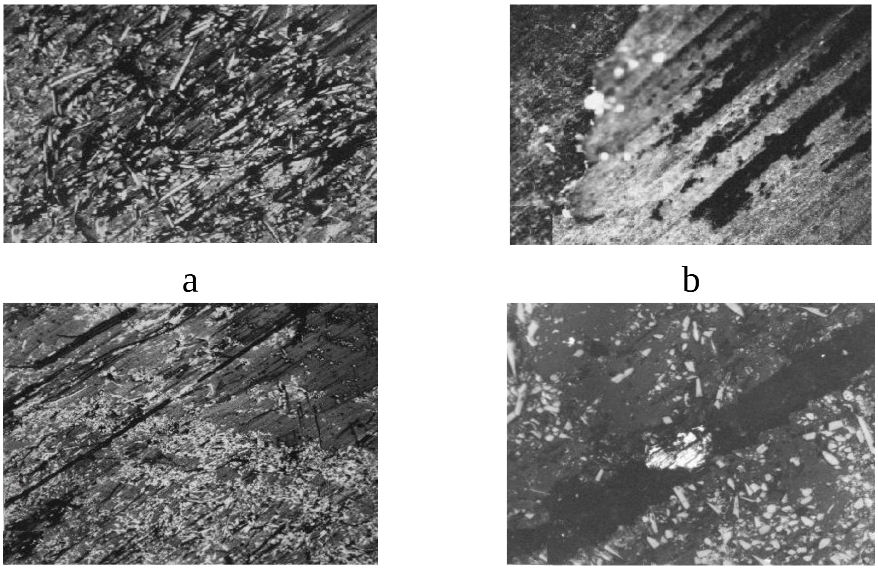


Fig. 2.39: Particles microstructure of the products' wear-out of the carbon plastics, based on polyarylate, reinforced by 25 mass % of uglen. Enhance: × 500

Friction coefficient takes on minimum values at the load 0.4 MPa and 1 m/s (0.18) sliding speed. Friction coefficient decreasing at sliding speed enhance from 0.5 to 1 m/s at the 0.4 MPa load caused on the one hand because of the friction linking decreasing carbon plastics – steel, on the other, increasing of the tangential component of the sliding speed, which contribute to effective outwearing particles derivation from the friction zone. However, at the sliding speed increasing up to 2 m/s, friction coefficient starts raising, it defined by the temperature enhance in the contact zone polymer steel bowl. Minimization effect of the friction coefficient in speed diapason 1 and 1.5 m/s decreases with the load enhance up to 0.6 MPa, and at the load of 0.8 MPa it disappears at all. Similarly to the friction coefficient, the intensity of the carbon plastics linear outwearing also changes, but intensity of its enhance increases significant in the area of the maximum loads and speeds (P = 0.6 – 0.8 MPa, v = 1.5–2 m/s).

In average, with load enhance up to 0.8 MPa, the intensity of the linear outwearing increases in 1.6–1.9 times with researched speed interval. It can be explained by the fact that high temperature develops in a conditions of the intensive slide speeds and high loads on the counterbody surface. It leads to emolliating of the binder surface coat (fig. 2.40a), and adhesion between wearing surfaces increases, as a consequence, wear-out of the polymer samples increases.



a b

c d

Fig. 2.40: Friction surface microstructure of the carbon plastic, reinforced by 25% mass of uglen, tested at specific loads 0.4 (a); 0.6 (c, d) и 0.8 (b) MPa and sliding speed 0.5 (a) and 2 m/s (b, c, d). Enhance: × 100 (в); 160 (a, b) and 500 (d)

It is known that the polymer wear-out is happened as a result of the fatigue fracture mechanism. First of all, such mechanism caused by quantum nature of the friction contact [196]. It means that polymer frequent deformation in single spots of friction contact, which leads to destruction and following material separation is happened during external friction. Degree and frequency of the deformation depend on geometry and surface properties, and also on sliding speed, temperature and pressure.

Pointed above is confirmed by the results of the research. Studying of the carbon plastics friction surface shows that the smooth glassy surface with the carbon fibers distributed at random and lengthwise stripes on the friction surface is made at abrasion (P = 0.4 MPa, v = 0.5 m/s) (fig. 2.40a).

At the exploitation regimes stiffening on the plastics friction surface, we can see significant changes (fig. 2.40 b, c, d), which consists in failing of the reinforcing filler random location in the binder structure, and also its pulling out of the polymer matrix and orientation along counterbody direction. As we mention above, it has established by the binder surface coat emolliating.

Further increasing of the load regime of the carbon plastics tests leads to seizing zone enhance, as a result of that the intensive stripes of ploughing is made on the sample surface. We can see a torn off metal particle of the counterbody in one of these stripes. This character of wear-out proclaimed that adhesive mechanism of outwearing takes place at the load of 0.8 MPa.

In a whole studying of the exploitation regimes influence on the wear-out of the composites with optimal uglen content shows that the working capacity criteria of PV composites at dry friction increases in 1.3 times (up to 1.6 MPa · m/s) in a result of polyester reinforcing. It allows using the material in wider diapason of sliding speeds and load, while it doesn't exceed 0.8 MPa · m/s for the carbon plastics based on polyvinylchloride (Table 2.22).

Table 2.22: Criteria of the carbon plastics working capacity based on polyarylate [197-199]

Binder			
Polyarylate	Polyvinylchloride	Oxetane resin	Polypropylene
1.6	0.4	0.6	0.8

Considering that carbon plastics have better complex of tribological properties, carbon plastics were chosen for the studying of the influence of the dress nature on the carbon plastics friction and wear-out. Test data of the carbon plastics at water and oil dress is presented in Table 2.23.

The researched data proclaim that composites friction coefficient takes on an extraordinary low values (0.002–0.003) at the dress presence. Dress using also lets increase load regime of plastics up to $PV = 9$ MPa · m/s, at the same time, for example, details made from bronze OCS 5-5-5 go out at $PV = 4$ MPa · m/s [200]. It is established that the lowest values of the friction coefficient is seen in researched diapason of specific pressures at sliding speed 1.3 m/s. In this case the example has smooth glassy surface without visible defects. During the tests we found that the surface roughness of the counterbody is decreased both with oil dressing, and with water dressing: before tests it was $R_a = 0.36$ micrometers, after tests –

0.33 micrometers. Probably, it specified by the fact that wear-out particles serve as polishing agent when they get in a lubricating fluid.

Table 2.23: Exploitation regimes influence on tribological properties of the carbon plastics, reinforced by 25 mass % of uglen at water and oil dressing

V, m/s	Load, MPa											
	1.25		1.87		2.5		3.12		3.75		4.37	
	f	*T*	*f*	*T*	*f*	*T*	*f*	*T*	*f*	*T*	*f*	*T*
Dress – oil												
0.8	0.006	14	0.032	16	0.030	18	0.033	22	0.034	25	0.100	34
1.3	0.003	18	0.008	20	0.021	24	0.026	26	0.034	28	0.038	32
2.6	0.003	23	0.012	26	0.033	31	0.053	34	0.048	40	0.051	49
Dress – water												
0.8	0.006	14	0.032	16	0.030	18	0.033	22	0.034	25	0.100	34
1.3	0.003	18	0.004	20	0.003	21	0.007	22	0.005	23	0.050	23
2.6	0.002	23	0.002	23	0.003	23	0.005	26	0.010	28	0.017	31

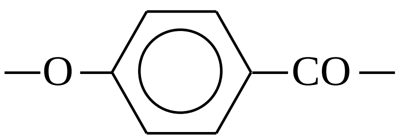
Researches of the fluid deflecting determination index show that the water and oil deflecting coefficients are 1.3342 and 1.4941, while they decrease up to 1 and 1.4934 accordingly after the research.

Chapter 3. Composites based on polyarylate reinforced by the liquid-crystalline fibers

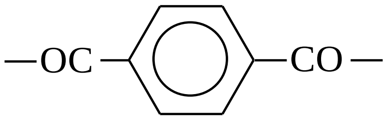
Throughout the last decades, polymer composites based on organic polymers, reinforced by the glass and carbon fibers, applied industrially instead of the metal alloys. However, as the results of our research show, we can see the maximum effect of the composites exploitation characteristics enhance, when we use liquid-crystalline fibers (LCF) during polymer binder reinforcing [201-202].

Liquid-crystalline fiber is self-reinforcing materials, which consist of rigid and semi-rigid molecules, which can orient in regard to each other in the recast process. It impacts a unique properties to them, like long working capacity at the 493-513K, high chemical and heat resistance, low temperature coefficient of the thermal expansion, good dielectric characteristics, low water sorption and good molding capacity. Thanks to the valuable complex of properties, these polymers open powerful capabilities for creating new composites.

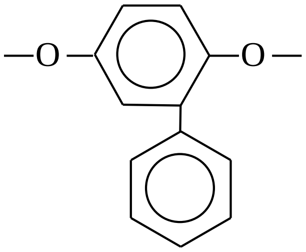
For the polyarylate reinforcing we used liquid-crystalline fibers, consisted of the n-hydroxybenzonic and terephthalic acids components, dihydroxydiphenyl with the following recipe and at the indicated ratio of the components:



10



45



45

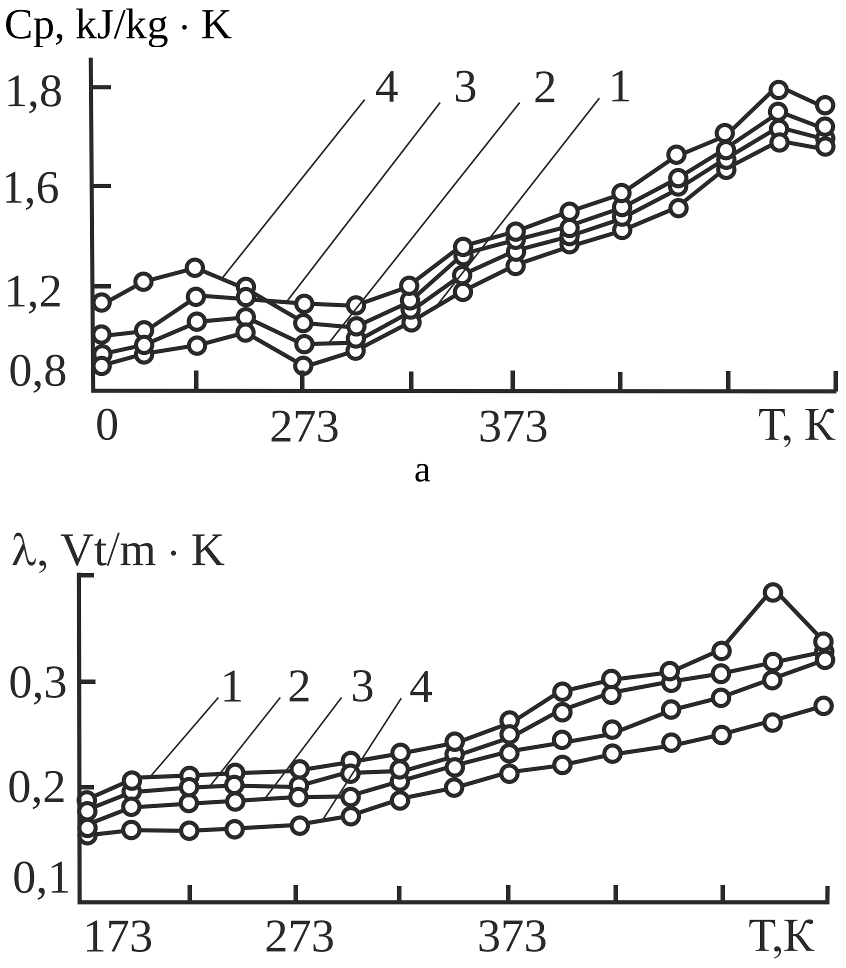
Components of the terephthalic acid and n-hydroxy acid included in the fiber composition provide rather high rigid chain. Fiber melting temperature is 280°C, density – 1.4 g/cm^3. As-spun liquid-crystalline fibers, without heat treatment, have insufficient strength and breaking strain. Apparently, the main reason of the slight mechanical index is a low molecular mass of the polymer. For increasing the molecular mass and polymer macromolecules orientation degree they were exposed to a long vacuum heat treatment. As-spun fibers are elaborated by aqueous slurry of barium sulfate ($BaSO_4$) and alkaline silica SiO_2 in order to prevent agglutinating. As far as the process of fiber reinforcement is longstanding, to reduce time of its heat treatment, the liquid-crystalline fibers are penetrated with aqua solution of potassium iodide (KI), which was used as activator (Table 3.1).

Table 3.1: Heating conditions and properties of the liquid-crystalline fibers

№	Temperature vacuum treatment ,°C	Strength, Sn/tex	Tnsile elongation, %	Impreg-nating solution
1	20-290	174.8	6.8	KI and SiO_2
2	–	67.7	3.1	0,2 % $BaSO_4$
3	20-290	152	6.0	1 % KI in water and $BaSO_4$
4	20-290	94.84	3.18	–

Preparing of compositions with the liquid-crystalline fibers content of 20 mass % is made by the approach of dry mixing in a rotating electromagnetic field. The prepared mixtures were treated into the block item by the compression pressing approach. Studying of the specific heat capacity and thermal conduction coefficient was made according to GOST 23630-79 in the temperature interval of 298-523 K on the measures IT-C-400 and IT-λ-400. Heat resistance according to Vicat is determined by GOST 15088-83 on the PTB-1-PG measure in a liquid medium in the temperature range of 298-473 K; temperature coefficient of the linear dilatation (TCLD) – on the dilatometer DKV-5AM in the tempera-ture interval of 293-1173 K. Study of the composites samples on impact resistance was held in accordance with GOST 4647-80 by Charpy approach on pendulum impact machine KM-04. Determi-nation of the yield pressure at compression, specific deformation at destruction (GOST 4651-78) was made on the FP-100 test machine. Tribological characteristics of materials were studied on the 2070 CMT-1 test machine with following parameters: kinetics of the movement – sliding of the polymer sample at steel counterbody with the diameter of 50 mm (50 $HRC_э$, R_a – 0.36 micrometers) at rotation in a dry friction regime; speed – 1 m/s; load on friction couple – 1.0 MPa; slide distance – 1000 m. Specific wear resistance during outwearing of abrasive particles, which were held nonrigidly, were determined according to GOST 23.208-79 on the friction machine SMC-2.

Data of the thermophysical research (fig. 3.1 a, b) show that in all researched temperature interval during adding liquid-crystalline fibers in polymer heat conduction coefficient reduces so as specific heat capacity, besides more intensivefor the composites, contented fiber without proofing.



a

b

Fig. 3.1: Temperature dependence of the specific heat capacity (a) and thermal conduction (b) of polyarylate (1) and composites, reinforced by liquid-crystalline fibers № 1 (2), 2 (3), 3 (5) and 4 (5)

It lets us recommend to use developed plastics as insulating materials. In addition to this, it was established that polyarylate reinforcing with heat resistant fibers let increase heat resistance at composites penetration. So, reinforcing of the base polymer by liquid-crystalline fibers 1, 2, 3, and 4 increases this thermophysical parameter on 5, 6, 15 and 8 degrees accordingly. Fiber, finished by the $BaSO_4$ and KI dispersion incre-ases heat resistance according to Vicat in a high degree. Character of the deformation curves changes of the binder samples and composites is the same: material deformation increases with temperature enhance, however it takes notice that deformation on the curves in the 300-400°C interval have negative sign. The last one proclaims the fact that the temperature indicator doesnt collapse in the sample, but on the contrary it rises insignificantly under its surface. Apparently, some residual stress, relaxation of which we can see in the process of thermomechanical testing happen in the composites, which consist of the binder and liquid-crystalline fibers with different heat conduction and heat diffusivity.

Together with the heat resistance enhance, the fact that during polyester reinforcing by liquid-crystalline fibers 2, 3 and 4 we can see a reduction of the thermal linear dilatation in the temperature interval of 293–473 K according to 2.03–1.98; 2.2–1.5 and 1.7–2.2 times was established (Table 3.2).

In comparison with the base polyester, Rockwell hardness and comparative wear resistance of the developed materials change a little; the impact resistance decreases and this fact is common for the materials, reinforced by fibrous filler (Table 3.3). Independent from liquid-crystalline fibers type, flexural yield stress at compression increases in comparison with the binder. It takes maximum values in case of reinforcing by liquid-crystalline fiber 2. Curves of the dependence yield strength at compression ($\sigma_{st.}$) – tensile strain (ε) of the composites, according to the Hertzberg classification, refer to the second type. At the first straight-line segment at small values, stiffening and deformation are proportional to each other (describe by the Huck law) and characterize material spring deformation at small deformation values (fig. 3.2b). Parabolic segment of the curve, describing homogeneous plastic deformation follows next [188].

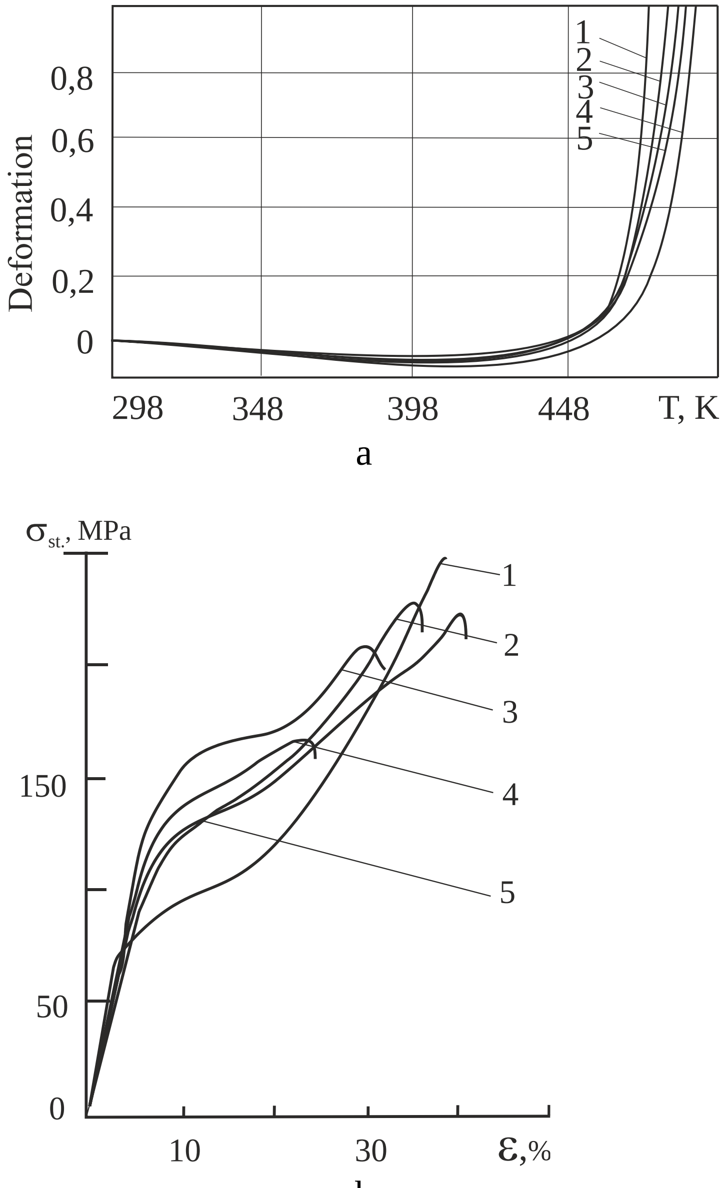
Table 3.2: Temperature coefficient of the linear dilatation of the composites based on polyarylate, reinforced by liquid-crystalline fibers

Temperature, K	$\alpha \cdot 10^{-6}$, K^{-1}			
	Polyaryate	Fiber type		
		2	3	4
293-323	60.90	30.00	28.60	35.70
293-348	66.36	36.45	34.87	37.86
293-373	68.50	39.85	39.86	38.60
293-398	69.66	41.40	41.52	40.40
293-423	70.36	44.00	44.00	42.80
293-448	71.56	46.40	46.62	44.03
293-473	71.00	35.90	46.42	31.73

Research of the material failure mode at compression shows that the polyarylate samples creep plastically and assume a barrel shape. They also don’t perish in all deformation diapason. As for the composites, they perish delicately: there are inclines (approximately at the angle of 45° to the samples pad) cracks, directed parallel to the squares, in which there is big shearing strength on the samples. It is an indirect proof that these composites have high resistance to the shift. Results of the physical and mechanical researches bespeak that composite, contented liquid-crystalline fiber 3 has the optimal complex of properties. So, in particular,

Table 3.3: Fiber nature influence on physical and mechanical and tribological properties of the composites based on polyarylate

Index	Polyarylate	Fiber type			
		1	2	3	4
Indurate according to Rockwell HR_α	104	–	101.3	104.2	103.7
Comparative wear resistance	0.21	–	0.20	0.18	0.20
Impact resistance, kJ/m^2	62.4	–	20.7	21.9	21.5
Flexural yield stress at compression, MPa	95	128	155	140	148
Coefficient of the friction	0.6	0.6	0.7	0.4	0.6
Weigh detrition, mg	7.8	14.2	13.01	5.05	11.3



a

b

Fig. 3.2: Heat resistance according to Vicat (a) and curves of stiffening – deformation (b) of the composites, based on polyarylate, reinforced by liquid-crystalline fibers: № 1 (2); 2 (3); 3 (4); 4 (5)

samples from the pointed material have maximum impact resistance, rather high value of the yield strength at compression in comparison with plastics, reinforced by another liquid-crystalline fibers. Study of the exploitation regimes influence on the friction coefficient of the binder and composite, reinforced by liquid-crystalline fiber 1 (Table 3.4 show that minimum values of this parameter are indicative for the researched materials at specific pressure of 1.0 MPa. That's why further tribological researches of the composites was continued at this load. It is found that significant reduction of the friction coefficient is happened only during binder reinforcing by liquid-crystalline fiber 3 (in 1.5 times); in addition to this, composites abrasive resistance increases on 29 %.

Table 3.4: Specific pressure influence on friction coefficient of the composite based on polyarylate

Specific pressure, MPa		
0.5	1.0	1.5
Polyarylate		
1.0	0.6	0.7
Polymer composite		
0.8	0.6	0.7

In general, according to the test results, we can conclude that polyester binder reinforcing by liquid-crystalline fibers let receive new composites with improved exploitation characteristics. It ought to be noted that the additional fiber processing by the potassium iodide solution let improve filler properties significantly. Research data proclaim that the composites, reinforced by liquid-crystalline fiber 3 have optimal complex of exploitation characteristics. It allows recommend this composite for using as a material for constructional purpose [203].

Chapter 4. Composites based on polyarylate filled with oxynitride-silicon-yttrium

A big range of polymer matrices, reinforcing fibers with different elastic-strength properties and dispersed fillers let create polymer composites with complex of properties, which corresponds to the character and conditions of parts and construction work more completely.

To receive new plastics, polyarylate was filled by ultradisperse powdered filler-oxynitride-silicon-yttrium. Properties of the used filler is shown in the Table 4.1.

Table 4.1: Properties and composition
of the oxynitride-silicon-yttrium

Filler	Dimensions of the particles, mcm	Specific surface	Chemical preparation
Oxynitride silicon-yttrium Si_3N_4-Y_2O_3	0.008–0.12	42.5	32.3 % N, 4.0 % Si, 9.5 % Y_2O_3

Oxynitride powder was received by plasma-chemical approach [204]. As compound, received by this approach, have increased chemical and structural activity, as filler content doesn’t increase

10 mass % in researched composite. Increased chemical activity of the filler is connected with the presence of the big amount of uncompensated links of different nature on the particles' surface [205].

Thermophysical researches show the same character of temperature dependence (Fig. 4.1) of the binder specific heat capacity and composites in researched temperature interval (173–573K) as in the conditions of low temperatures (173–298 K), as monotonous enhance of this parameter up to 423K is happened at increased temperatures. For the binder and composite with filler content of 0.2 mass % in transition area of the polymer from glassy state into high elastic state, specific heat goes through the maximum at the temperature of 498 K, and after that it decreases sharply; for the composites with the filler content in amount of 5 and 10 mass % the leap of heat capacity shifts in a side of lower temperatures (473K). Increment addition of the heat capacity (Table 4.2) during composites transition from glassy state into high elastic at the glass transition temperature, decreases at the presence of the ultradisperse filler (except composite with oxynitride content of 0.2 mass %), provided that the decrement value ΔC_p can be semiquantitative measure of the boundary layers relative content in the filled system. Data of leap calculation ΔC_p in the area of the composites' phase transitions is showed in the Table 4.2.

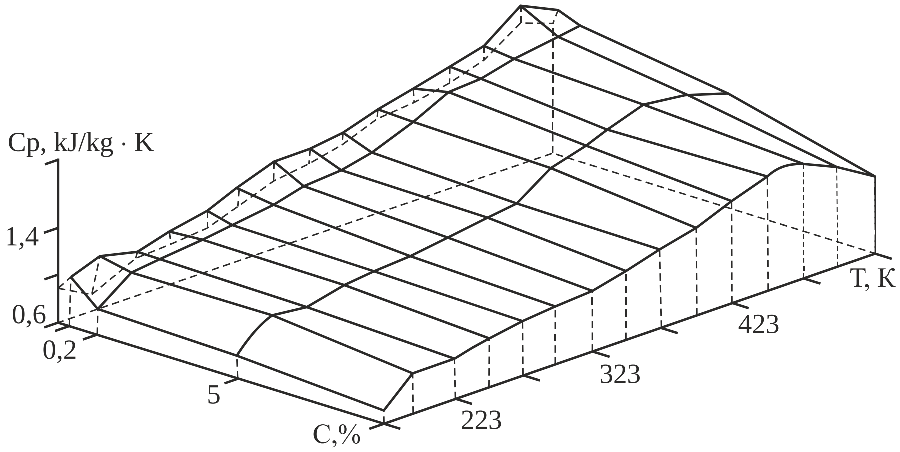


Fig. 4.1: Temperature dependence on specific heat capacity of the polyarylate and composites on its base, filled 0.2; 1; 5 and 10 mass % of oxynitride silicon-yttrium

Estimation of the ultadisperse filler influence on this thermo-physical index let us mark that at its content in amount of 0.2 mass % we can see anomalous declination of the heat capacity. So, independently from the temperature test on concentration dependences of specific heat capacity we can see maximum at oxynitride silicon-yttrium content of 0.2 mass %, in other words we can see so called “small additives effect”, which is distinctive for the polymers with filler content in amount of less than 1 mass % [206].

Table 4.2: Value of the composites heat capacity leap based on polyarylate, kJ/kg · K

Oxynitride silicon-yttrium content, mass %				
–	0.2	1	5	10
0.17	0.21	0.16	0.14	0.11

Apparently, there are some structural changes in a polymer binder at small amount of reinforcing filler in the composite. It causes the enhance of the ΔC_p leap in the area of phase transitions in comparison with polyarylate.

With further growing of the oxynitride silicon-yttrium crowding up to 1 mass % and more ΔC_p starts decreasing sharply, it can be connected with the enhance amorphic polymer part involved into transition layers, and with the disclusion of this share of molecules' segments from the number participating in glassing. Such supposition allowed to evaluate approximate thickness of a transition layer (Table 4.3).

Table 4.3: Thickness of the boundary layer of composites based on polyarylate, Å

Content of the oxynitride silicon-yttrium, mass %		
1	5	10
364	987	1686

As data from the tables 3.2 and 3.3 show us, the enhance degree of the filler polyarylate from 1 to 10 mass % leads to decrease of ΔC_p and thickness of the boundary layer polymer binder-filler increases.

In a whole, according to the results of the specific heat capacity of the composites based on polyarylate research, we should mention that filling of the polyester binder by ultradisperse mineral oxynitride silicon-yttrium, let us decrease this thermophysical index on 10-18 % in average, hypothetically, as a result of segment mobility limitation.

Decreasing of the specific heat capacity in researched temperature interval is accompanied by increasing of the composites heat conduction coefficient in 1.2–1.4 times in average (Table 4.4), what is more, the bigger degree, the higher filler content.

Table 4.4: The coefficient of the composites heat conduction on the base of polyarylate

Temperature, K	Content of the oxynitride silicon-yttrium, mass %				
	–	0.2	1	5	10
223	0. 22	0,23	0.24	0.25	0.26
323	0.25	0.26	0.28	0.29	0.30
423	0.31	0.33	0.34	0.34	0.36
523	0.35	0.38	0.39	0.40	0.42

Studying of the tribological properties of developed composites was made on the SMC-1 friction machine in dry friction regime at specific load of 0.5–1.5 MPa and sliding speed of 1.0 m/s; slip distance was – 1 km, disk, manufactured from 45 steel with thickness after 50 HRC heating, was used as a counterbody. Heat conduction coefficient of the composites is determined on the

IT-λ-400 according to GOST 23630.2-79 in the temperature interval of 173-523 K. Determination of the destruction stiffening at compression, specific deformations at destruction were made according to GOST 4651-78 on the FRZ-100/1 test machine. Impact resistance was determined according to Charpy approach and GOST 4647-80 on the impact pendulum-type testing machine KM-04.

It is known that the physical and mechanical characteristics of the filled plastics are determined by the polymer, which is used as a binder. However, filler and doping agents influence significantly over the wear resistance and coefficient of friction: they change their material characteristics in rather wide range and perform function of a frame in the compositions.

Considering the fact that there is up to 10 mass % of the filler in the researched composites, changes of the composites tribological properties in dependence on percentage content of oxynitride silicon-yttrium can be explained by binder structure transformation. Meanwhile a small amount of the reinforcing filler influence significantly over the polymer structure. Analysis of the tribological research data (Table 4.5 and Fig. 4.2-4.4) shows that in all researched load interval just a small degree of the filling (0.2 mass %) decrease significantly the coefficient of friction and temperature in a contact zone polymer binder – counterbody. So, oxynytride adding in amount of 0.2 mass % at the load of 0.5; 1.0 and 1.5 MPa decreases coefficient of friction in comparison with the binder on 30; 16.7 and 14.3 % accordingly. However, lower values of the coefficient of friction is distinctive for the composites contented 10 mass % of pointed filler.

Research results analysis of the specific load influence on the composites tribological properties (Table 4.5 and Fig. 4.2-4.4) shows that developed plastics can be successfully operated in rather rigid conditions: at the criteria value *PV* up to 1.5 MPa · m/s.

Table 4.5: Specific load and filler content influence on tribological characteristics of the composites based on polyarylate

Load, MPa	Content of the oxynitride silicon-yttrium, mass %				
	–	0.2	1	5	10
Coefficient of friction					
0.50	1.00	0.70	0.80	0.80	0.60
Temperature in the contact area, K					
0.50	345	333	343	331	333
Weigh detrition, mg					
0.50	2.6	3.6	2.7	1.4	18.1

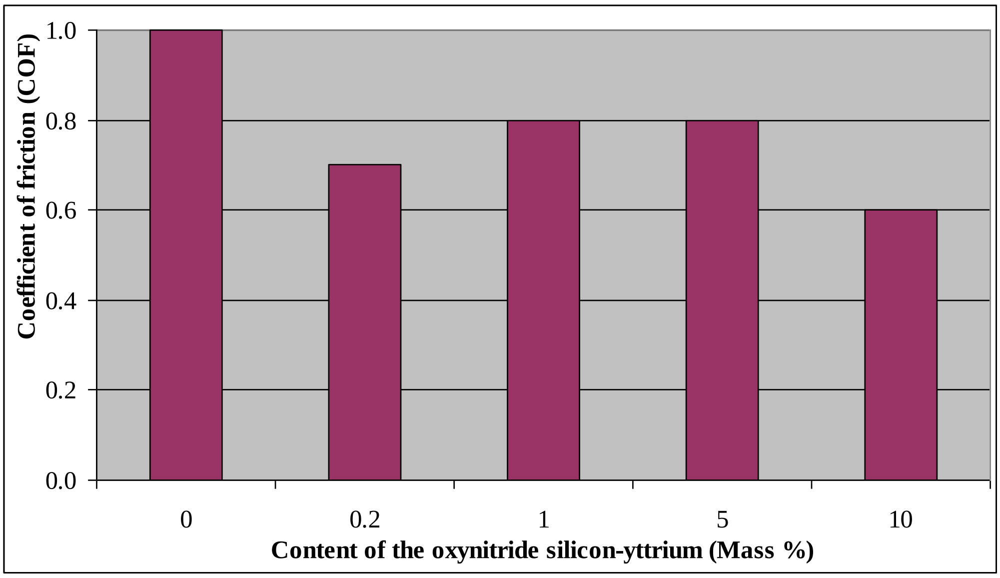


Fig. 4.2: Graphical representation of dependencies coefficient of friction from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

Study of the load influence on composites tribological properties shows that polyarylate filling by oxynitride silicon-yttrium provides decreasing of the coefficient of friction and temperature in a contact zone at composites friction along steel counterbody in all researched diapason of loads. It takes notice the fact that the most significant decreasing of the coefficient of friction (in 1.4–1.9 times) we can see at the load of 1.5 MPa.

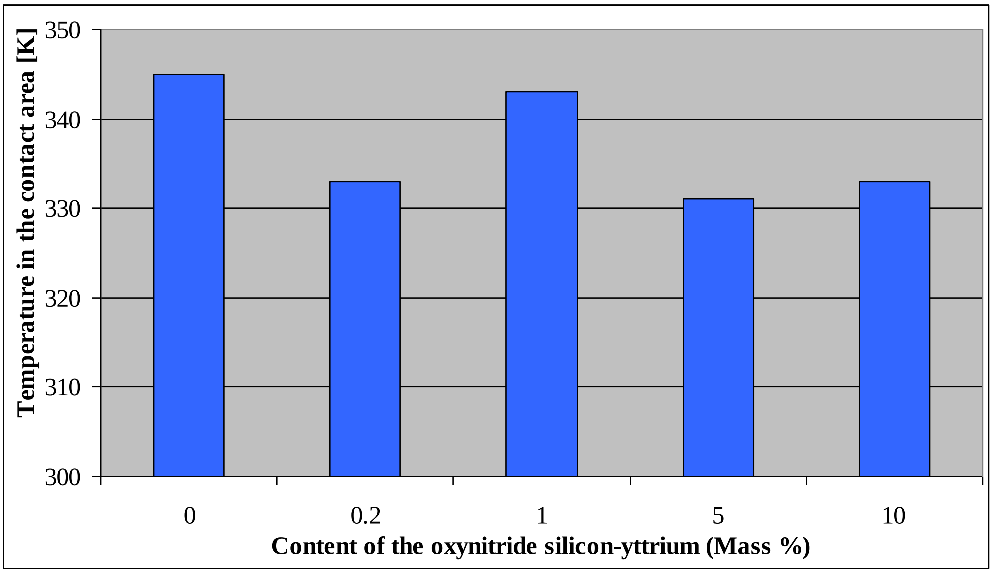


Fig. 4.3: Graphical representation of dependencies temperature in the contact area from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

Coefficient of friction dependence on specific load (friction law) is determined, mainly, by the changing with load of the actual contact square. Tanaka [206] shows that the friction of the rigid polymer connected to their deformational properties in a contact zone, frictional force is proportional to the contact square. Characterizing the filler influence on the composites wear-off we can note that at the load less than 0.5 MPa and oxynitride silicon-yttrium content less than 5 mass % the composites outwearing is higher than the base polymer has.

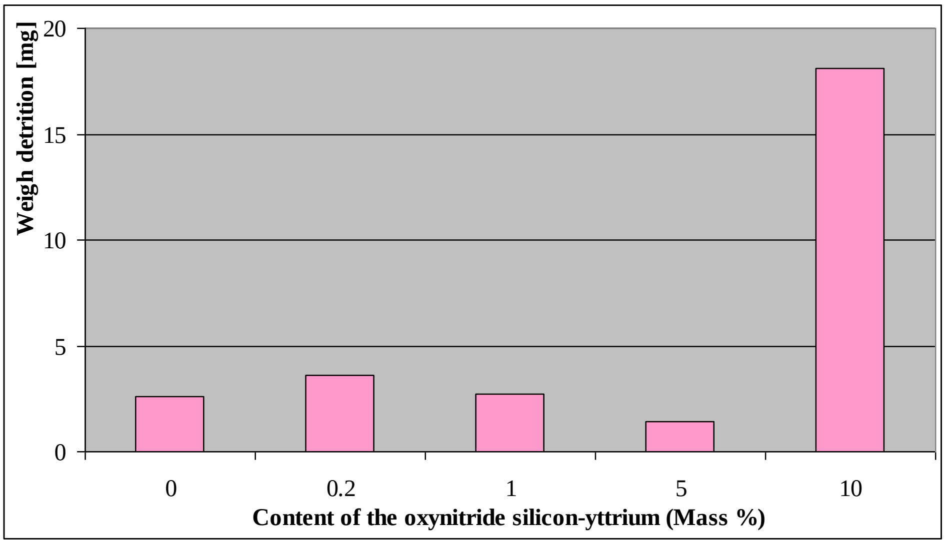


Fig. 4.4: Graphical representation of dependencies weigh detrition from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

Research of the friction surface microstructure (Fig. 4.5) after its failure shows that the reason of this is attainment of the temperature close to binder melting temperature in a contact zone. In addition to the reducing of coefficient of friction, the growth of filler amount provides temperature decreasing in a contact zone polymer–counterbody. It can be explained by the heat conduction increasing of the developed composites and as a result, the best heat removal from the friction zone.

The results of the thermophysical research [207] show that the polyarylate filling provides the growth of the composites heat conduction coefficient in all researched temperature interval (173–523 K).

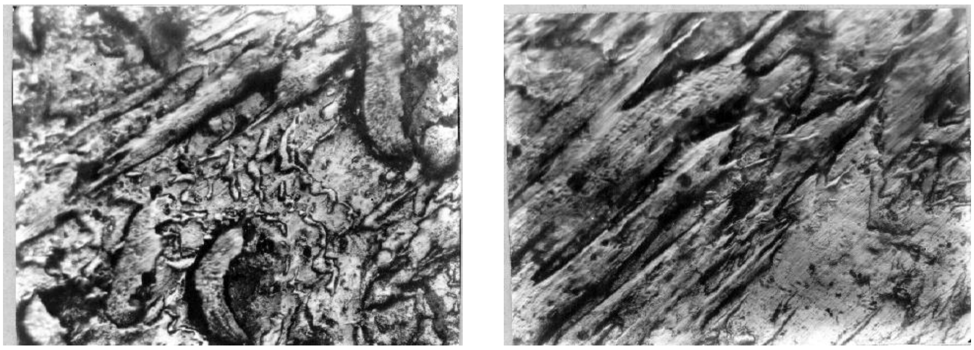


Fig. 4.5: Friction surface microstructure of the composites based on polyarylate after the tests in dry friction regime

In addition to improvement of the tribological and thermo-physical properties, the improving of the physical and mechanical properties is distinctive for the developed composite materials (Table 4.6, Fig. 4.6-4.10).

So, for the composites contented 1, 5 and 10 mass % of oxynitride silicon-yttrium, the modulus of elasticity increases at the compression in 2.8; 10 and 33.3 % times accordingly. It is noticed that the out-rigger reduces in comparison with polyester modulus of elasticity at filler content in amount of 0.2 mass %. Apparently, it can be explained by the fact that insignificant content of the oxynitride silicon-yttrium influence on the polymer structure (probably, it makes large fibrillous structure of material), and this,

Table 4.6: Mechanical characteristics of the composites based on polyarylate

Index	Content of oxynitride-silicon-yttrium, mass %				
	–	0.2	1	5	10
Elasticity modulus at compression, MPa	2400	1880	2160	2320	2800
Ultimate tensile strength at compression, MPa	243	240	245	243	243
Tensile strain, %	27	36	35	23	31
Destruction work, kJ	8900	10540	11520	7410	10180
Impact resistance, kJ/m^2	62.4	67.2	51.4	30.5	18.7

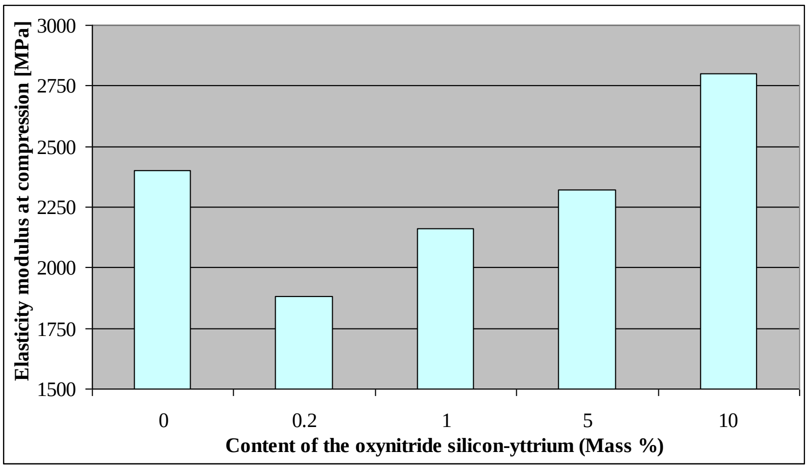


Fig. 4.6: Graphical representation of dependencies elasticity modulus at compression from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

in its turn, leads to decreasing of this index. Delicate destruction of the samples (Fig. 4.5) is noticed for the composites in a result of creating linear (for the composites, contented 5 and 10 mass % of filler) and inclined cracks-approximately 45° to the rapture pad samples (for the composites, contented 0.2 and 1 mass % of oxynitride silicon-yttrium). Inclined cracks is parallel to squares, in which the biggest shearing strengths function, in other words, these materials will have the biggest resistance to shift and impact resistance. The last one is confirmed by the data from the Table 4.6.

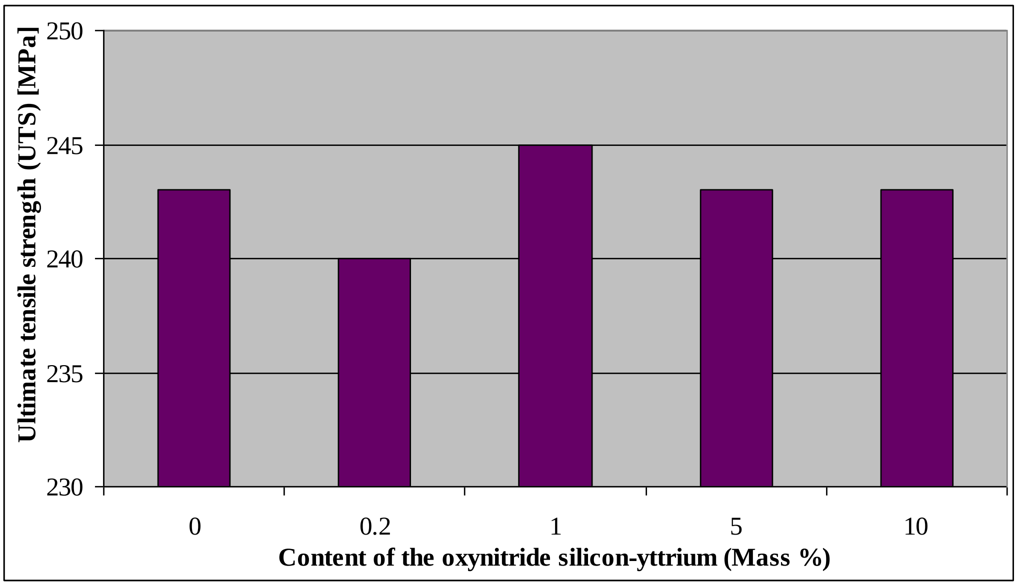


Fig. 4.7: Graphical representation of dependencies ultimate tensile strength at compression from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

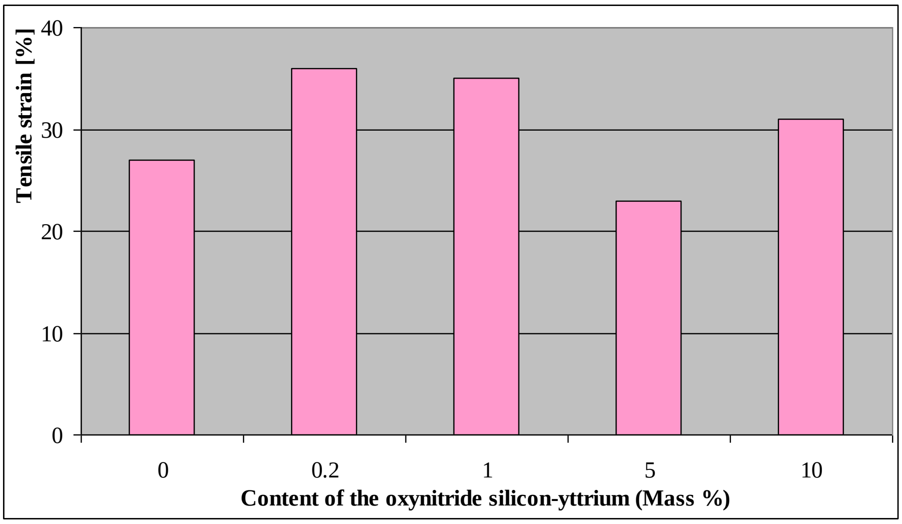


Fig. 4.8: Graphical representation of dependencies tensile strain from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

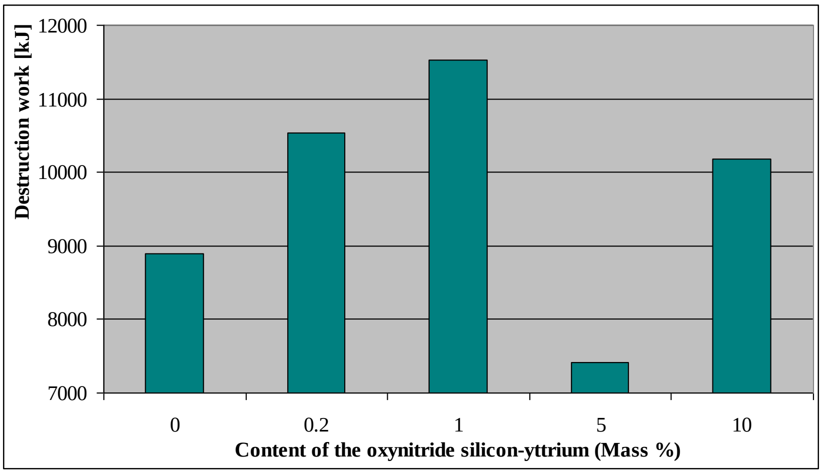


Fig. 4.9: Graphical representation of dependencies destruction work from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

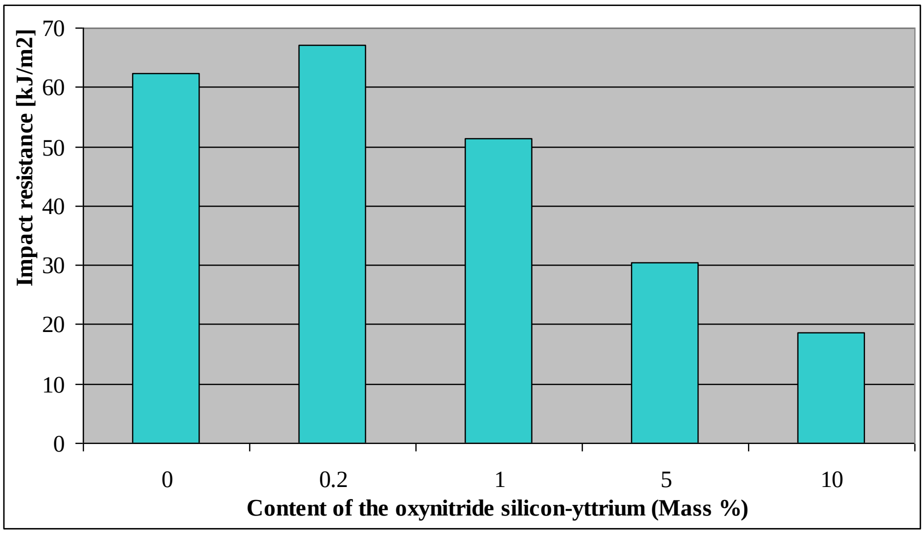


Fig. 4.10: Graphical representation of dependencies impact resistance from the composites based on polyarylate filled with different content of the oxynitride-silicon-yttrium

In one embodiment, the end-capped polyarylate comprising structural unit II is isolated by removing the solvent from a solution of the end-capped polyarylate. Suitable solvent removal techniques include, but are not limited to, distillation, air-drying, drum drying, devolatilizing extrusion, and the like. Other techniques for isolation of the end-capped polyarylate may also be effected. Such techniques include, but are not limited to precipitation into a non-solvent, followed by filtration. Filtration include sintered metal filtration, vacuum filtration, suction filtration, gravity filtration, decantation and centrifugation.

CONCLUSIONS

The results of given complex researches let us to make following conclusions:

- Regularities of thermal, physical and mechanical properties of polyarylate changes from technological parameters were established. The opportunity of using of mathematical models of different mechanisms of heterogeneous processes for the determination of optimal kinetic parameters thermal oxidative breakdown of the polyarylate and composites on its base were shown.
- The main regularities of the processes, which were held on the boarder of phase separation polymer – discontinuous fiber and their main exploitation characteristics of composites were studied. It was found that the presence of the boundary layers in researched systems influences significantly on the composite structure. It is shown that composites, reinforced by fibers, close their chemical structure to binder have maximum values of boundary layers fractures.
- In a result of complex research of fibrous filler influence on thermophysical, physical, mechanical and tribological characteristics and the structure of glass-, carbon- and organic plastics on the base of polyarylates compounds of

composite materials were optimized. It was found that composites, reinforced by 25 mass % of carbon fiber and 15 mass % of organic and glass fibers have the best complex of exploitation characteristics.

- It was established that polyarylate reinforcing by uglen fiber leads to specific heat capacity reducing (on 5-16 %), temperature coefficient of linear dilatation (in 1.4-7.3 times), friction coefficient (in 1.7-3.2 times) and intensity of linear outwearing (in 5-24 times), and it also provides increasing of the heat conduction coefficient (on 10-37 %), flintiness according to Brinell (on 11-27 MPa). Using vniivlon fiber as reinforcing filler increases tensile strength at compression on 42-85 MPa and let us to receive crashworthiness composites with impact resistance of 50-60 kJ/m^2. Composites, based on polyarylate and terlon differ by increased dynamic modulus of elasticity. It was established that developed composites can work stable at the working capacity criteria PV value not less than 1.6 MPa · m/s – in dry friction regime and 9 MPa · m/s – at water and oil dressing.
- It is shown that the nature of fibrous filler influence significantly on the changing of composites properties. We can range fillers according their influence on properties improving: according tribotechnical criteria: carbon fiber > vniivlon; at strength – vniivlon > glass fiber > carbon fiber.

- Polyarylate reinforcing by liquidcrystalline fibers let us to receive new composite materials with improved properties. Additional processing of liqudcrystalline fiber with potassium iodide let improve filler exploitation characteristics significantly. Research results show us that composite, reinforced by processed liquid-crystalline fiber has the optimal complex of properties. Heat resistance according to Vicat and wear resistance of this composite is higher on 15 degrees and 29 %, and temperature coefficient of linear dilatation and friction coefficient is lower more than in 2 times and 33 % then polyarylate has.
- Using as a filler ultradisperse oxynitride silicon-yttrium, which has increased chemical and structural activity and was received by plasma-chemical approach, let us to enhance thermophysical and tribological characteristics of polyarylate. So, filling of the polyester binder by ultra-disperse filler, let increase its heat conduction almost in 1.5 times and decrease its friction coefficient on 14-30 %.
- In a whole, reinforcing of polyarylate polyesterby discontinuous chemical and liquidcrystalline fibers, and also ultradisperse filler let receive new polymer composite materials for construction purpose, which are able to work in a machines and mechanisms friction units in conditions of raised temperatures, specific loads and sliding speeds.

REFERENCES

[1] *Perspektiven technischer Kunststoffe // Konstruktionspraxis, № 6, 1992, PP. 10-11.*

[2] *Karandikar H.M., Mistree F.: Tailoring composite materials though optimal selection of their constituents // Trans. ASME J. Mech. Des., 114, № 3, 1992, PP. 451-458.*

[3] *Peter Ralf: Verbundwerkstoffe mit polymeren Matrices. Leichtgewichtig und hoch belastbar // Chem. Ind., 114, № 12, 1991, PP. 52-55.*

[4] *Archibald D.A., Schwarz J.W., Wanamaher J.L.: Reducing the cost of thermoplastic composite structures // Proc. Amer. Soc. Compos., 4th Techn. Conf., Bracksburg, Oct. 3-5, 1989, PP. 593-601.*

[5] *Chang Ike Y.: Thermoplastic matrix composites development update // 37th Int. SAMPE Symp. and Exhib. "Mater. Work. For You 21st Cent.", Anaheim, Calif., 1992, PP. 1276-1290.*

[6] *Сугиура Мотоюки: Тенденции разработки агентов для улучшения совместимости компонентов полимерных сплавов // Kogyo zairyo = Eng Mater. 39,* № *15, 1991, C. 40-45.*

[7] *Заявка 1-74259 Япония, МКИ С 08 L 67/00. Композиция полностью ароматического сложного полиэфира / Mitsui Petrochem.Ind. Ltd. (Япония), №62-227552, Заявл. 12.09.87, Опубл. 20.03.89, ИСМ 3/61, 1990, С. 94.*

[8] *Патент 5115046 США, МКИ С 08 L 67/02. Полимерные композиции на основе взаимосовместимых смесей полиамидов и полиарилатов. Amoco Corp. (США), №695937, Заявл. 06.05.91, Опубл.19.05.92, ИСМ 23/42, 1993, С. 145.*

[9] *Заявка 61-54823 Япония, МКИ С 08 L 67/02. Малогорючая полимерная композиция. Юнитика К.К. (Япония), № 52-8347, Заявл. 27.01.77, Опубл. 25.11.86, ИСМ 19/61, 1987, С. 89.*

[10] *Аскадский А.А. Физико-химия полиарилатов. М.: Химия, 1968, 216 с.*

[11] *Чигвинцева О.П., Буря А.И.: Свойства ароматических полиэфиров полиарилатов // Вопросы химии и химической технологии, №4, 2002, С. 60-69.*

[12] *Коршак В.В.: Практикум по технологии полимерных материалов. Часть II. Поликонденсационные и химически модифицированные полимерные материалы. М.: Высшая школа, 1977, С. 104.*

[13] *Perspektiven technischer Kunststoffe // Konstruktionspraxis. - 1992. - № 6. - PP.10-11.*

[14] *Tailoring composite materials though optimal selectoin of their constituents / Karandikar H.M., Mistree F. // Trans. ASME J. Mech. Des. - 1992. - 114, № 3.- PP. 451-458.*

[15] *Peter Ralf. Verbundwerkstoffe mit polymeren Matrices / Leichtgewichtig und hoch belastbar // Chem. Ind. - 1991. - 114, № 12.- PP.52, 54-55.*

[16] *Reducing the cost of thermoplastic composite structures / Archibald D.A., Schwarz J.W., Wanamaher J.L. // Proc. Amer. Soc. Compos.: 4th Techn. Conf., Bracksburg, Va, Oct. 3-5, 1989, Lancaster (Pa.), Basce, 1989. - PP. 593-601.*

[17] *Chang Ike Y. Thermoplastic matrix composites development update // 37th Int. SAMPE Symp. And Exhib. "Mater. Work. For You 21st Cent.", Anaheim, Calif., March 9-12, Covina (Calif.), 1992. - PP. 1276-1290.*

[18] *Введение к новым материалам. Пластики с уникальными свойствами / Коба M. // Puranto enjinia = Plast. Eng. - 1993. - 25, № 1. - PP. 63-68.*

[19] *Новые типы пластмасс для тяжелых условиях работы [Neue Polyarylate für Hochleistungsanwendungen] // Kunststoffe. - 1994. - 84, № 8. - PP. 1015-1019 .*

[20] *Успехи в области синтеза элементоорганических полимеров / Под ред. В.В.Коршака. - М.: Наука, 1988. - 320 с.*

[21] *High-temperature engineering resins: New materials, better performance, new uses, but are there too many producers // High-tech. Mater. Alert. - 1991. - 8, № 11.- PP. 5-6.*

[22] *Werdingen. High temperature performing plastics // ATA Ind. Automot. - 1991. - 44, № 11 .- PP. 757-762.*

[23] *High temperature engineering thermoplastics march towards the future / Massey E.M. // ANTEC'90: Plast. Environ.: Yesterday, Today and Tomorrow. Soc. Plast. Eng.: 48th Annu. Techn. Conf. And Exhib., Dallas, Tex., May 7-11, 1990, PP. 1648-1651.*

[24] *Конструкционные пластмассы / Есида Харуо // JETI: Jap. Energy and Technol. Intell. - 1991. - 39, № 1 - PP. 167.*

[25] *Robenson L.M. Recent advanced in polymer blend technology // Multiphase Macromol. Syst.: Proc. Int. Symp. 14th Bienn. Meet. Div. Polym. Sci. Amer. Chem. Soc., San Diego, Calif., Nov. 19-23, 1988, New York, London, 1989. - PP. 177-212.*

[26] *Joyce R.P. Tailor - made plastics // Des. News. - 1992. - 48, № 9. - С. 80, 84-86.*

[27] *Сугиура Мотоюки. Тенденции разработки агентов для улучшения совместимости компонентов полимерных сплавов // Kogyo zairyo = Eng. Mater.- 1991. - 39, № 15. - С. 40-45.*

[28] *Заявка 1-74259 Япония, МКИ C 08 L 67/00. Композиция полностью ароматического сложного полиэфира / Mitsui Petrochem. Ind. Ltd.(Япония). - №62-227552; Заявл. 12.09.87; Опубл. 20.03.89, ИСМ 3/61. - 1990, С. 94.*

[29] *Пат. 5115046 США, МКИ C 08 L 67/02. Полимерные композиции на основе взаимосовместимых смесей полиамидов и полиарилатов / Amoco Corp. (США). - №695937; Заявл. 06.05.91; Опубл.19.05.92,ИСМ 23/42. - 1993, С. 145.*

[30] *Заявка 61-54823 Япония, МКИ C 08 L 67/02. Малогорючая полимерная композиция / Юнитика К.К. (Япония). - № 52-8347; Заявл. 27.01.77; Опубл. 25.11.86, ИСМ 19/61. - 1987, С. 89.*

[31] *Заявка 0291997 США, МКИ C 08 L 77/00. Улучшенные термопластичные полиамид-полиарилатные композиции / E.I. Du Pont de Nemours and Company (США). - № 88108123; Заявл. 20.05.88; Опубл. 23.11.88, ИСМ 13/61. - 1989, С. 29.*

[32] *Заявка 62-944 Япония, МКИ С 08* L *67/02. Полимерная композиция и способ получения / Юнитика К.К. (Япония). - № 52-160047; Заявл. 29.12.77; Опубл. 10.01.87, ИСМ 23/61. - 1987, С. 93.*

[33] *Заявка 64-11070 Япония, МКИ С 08* L *67/02. Формуемая композиция / Юнитика К.К. (Япония). - № 56-76291; Заявл. 19.05.81; Опубл. 23.02.89, ИСМ 24/61. - 1989, С. 119.*

[34] *Пат. 5037900 Япония, МКИ С 08* L *67/02. Полимерные композиции на основе смеси полиарилата, полиамида, полиэтилентерефталата и эпоксидной смолы /* Kawasaki Steel Corp. *(Япония). - № 450222; Заявл. 12.12.89; Опубл. 06.08.91, ИСМ 6/42. - 1993, С. 137.*

[35] *Заявка 2-206650 Япония, МКИ С 08* L *77/00. Композиции на основе найлона 46 / Юнитика К.К. (Япония) . - № 1-26345; Заявл. 03.02.89; Опубл. 16.08.90.*

[36] *Заявка 88/00220 США, МКИ С 08* L *71/00. Добавление полиоксиэфира к смесям полиарилата и полиамида /* Amoco Corp. *(США). - № 87/01482; Заявл. 23.06.87; Опубл. 14.01.88, ИСМ 20/61. - 1988, С. 12.*

[37] *Заявка 4-353558 Япония, МКИ С 08* L *67/03. Полимерная композиция. /* Unitica Ltd. *(Япония). - № 3-157660; Заявл. 31.05.91; Опубл. 8.12.92, ИСМ 6/42. - 1994, С. 61.*

[38] *Заявка 62-14579 Япония, МКИ С 08 L 67/02. Огнестойкая композиция / Юнитика К.К. (Япония). - №53-8663; Заявл.27.01.78; Опубл.02.04.87, ИСМ 5/61.- 1988, С. 80.*

[39] *Заявка 5-070668 Япония, МКИ С 08 L 67/03. Огнестойкая композиция / Юнитика К.К. (Япония). - № 59-239116; Заявл. 13.11.84; Опубл. 05.10.93, ИСМ 7/42. - 1996, С. 20.*

[40] *Заявка 61-183353 Япония, МКИ С 08 L 67/02. Композиция, устойчивая к надрезам, ударам и термодеструкции / Unitica Ltd. (Япония). - № 60-24257; Заявл. 08.02.85; Опубл. 16.08.86, ИСМ 1/61. - 1988, С. 91.*

[41] *Заявка 0451769 Япония, МКИ С 08 L 67/03. Термопластичная полимерная композиция / Kanegafuchi Kagaku Kogyo К.К. (Япония). - № 91105562; Заявл. 09.04.91; Опубл. 16.10.91, ИСМ 4/42. - 1993, С. 44.*

[42] *Заявка 3-2264 Япония, МКИ С 08 L 67/02. Композиция на основе полимера, модифицированного изоцианатом / Kanegafuchi Kagaku Kogyo К.К. (Япония). - № 64-137975;Заявл.31.05.89; Опубл. 08.01.91, ИСМ 3/42. - 1992, С. 86.*

[43] *Заявка 2-308849 Япония, МКТ С 08 L 67/03. Композиции на основе модифицированных полиарилатов / Канэга-фути кагаку коге К.К. (Япония).- №1-129061; Заявл. 23.05.89; Опубл. 21.12.90.*

[44] *Заявка 2-292359 Япония, МКИ С 08 L 67/02. Эпоксидированные полимерные композиции / Kanegafuchi Chem. Ind. Co. Ltd. (Япония). - № 64-111641; Заявл. 28.04.89; Опубл. 03.12.90, ИСМ 2/42. - 1992, С. 84.*

[45] *Пат. 4769403 США, МКИ С 08 L 67/02. Термопластичные полиарилатные композиции / E.I. Du Pont de Nemours and Company (США). - №920328; Заявл. 17.09.86; Опубл. 06.09.88, ИСМ 11/61. - 1989, С. 48.*

[46] *Пат. 4621122 США, МКИ С 08 L 63/00. Порошок для нанесения термостойких электроизоляционных покрытий / Minnesota Mining and Manufacturing Company (США). - № 708701; Заявл. 06.03.85; Опубл. 04.11.86, ИСМ 17/61. - 1987, С. 76.*

[47] *А.с. 80233 СССР, МКИ С 08 L 63/00. Эпоксидно-полиарилатная композиция / Ин-т элементоорган. Соед. АН СССР (СССР). - №2770114; Заявлено 13.04.79; Опубл. 70.02.81 // РЖ. 19Т. - 1981. - № 16. - С. 17, 114П.*

[48] *Заявка 60-96644 Япония, МКИ С 08 L 67/02. Термостойкая композиция, полученная добавление низкоплавкой полиэфирной смолы к сложному ароматическому полиэфиру и ее применение в электронике / Mitsui Toatsu Kagaku K.K. (Япония). - №58-202819; Заявл. 31.10.83; Опубл. 30.05.85, ИСМ 6/61. - 1987, С. 107.*

[49] *Заявка 0258053 США, МКИ С 08 L 67/02. Полиарилат с низкой изнашиваемостью / Celanese Engineering Resins (США). - № 87307; Заявл. 27.08.87; Опубл. 02.03.88, ИСМ 20/61. - 1988, С. 30.*

[50] *Заявка 3-20347 Япония, МКИ С 08 L 27/12. Антифрикционные материалы / Мицубиси дэнки К.К. (Япония). - №1-152961; Заявл. 15.06.89; Опубл. 29.01.91.*

[51] *Заявка 2-219849 Япония, МКИ С 08 L 27/12. Композиции на основе синтетических полимеров для изготовления трущихся, антифрикционных изделий / Оирэсу коге К.К. (Япония). - №64-41454; Заявл. 21.02.89; Опубл. 03.09.90.*

[52] *Заявка 0320903 США, МКИ С 08 L 67/02. Улучшенная пресс-композиция на основе полиарилата / E.I. Du Pont de Nemours and Company (США).- № 88120897; Заявл. 14.12.88; Опубл. 21.06.89, ИСМ 3/61. - 1990, С. 41.*

[53] *Заявка 0372919 США, МКИ С 08 G 63/91, 63/64. Блокировка концевых карбоксигрупп полиарилатов с помощью ароматических карбонатов / E.I. Du Pont de Nemours and Company (США). - № 89312625; Заявл. 06.12.89; Опубл. 13.06.90, ИСМ 7/42.-1991, С. 26.*

[54] *Заявка 1-60057 США, МКИ С 08 L 67/00, 69/00. Композиция на основе поликарбонатов и полностью ароматических полиэфиров / Селаниз Корп. (США).- №56-103446; Заявл.03.07.81; Опубл. 20.12.89, ИСМ 16/61. - 1990, С. 109.*

[55] *Заявка 0279091 США, МКИ С 08 G 63/18. Полиарилаты на основе фенолфталеина и содержащие их композиции / Chevron Research Company. (США). - № 87301368; Заявл. 17.02.87; Опубл.24.08.88, ИСМ 6/61. - 1989, С. 18.*

[56] *Заявка 62-169848 Япония, МКИ С 08 L 67/02. Содержащая полиарилат композиция / Nippon Ester Co. Ltd. (Япония). - № 61-10596; Заявл. 21.01.86; Опубл. 27.07.87, ИСМ 23/61. - 1988, С. 80.*

[57] *Заявка 3-14865 Япония, МКИ С 08 L 69/00, С 08 К 3/24. Термопластична полимерная композиция / Teijin Chem. Ltd. (Япония). - № 64-148375; Заявл. 13.06.89; Опубл. 23.01.91, ИСМ 7/42. - 1992, С. 80.*

[58] *Заявка 1-60061 Япония, МКИ С 08 L 67/02. Полимерная композиция / Тэйдзин касэй К.К. (Япония). - №56-128800; Заявл.19.08.81; Опубл. 20.12.89, ИСМ 16/61.- 1990, С. 109.*

[59] *Заявка 88/03156 США, МКИ С 08 L 67/02. Изделия на основе смесей поликарбоната, полиарилата и полиалкилентерефталата / Amoco Corp. (США). - № 87/02786; Заявл. 23.10.87; Опубл. 05.05.88, ИСМ 23/61, 1988, С. 18.*

[60] *Заявка 3-239751 Япония, МКИ С 08 L 63/00. Добавки для увеличения совместимости термопластичных полимеров / Тосо К.К. (Япония). - №2-36372; Заявл. 19.02.90; Опубл. 25.10.91.*

[61] *Заявка 0338269 США, МКИ С 08 L 67/02. Стойкие к действию растворителей совместимые осоставы полифениленоксидов и смесей термопластичных сложных полиэфиров / General Electric Company. - №89105022; Заявл. 21.03.89; Опубл. 25.10.89, ИСМ 11/61, 1990, С. 33.*

[62] *Пат. 5091472 США, МКИ С 08 L 51/00. Совместимая, стойкая к растворителям композиция на основе полифениленоксида и термопластичного полиэфира / General Electric Company (США). - №478864; Заявл. 12.02.90; Опубл. 25.02.92.*

[63] *Пат. 5049615 США, МКИ С 08 L 53/02. Полииндановые добавки, улучшающие переработку конструкционных термопластов /* Hercules Inc. *(США). - №448394; Заявл.11.12.89; Опубл. 17.09.91.*

[64] *Пат. 5100973 США, МКИ С 08 L 67/03. Полимерные композиции на основе смеси полиарилэфиркетона и полиарилатов /* Amoco Corp. *(США). - №528095; Заявл. 23.05.90; Опубл. 31.03.92, ИСМ 20/42. - 1993, С. 115.*

[65] *Пат. 4908418 США, МКИ С 08 L 67/02. Трехкомпонентные полимерные композиции /* General Electric Company *(США). - №344007; Заявл. 29.01.82; Опубл. 13.03.90, ИСМ 10/42. - 1991, С. 63.*

[66] *Пат. 4908419 США, МКИ С 08 L 67/02. Полимерные композиции на основе смеси полиэфиримидов и полиарилатов /* General Electric Company *(США). - № 344012; Заявл. 29.01.82; Опубл. 13.03.90, ИСМ 10/42. - 1991, С. 63.*

[67] *А.с. 1642738 СССР, МКИ С 08 L 67/02. Полимерная композиция / ИНЭОС АН СССР, НПО “Полимерсинтез” (СССР). - № 4682407; Опубл. 19.04.89, ДСП. - 6 с.*

[68] *Пат 4920005 США, МКИ В 32 В 27/34. Ароматические полимерные композиции /* Raychem Corp. *(США). - № 355937; Заявл. 23.05.89; Опубл. 24.04.90.*

[69] *Заявка 0357232 США, МКИ С 08 J 7/04. Композиты из ароматических полибензимидазолов и полиарилатов и способ их изготовления / Hoechst Celanese Corp. (США). - № 89307792; Заявл.01.08.89; Опубл. 03.08.88, ИСМ 24/61. - 1990, С.16.*

[70] *Заявка 3-2220 Япония, МКИ С 08 G 81/00. Полимеры для контактных линз / Mitsubishi Rayon Co. Ltd. (Япония). - №64-135764; Заявл.31.05.89; Опубл. 08.01.91, ИСМ 3/42. - 1992, С. 73.*

[71] *Заявка 62-56908 Япония, МКИ С 08 L 67/02. Полимерная композиция / Юнитика К.К. (Япония). - № 55-162251; Заявл. 17.11.80; Опубл. 27.11.87, ИСМ 22/61. - 1988, С. 90.*

[72] *Заявка 63-18622 Япония, МКИ С 08 L 67/02. Композиция смол / Юнитика К.К. (Япония). - № 55-160188; Заявл. 13.11.80; Опубл. 19.04.88, ИСМ 5/61. - 1989, С. 135.*

[73] *Заявка 5-068507 Япония, МКИ С 08 L 67/00. Изделия для микроволновых и электрических печей / Сумитомо кагаку коге К.К. (Япония). - №59-121074; Заявл. 12.06.84; Опубл. 29.09.93, ИСМ 7/42. - 1996, С. 18.*

[74] *Koser Uwe, Stollbrink Kuno K.U. Matrixloser Faser-verbund: Ein neuaartiger Hochleistungs verbundwerkstoff ous LC-Polymeren // DLR-Nachr, 1993, № 72, С. 16-21.*

[75] *Тенденции разработок высокомодульных материалов / Танака Тацундо // Kinzoku Metals and Technol.* - 1992. - *62, № 4, С. 19*-26.

[76] *Заявка 92/03506 США, МКИ С 08 L 67/03. Самоупрочненный композит на основе термотропных жидкокристаллических полиэфиров /* The University *of* Akron. *(США). - № 91/05787; Заявл. 15.08.91; Опубл. 05.03.92, ИСМ 10/42. - 1993, С. 116.*

[77] *Пахаренко В.А. и др. Термостойкие полимеры.- К.: Общво "Знание"* . - 1984. - *45 с.*

[78] *Химический энциклопедический словарь / Под ред. И.Л. Кнунянца. М.: "Советская энциклопедия",* 1986, *С. 82*-84.

[79] *Заявка 62-45263 Япония, МКИ С 08 L 67/02. Способ получения формованных изделий из полиэфирных смол / Тэйдзин К.К. (Япония). - № 53-82875; Заявл. 10.07.78; Опубл. 25.09.87, ИСМ 18/61. - 1988, С. 101.*

[80] *Заявка 2-274756 Япония, МКИ С08 L 67/02. Полимерные композиции / Тосо К.К. (Япония). - № 1-95319; Заявл. 17.04.89; Опубл. 08.11.90.*

[81] *Заявка 3-237154 Япония, МКИ С 08 L 69/00. Термопластичные композиции / Тэйдзин касэй К.К. (Япония). - №2-33350; Заявл.14.02.90; Опубл. 23.10.91.*

[82] *Пат. 5104925 Япония, МКИ 08 L 37/00. Композиции на основе синтетических полимеров / Nippon Oil and Fast Co. Ltd. (Япония). - №406499; Заявл. 13.09.89; Опубл. 14.04.92.*

[83] *Заявка 3-91556 Япония, МКИ С 08 L 59/00. Электропроводящие полимерные композиции / Район К.К. (Япония). - №1-228941; Заявл. 04.09.89; Опубл. 17.04.91.*

[84] *Пат. 4851467 США, МКИ С 08 К 3/04. Формовочные композиции на основе ароматических полимеров с добавкой технического углерода / Amoco Corp. (США).- №179048; Заявл. 03.04.88; Опубл. 25.07.89, ИСМ 22/61. - 1990, С. 6.*

[85] *Заявка 413550 ФРГ, МКИ В 32 7/02. Оптические элементы / Institut fϋr neue Materialin gemeinnützide GmbH (ФРГ). - №4130550; Заявл. 13.09.91; Опубл. 18.03.93.*

[86] *Справочник по пластическим массами / Под ред. Гарбара М.И. - М.: Химия, 1969. - Т.2. - 517 с.*

[87] *Кацнельсон И.Ю., Балаев Г.А.. Пластмассы: Свойства и применение. Справочник . Л. : Химия, 1978. - 384 с.*

[88] *А.с. 975752 СССР, МКИ С 08 L 67/02 Антифрикционная композиция (ее варианты) / ИНЭОС АН СССР (СССР).- №3297895; Заявл.08.06.81; Опубл. 23.11.82, Бюл. № 43.*

[89] *Пат. 5091464 США, МКИ С 08* L *67/03. Полимерные композиции с улучшенной технологичностью при формовании /* Amoco Corp.*(США). - №629826; Заявл. 19.12.90; Опубл. 25.02.92; ИМС 18/42. - 1993, С. 139.*

[90] *Заявка 1-74257 Япония, МКИ С 08* L *67/00, С 08 К 7/14. Композиция на основе полностью ароматического сложного полиэфира /* Mitsui Petrochem Ind. Ltd. *(Япония).- № 62-229376; Заявл. 12.09.87; Опубл. 20.03.89, ИСМ 3/61. - 1990, С. 94.*

[91] *Заявка 61-203162 Япония, МКИ С 08* L *67/02. Прочная, хорошо формуемая, термостабильная при плавлении, безусадочная композиция с высоким модулем упругости на основе ароматического сложного полиэфира и волокон титаната калия /* Sumitomo Chem. Co. Ltd.*(Япония). - № 60-42464; Заявл. 04.03.85; Опубл. 09.09.86,* BCV *8.61. - 1988, С.79.*

[92] *Заявка 1-74257 Япония, МКИ С 08* L *67/00. Композиция на основе полностью ароматического сложного полиэфира /* Mitsui Petrochem Ind. Ltd. *(Япония). - №62-229376; Заявл. 12.09.87; Опубл. 20.03.89, ИСМ 3/61. – 1990, С. 94.*

[93] *Заявка 0284300 Япония, МКИ С 08 L 59/00. Армированная полимерная формовочная композиция /* Polyplastics Co. Ltd. *(Япония). - №88302376; Заявл. 18.03.88; Опубл. 28.09.87, ИСМ 9/61. - 1989, С. 21.*

[94] *А.с. 1694603 СССР, МКИ С 08 L 67/02. Полимерная композиция / Днепропетровский сельскохозяйственный институт, институт общей и неорганической химии АН БССР (СССР). - № 4661348; Заявл. 10.03.89; Опубл. 30.11.91, Бюл. № 44, 6 с.*

[95] *Пат. 5011879 Япония, МКИ С 08 К 5/10. Конструкционные полимерные материалы и композиции для их изготовления /* Sekisui Kagaku Kogyo K. *(Япония). - № 356725; Заявл. 25.05.89; Опубл. 30.04.88.*

[96] *А.с. 523127 СССР, МКИ С 08 L 67/02. Полимерная композиция для термостойкой электроизоляционной бумаги / ВНИИСС, Ленинградская бумажная фабрика Госзнак и ИНЭОС АН (СССР). - №1856318; Заявл. 06.12.72; Опубл. 30.07.76, Бюл. № 28, 4 с.*

[97] *Заявка 5-064182 Япония, МКИ С 08 L 67/00. Изделия для электроплит / Сумитомо кагаку коге К.К. (Япония). - № 84-121522; Заявл. 13.06.84, ИСМ 5/42. - 1996, С. 23.*

[98] *А.с. 204574 СССР, МКИ С 08 67/02. Способ получения пластмассы / ИНЭОС АН СССР (СССР). - № 1072949; Заявл. 29.04.66; Опубл. 15.06.79, Бюл. № 22. - 6 с.*

[99] *Влияние содержания* MoS_2 *на термические свойства полиарилата ДВ / Г.Ф. Зюзина, Н.К. Виноградова, И.А. Грибова и др. // Пластмассы. - 1993, № 6. - С. 42-45.*

[100] *Заявка 62-28176 Япония, МКИ С 08 L 67/02. Стабилизированная композиция на основе ароматических полиэфиров / Сумитомо кагаку коге К.К. (Япония).- №53-67943; Заявл.05.06.78; Опубл.18.06.87, ИСМ 11/61. - 1988, С.84.*

[101] *А.с. 1259662 СССР, МКИ С 08 L 67/02. Полиарилатная композиция / ИНЭОС АН СССР (СССР). - № 3794693; Заявл. 26.06.84, ДСП.*

[102] *Заявка 3-41132 Япония, МКИ С 08 К 9/04. Антипирены и трудновоспламеняющиеся композиции / Кева кагаку коге К.К. (Япония). - № 1-177763; Заявл. 10.07.89; Опубл. 21.02.91.*

[103] *Заявка 4-47709 Япония, МКИ С 08 L 67/00. Композиция на основе ароматического полиэфира / Эн-Ти-Эн К.К. (Япония). - № 61-138941; Заявл. 14.06.86; Опубл. 04.08.92, ИСМ 8/42. - 1994, С. 48.*

[104] *А.с. 523127 СССР, МКИ С 08* L 67/02. *Полимерная композиция для термостойкой электроизоляционной бумаги / ВНИИСС, Ленинградская бумажная фабрика Госзнак и ИНЭОС АН (СССР). - №1856318; Заявл. 06.12.72; Опубл.30.07.76, Бюл. № 28, 4 с.*

[105] *Заявка 5-064182 Япония, МКИ С 08* L 67/00. *Изделия для электроплит / Сумитомо кагаку коге К.К. (Япония). - № 84-121522; Заявл. 13.06.84, ИСМ 5/42.- 1996, С. 23.*

[106] *Заявка 60-86156 Япония, МКИ С 08* L *67/02. Композиция с высокой скоростью кристаллизации /* Nippon Ester K.K. *(Япония). - № 58-194819; Заявл.* 18.10.83; *Опубл. 15.05.85, ИСМ 3/61.- 1987, С. 75.*

[107] *А.с. 1654305 СССР, МКИ С 08* J 5/06. *Способ получения композиционного материала / Институт механики металлополимерных систем АН БССР (СССР). - №4627522; Заявл. 22.12.88; Опубл. 07.06.91, Бюл. № 21, 6 с.*

[108] *Заявка 0323160 Япония, МКИ С 08* G *63/60. Пленки из полностью ароматического полиэфира и способ их приготовления /* Mitsui Petrochemical Industries Ltd. *(Япония). - № 8312223; Заявл. 22.12.88; Опубл. 05.07.87, ИСМ 4/61. - 1990, С. 25*

[109] *Пат. 5140093 США, МКИ С 08 G 63/00. Способные к переработке из расплава термотропные полиэфиры с фторированными соединительными группами / Hoechst Celanese Corp. (США). - № 729968; Заявл.15.07.91; Опубл.18.08.92, ИСМ 6/42. - 1994, С. 96.*

[110] *Заявка 3542813 ФРГ, МКИ С 08 G 63/60. Полностью ароматические полиэфиры, их получение и применение / BASF AG. - №3542813; Заявл. 04.12.85; Опубл. 11.06.87, ИСМ 3/61. - 1988, С. 39.*

[111] *Пат. 5185116 США, МКИ В 29 С 47/90. Получение формованной структуры полиарилатных сополимеров / E.I. Du Pont de Nemours and Co. (США). - №715599; Заявл. 14.06.91; Опубл. 09.02.93.*

[112] *Пат. 5053180 США, МКИ В 29 С 55/16. Процесс деформирования аморфных полимеров / Aluminium Co. America (США). - № 387170; Заявл. 31.07.89; Опубл. 1.10.91.*

[113] *Пат. 5360829 Япония, МКИ С 08 J 9/04. Листовой полиэфирный пенопласт и способ его получения / Kanebo Ltd. (Япония). - № 184256; Заявл. 21.01.94; Опубл. 01.11.94, ИСМ 42/24. - 1995, С. 60.*

[114] *Neue Polyarylate für Hochleistungsanwendungen // Kunststoffe. - 1994. - 84, № 8. - C. 1015-1019.*

[115] *Заявка 3-7314 Япония, МКИ C 08 G 63/88. Способ получения полностью ароматического сложного сополиэфира /Tosoh Corp.(Япония). - №64-134768; Заявл. 04.02.90; Опубл. 07.01.91, ИСМ 3/42. – 1992, С. 71.*

[116] *Заявка 61-261320 Япония, МКИ C 08 G 63/68. Полиарилаты / Nippon Ester Co. Ltd.(Япония). - № 60-103100; Заявл. 15.05.85; Опубл. 19.11.86, ИСМ 18/61. - 1988, С. 62.*

[117] *Заявка 2-235935 Япония, МКИ C 08 J 5/18. Субстраты из жидкокристаллических высокомолекулярных соединений / Кэнон К.К.(Япония). - №64-56028, Заявл. 10.03.89; Опубл.18.09.90.*

[118] *Заявка 4028210 ФРГ, МКИ C 08 J 7/12. Поверхностная обработка изделий из жидкокристаллических полимеров / BASF AG (ФРГ). - №4028210, Заявл. 06.09.90; Опубл. 12.03.92.*

[119] *Пат. 4623710 Япония, МКИ C 08 G 63/18. Формовочная композиция на основе ароматического полиэфира / Kanegafuchi Kagaku Kogyo K.K. (Япония). - №762169; Заявл. 05.08.85; Опубл. 18.11.86, ИСМ17/61. - 1987, С.61.*

[120] *Мацумобо Йосицэ. Модификация поверхности пластмасс коротковолновым ультрафиолетовым излучением // Join. Assemsl. Eng. - 1991. - 7, № 8. - С. 104-108.*

[121] *Заявка 2-169636 Япония, МКИ С 08 J 7/00. Способ изготовления формованных изделий с антистатическими свойствами / Сумитомо дэнки коге К.К. (Япония). - № 63-325110; Заявл. 22.12.88; Опубл. 29.06.90.*

[122] *Бюллер К.У. Тепло- и термостойкие полимеры : Пер. с нем. - М.: "Химия", 1984. - 1056 с.*

[123] *Пат. 655731 Швейцария, МКИ С 08 G 63/22. Способ получения линейных ароматических сложных полиэфиров / Ems-Inventa AG.(Шверцария). - № 4892/82; Заявл. 16.08.82; Опубл. 15.05.86, ИСМ 4/61. - 1987, С.110.*

[124] *Заявка 93/22361 Япония, МКИ С 08 G 63/00. Полимер эфира, способ получения и электрофотографический фоторецептор на его основе / Idemitsu Kosan Co. Ltd. (Япония). - №93/00576; Заявл. 30.04.93; Опубл. 11.11.93, ИСМ 8/42. – 1995, С. 71.*

[125] *Пат. 5162485 США, МКИ С 08 G 63/00. Дифенольные полиэфиры для матриц фотоприемников / Xerox Corp. (США). - №626849; Заявл. 13.12.90; Опубл. 10.11.92.*

[126] *Hilton L.K., Spray J.L. The use of polymers for enviromental protection of a photovoltaic array // ANTEC' 90, P. 1956-1959.*

[127] *Заявка 2-238021 Япония, МКИ C 08 G 63/672. Полностью ароматические сложные полиэфиры и композиции на их основе / Порипурасутицукусу К.К. (Япония). - № 1-60231: Заявл.13.03.89; Опубл. 20.09.89.*

[128] *Заявка 92/03493 США, МКИ C 08 G 63/193. Ароматический полиэфир высокой чистоты, пленки и другие продукты и изделия на его основе и способ получения пленки / Isonova Technische Innovationen Gesellschaft M.B.H. (США). - № 91/01631; Заявл. 28.08.91; Опубл. 05.03.92, ИСМ 10/42. - 1993, С. 113.*

[129] *Doи Осату. Полимерные сплавы на основе полиарилатов // Kogyo гairyo = Eng. Mater., 1991, 39, № 15, С. 58-64.*

[130] *Заявка 3629209 ФРГ, МКИ C 08 G 63/60. Полностью ароматические термотропные сложные полиэфиры / BASF AG (ФРГ). - №3629209; Заявл. 28.08.86; Опубл. 03.03.88, ИСМ 19/61. - 1988, С. 29.*

[131] *Заявка 2-219849 Япония, МКИ C 08 L 27/12. Композиции на основе синтетических полимеров / Оирєсу коге К.К.. - № 64-41454; Заявл. 21.02.89; Опубл. 03.09.90.*

[132] *Заявка 2233661 Великобритания, МКИ С 08 J 5/16. Износостойкое изделие / T & N Technology Limited (Великобритания). - № 8915475; Заявл. 06.07.89; Опубл. 16.01.91, ИСМ 3/42. - 1993, С. 49.*

[133] *А.с. 1287545 СССР, МКИ С 08 G 63/18. Способ получения сложных сополиэфиров / Кемеровское НПО “Карболит” (СССР). - №3799016; Заявл. 05.10.84, ДСП, 6 с.*

[134] *Burya A.I., Kobets A.S., Volokhina A.V., Raskian A.B. Friction and wear of carbon fibre reinforced based on liquid crystallins polymers // Proc. Int. Simp. Tribology Frict. Mater. Yaroslavi, 1991: YAROFRI-91, Vol. 2.*

[135] *Заявка 1-40851 Япония, МКИ С 08 J 5/18. Способ формования ароматического полиэфира / Тэйдзин К.К. (Япония). - №5714723; Заявл.03.02.82, Опубл.31.08.89, ИСМ 10/61. - 1990, С. 79.*

[136] *Заявка 3842551 ФРГ, МКИ С 08 G 63/60. Термотропные ароматические полиэфиры, способ их получения и применение / Bayer AG (ФРГ). - № 3842551; Заявл. 17.12.88; Опубл.21.06.90, ИСМ10/42. - 1991, С. 47.*

[137] *Пат. 5073176 США, МКИ В 01 D 53/22. Газораспределительные мембраны на основе сложных полиэфиров дикарбоновых кислот и полиамидов / E.I. Du Pont de Nemours and Co. (США). - № 609443; Заявл. 05.11.90; Опубл. 17.12.91.*

[138] *Пат. 5013332 США, МКИ В 01 D 53/22. Мембраны, образованные из жестких полиарилатов /Air Products and Chemicals Inc.(США).- №518450; Заявл. 03.05.90; Опубл. 07.05.91.*

[139] *Пат. 5317077 США, МКИ С 08 G 63/00. Полиарилаты с содержанием производных природных аминокислот α-тирозина / Rutgers The University of New Jersey (США). - №39929; Заявл. 29.03.93; Опубл. 31.05.94, ИСМ 18/42. - 1995, С. 49.*

[140] *Полиарилаты открывают новые технические возможности полимеров // Poliarilato offre molte opportunita nel campo dei tecnopolimeri. "Mater. Plast. End elast.", 1980, № 5.*

[141] *Заявка 3-2220 Япония, МКИ С 08 G 81/00. Полимеры для контактных линз / Mitsubishi Rayon Co.Ltd. (Япония). - №64-135764; Заявл. 31.05.89; Опубл. 08.01.91, ИСМ 3/42. – 1992, С. 73.*

[142] *Табути Нобухидэ. Полиарилаты “U-полимеры” / “JETI: Jap. Energy and Technol. Intell”, 1986, 34, №6, С. 69-72.*

[143] *Заявка 1-170619 Япония, МКИ C 08 G 63/66. Сложный сополиэфир. / Mitsubishi Kasei Corp. (Япония). - №62-32950; Заявл. 25.12.87; Опубл. 05.07.89, ИСМ 9/61. - 1990, С. 52.*

[144] *Пат. 5132336 США, МКИ C 08 K 3/34. Полимерные композиции для печного оборудования / Amoco Corp. (США). - №697809; Заявл. 09.05.91; Опубл. 21.07.92, ИСМ 4/42.- 1994, С. 94.*

[145] *Заявка 0455313 Япония, МКИ C 08 L 67/00. Противень для печей с электромагнитным нагревом / Nippon Petrochemicals Company Limited (Япония). - №91303550; Заявл. 19.04.91; Опубл. 23.10.91, ИСМ 1/42. - 1993, С. 38.*

[146] *Пилиповский Ю.Л., Грудина Т.В., Сапожникова А.Б.: Композиционные материалы в машиностроении. К.: “Тэхника”, 1990, 141 с.*

[147] *Практикум по технологии полимерных материалов / Под ред. Коршака В.В. М.: Высшая школа. Часть II. Поликондесационные и химически модифицированные полимерные материалы, С. 104.*

[148] *Ермоленко И.Н., Люблинер И.П., Гулько Н.В. Элементоуглеродные угольные волокнистые материалы. Минск: Наука и техника, 1982, 272 с.*

[149] *Конкин А.А.: Углеродные и другие жаростойкие волокнистые материалы. М.: Химия, 1974, 376 с.*

[150] *Левит Р.М.: Химическая структура углеродных волокон // Химические волокна.* № *3, 1979, С. 23-26.*

[151] *Конкин А.А., Азарова М.Т., Волкова Н.С.: Углеродные волокнистые материалы // Химические волокна. № 3, 1977, С. 65-66.*

[152] *Таблица-вклейка. Термостойкие и жаростойкие волокна // Химические волокна, № 3, 1975.*

[153] *Волохина А.В., Калмыкова В.Д.: Получение высокопрочных и термостойких синтетических волокон // Итоги науки и техники. Серия: Химия и технология высокомолекулярных соединений, Т. 15, 1981, С. 3-61.*

[154] *Гуняев Г.М.: Структура и свойства полимерных волокнистых композитов. М.: Химия, 1981, С. 232.*

[155] *Chigvintseva O.P., Petrushina G.A., Tokar A.V./Structure research of composite materials // Nauka i Studia. Techniczne nauki. - N 7 (209) 2020. - Przemyśl: Nauka i studia, 2020. - PP. 14-21.*

[156] *Буря А.И., Чигвинцева О.П. Разработка и применение углепластиков полиарилата в конструкциях свеклоуборочных машин // Весник аграрной науки. – 1998. – № 8. – С. 56-60.*

[157] *Бурия А.И., Чигвинцева О.П., Бурмистр М.В. Новые полиарилатные композиции конструкционного назначения // Материалы научно-практической конференции "Наука, техника и высшее образование", Хургада, Египет, 21-28 февраля. - 2004. - С. 62-64.*

[158] *Burya A.I., Chigvintseva O.P., Suchilina-Sokolenko S.P. The influence of fibre's nature on interphasial phenomena in the structure of composition based on polyarylate // Prace Naukowe katedry budowy maszyn. Seria: Konferenje. Polymery i kompozyty konstrukcyjne. - 2000. - № 1. – PP. 107-112.*

[159] *Липатов Ю.С., Шилов В.В, Гомза Ю.П. и др. Рентгенографические методы изучения полимерных систем. - К.: Наукова думка, 1982. – 296 с.*

[160] *Альперин В.И., Корольков Н.В., Мотавкин А.В. и др. Конструкционные стеклопластики. - М.: Химия. - 1979. - 360 с.*

[161] *Буря А.И., Чигвинцева О.П. Перспективные стеклопластики на основе полиарилата // Сучасне машинобудування. - 1999. - № 2. - С. 28-32.*

[162] *Буря А.И., Чигвинцева О.П,, Олейник Г.С. Структурные исследования композитов на основе полиарилата // Композитные материалы, Том 2, № 1, 2008, С. 50-54.*

[163] *Липатов Ю.С.: Синтез и модификация полимеров, 1976, С. 175-182.*

[164] *Zuru A.A., Whitehead R., Griffiths D.L.: A new technique for determination of the possible reaction mechanism from non-isothermal thermodravimetric data. Thermochim.Acta, 164, (1990), pp. 285-305.*

[165] *Zsako J. Kinetic analysis of thermogravimetric data. XIV. Three integral method and their computer programs. J. Therm. Anal., V.19, 1980, PP. 333-345.*

[166] *Shestak Ya.: Theory of thermal analysis: Physical and chemical properties of inorganic compound. M.: Mir, 1987, 456 p.*

[167] *Coats A.W., Redfern G.P. Nature, 201, 1964, P. 68.*

[168] *Буря А.И., Чигвинцева О.П., Сытник С.В.: Исследование процесса термоокислительной деструкции сложного полиэфира полиарилат // Материалы, технологии, инструменты. Т. 3,* № *1, 1998, С. 34-37.*

[169] *Буря А.И.,Чигвинцева О.П., Сытник С.В.: Термостойкие композиты на основе полиарилата // Труды Международной научно-технической конференции “Полимерные композиты 98”, Гомель, 1998, С. 213-218.*

[170] *Тростянская Е.Б. Термоустойчивость пластиков конструкционного назначения. М.: Химия, 1980, 240 с.*

[171] *Привалко В.П.: Свойства полимеров в блочном состоянии. Справочник по физической химии полимеров. К.: Наукова думка, Т.2, (1984), с. 330.*

[172] *Годовский Ю.К.: Теплофизические методы исследований полимеров. М.: Химия, 1970, 216 с.*

[173] *Пахаренко В.А., Зверилин В.Г., Привалко В.П.: Теплофизические и реологические характеристики и коэффициенты трения наполненных термопластов. Киев: Наукова думка, 1983, 279 с.*

[174] *Буря А.И., Чигвинцева О.П.: Исследование теплофизических свойств композитов на основе полиарилата // Композиционные полимерные материалы, Т. XXII, № 1, 2000, С. 51-54.*

[175] *Привалко В.П., Липатов Ю.С., Керча Ю.Ю., Мозжухина Л.В. Калориметрическое исследование наполненных линейных полиуретанов. Высокомолекулярные соединения, А, Т.13,* № *1, 1971, С. 103-110.*

[176] *Липатов Ю.С.: Физическая химия наполненных полимеров. М.: Химия, 1977, С. 99.*

[177] *Соломко В.П., Пасько С.П.: Исследование удельной теплоемкости наполненного полистирола и полиметилметакрилата // Высокомолекулярные соединения. Т. (А)XII,* № *3, 1970, С. 681-686.*

[178] *Колупаев Б.С.: Физико-химия полимеров. Львов: Вища школа, 1978, 160 с.*

[179] *Кнунянц И.Л.: Химический энциклопедический словарь. М.: Советская энциклопедия, 1983, С.* 543.

[180] *Пивень А.Н., Гречаная Н.А., Чернобыльский И.И.: Теплофизические свойства полимерных материалов. К.: Вища школа, 1976, 180 с.*

[181] *Барановский В.М.: Теплофизические свойства модифицированных полимеров. К.: КГПИ, 1983, С.* 82-84.

[182] *Тугов И.И., Кострыкина Г.И.: Химия и физика полимеров: М.: Химия, 1989, 432 с.*

[183] *Буря А.И., Дорофеев В.Т., Соколенко В.Н., Бедин А.С.: Свойства и переработка ароматического полиамида днепролон-м // Вопросы химии и химической технологии, Вып.57, 1979, С.*109-111.

[184] *Буря А.И., Силкина С.П., Шустов Г.Б.: Исследование теплофизических свойств углепластиков на основе блок-сополимера БСП-7 // Поликонденсационные процесссы и полимеры, 1989, С.* 3-8.

[185] *Бартенев Г.М., Зеленев Ю.В.: Физика и механика полимеров. М.: Высшая школа, 1983, 391 с.*

[186] *Буря А.И.: Свойства и опыт применения углепластиков в сельхозмашиностроении. К.: Общество “Знание”, 1992, 28 с.*

[187] *Браутман Л.: Разрушение и усталость. М.: Мир, 1978, 483 с.*

[188] *Херцберг Р.В.: Деформация и механика разрушения конструкционных материалов. М.: Металлургия, 1989, 576 с.*

[189] *Буря А.И., Чигвинцева О.П.: Исследование динамических характеристик армированного полиарилата // Тезисы докладов конференции "Технологическое обеспечение работоспособности деталей машин, механизмов и инструмента", Киев, 1997,* С. 119-121.

[190] *Композиционные материалы на основе углеродных волокон и полимерных материалов // Обзорная информация. Серия: Промышленность химических волокон, 1979 , 55 с.*

[191] *Буря А.И., Чигвинцева О.П.: Исследование фрикционных свойств сложного ароматического полиэфира полиарилат // Тезисы докладов* V *Республиканской научной конференции студентов и аспирантов "Физика конденсированных сред", Гродно, 1997,* С. 193.

[192] *Бартенев Г.М., Лаврентьев В.В.: Трение и износ полимеров. Л.: Химия, 1972, 240 с*

[193] *Буря А.И., Чигвинцева О.П.: Влияние содержания органического волокна на фрикционные свойства армированных пластиков на основе полиарилата // Тезисы докладов конференции "Оснастка-97", 1997,* С. 48-49.

[194] *Burya A.I., Chigvintseva O.P.: The influence of fibre contents on the tribological carbon plastics properties on the base polyarylate // World Tribology Congress, London, UK, 1997, PP. 835*

[195] *Буря А.И., Чигвинцева О.П.: Разработка и применение углепластиков полиарилата в конструкциях свеклоуборочных машин // Вестник аграрной науки, №8, 1992, С. 56-60.*

[196] *Крагельский И.В.: Трение и износ. М.: “Машиностроение”, 1968, 480 с.*

[197] *Буря А.И., Леви А.Г., Молчанов Б.И., Захаров А.В.: Антифрикционные свойства углепластиков на основе полипропилена // Проблемы трения и изнашивания, Вып.30, 1986, С. 88-89.*

[198] *Буря А.И., Ткач Л.Н.: Свойства и применение углепластиков на основе пентапласта // Тезисы докладов II Всесоюзного совещания “Пентапласт – синтез, свойства, применение, производство”, Уфа, 1990, С. 32.*

[199] *Буря А.И.: Исследование свойств углепластиков на основе поливинилхлорида // Тезисы докладов конференции “Синтетические смолы и пластмассы. Технология производства и применение в отраслях промышленности”, Сколе - Киев: Знание, 1995, С. 46.*

[200] *Зиновьев Е.В., Левин А.Л., Бородулин М.М., Чичинадзе А.В.: Полимеры в узлах трения машин и приборов. М.: “Машиностроение”, 1980, 208 с.*

[201] *Буря А.И., Чигвинцева О.П.: Свойства ароматических полиэфиров полиарилатов // Вопросы химии и химической технологи, № 4, 2002, С. 60-69.*

[202] *Буря А.И., Чигвинцева О.П., Теренин В.И., Сытар В.И. Применение жидкокристаллических полимеров в качестве связующего и наполнителей композиционных материалов // Сборник научных трудов Международной научно-технической конференции "Композиционные матерылы", Киев, 1998, С. 111-112.*

[203] *Буря А.И., Чигвинцева О.П. Холодилов О.В., Теренин В.И. Эксплуатационные характеристики композитов на основе полиарилата, армированного жидкокристаллическими волокнами // "Теоретические и технологические основы упрочнения и восстановления изделий машиностроения", Минск, 2001, С. 234-238.*

[204] *Миллер Т.Н.: Плазмохимический метод и свойства порошков тугоплавких соединений // Неорганические материалы, Т. 15, № 4, 1979, С. 557-561.*

[205] *Рекомендации по применению фторопластовых композитов для уплотнительных устройств. Якутск: изд. ЯФ СО АН СССР, 1988, 56 с.*

[206] *Tapaka K. J.Phys. Soc., 16, № 60, 1961, P. 2003.*

[207] *Chigvintseva O.P., Predrad Predrag Dašić. Composites based on polyarylate filled with oxynitride-siliconyttrium // VI International Scientific and Practical Conference "Scientific achievements of modern society", United Kingdom, 5-7 February 2020, PP. 99-106.*

Scientific monography

Chigvintseva O., Dašić P.

THE RESEARCH OF POLYMER COMPOSITES BASED ON POLYARYLATE POLYESTER

Reader
Jelena Apostolović, Primary school “Jovan Popović”,
Kruševac, Serbia

Technical processing and design
Predrag Dašić, SaTCIP Publisher Ltd., Vrnjačka Banja
Jovan Dašić, SaTCIP Publisher Ltd., Vrnjačka Banja

Printable singer by 30.11.2019 Format 60×84 1/16. Offset Paper
Probation.printing.f. 10.5; Obl.-view. f. 5.1. Zam. Number
0112/2019 Circulation 300 copies

Printed by
Publisher Ltd. Vrnjačka Banja Serbia
36210 Vrnjačka Banja, Serbia
Tel/fax: +381 3 6 622454