IV МЕЖДУНАРОДНЫЙ ФОРУМ КЛЮЧЕВЫЕ ТРЕНДЫ В КОМПОЗИТАХ: НАУКА И ТЕХНОЛОГИИ

2 - 3 декабря 2021

IV INTERNATIONAL FORUM ADVANCES IN COMPOSITE: SCIENCE AND TECHNOLOGY

2 - 3 december 2021

ОНЛАЙН | VR | МИА “Россия сегодня” | МГТУ ИМ. Н.Э. БАУМАНА

ОНЛАЙН | VR | IIA "Rossiya Segonya"| BMSTU

МИР НАУКИ
ИЗДАТЕЛЬСТВО
2022

@compositeforum forum.emtc.ru/en/ composite-forum@emtc.ru

УДК 629.78-03, 620.2(15)
ГРНТИ 89.25.43, 50.51.15, 50.53.15, 47.09.48, 76.09.41
ББК 30
К 52

К 52 Ключевые тренды в композитах: наука и технологии 2021. IV Международный форум (Москва, 2–3 декабря 2021 г.) // Сборник трудов конференции — М.: Мир науки, 2022. — Режим доступа: https://izd-mn.com/PDF/67MNNPK22.pdf — Загл. с экрана.

ISBN 978-5-907603-66-0

DOI: 10.15862/67MNNPK22

Это ежегодная конференция, которая проводится с 2018 года в Москве, Россия. Организатором конференции является Московский государственный технический университет имени Баумана (МГТУ). Сайт конференции https://forum.emtc.ru/ru/. Площадка научно-практической конференции позволяет представить и обсудить последние научные достижения и мировые тенденции, обменяться свежими идеями, концепциями, методиками и инновационными теориями в области разработки и производства композиционных материалов.

Конференция была виртуальной.

Конференция включала пленарное заседание с 10 спикерами по 10 минут на каждого. А также доклады и дискуссии в 7 секциях по 5 часов, всего около 90 докладчиков.

Общая посещаемость составила около 3 000 человек.

ISBN 978-5-907603-66-0

Организационный комитет

- Нелюб Владимир, mail@emtc.ru (председатель)
- Бородулин Алексей, asb@emtc.ru
- Терешков Александр, atereshkov@emtc.ru
- Вырикова Анастасия, avyrikova@emtc.ru

Научный комитет

- Полежаев Александр, aleksandr.polejaev@gmail.com
- Плохих Андрей, plokhikh@bmstu.ru
- Курганова Юлия, kurganova_ya@mail.ru
- Галиновский Андрей, galcomputer@mail.ru
- Резник Сергей, sreznik@bmstu.ru
- Думанский Александр, aldumans@rambler.ru
- Малышева Галина, malyin@mail.ru
- Дмитриенко Юрий, dimit.bmstu@gmail.com

Редакционный комитет

- Бородулин Алексей
- Терешков Александр

Оглавление

Селезнев В.А., Чуков Н.А. Physical and mechanical characteristics of basalt plastic reinforcement 5

Симачев А.Д., Сторожук И.П., Павлюкович Н.Г., Платонова Е.О., Филатова Е.В., Шевцов В.Ю., Терешков А.Г. Copolysulfones with increased heat resistance 10

Павлюкович Н.Г., Кирейнов А.В., Третьяков И.В., Терешков А.Г., Сторожук И.П. Obtaining polymer composite materials using the solution technology for the manufacture of prepregs 18

Сторожук И.П., Орлов М.А., Богачев В.В., Калинников А.Н., Павлюкович Н.Г. Polyurethane protective and anti-icing coating for structures for various purposes 24

Сторожук И.П., Орлов М.А., Поликарпова И.А., Калинников А.Н., Павлюкович Н.Г. Polymer protective coatings for pipes and pipeline fittings in the oil and gas industry 30

Стоянова М.В., Новиков А.Д. The engineering rent specifics assessment for engineering industrial companies in the field of digital materials science 36

Стоянова М.В., Новиков А.Д. On the issue of new materials use in satellite communication systems economic efficiency assessing 43

Терешков А.Г. Polysulfones and fabric composite materials based on them 49

Селезнев В.А., Чуков Н.А., Дорофеев К.С. Digital system for designing matrixes of self-regulating heating cables 61

Вдовин Д.С., Бородулин А.С. Experience in evaluating the properties of fiberglass using a neural network and non-destructive testing method 68

Чэнь Я., Малышева Г.В. Technique for optimizing the curing mode of glass-reinforced plastic parts based on an epoxy binder 74

DOI: 10.15862/67MNNPK22-01

Seleznev Vyacheslav Aleksandrovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: vseleznev@emtc.ru

Chukov Nikolay Aleksandrovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: nchukov@emtc.ru

Physical and mechanical characteristics of basalt plastic reinforcement

Abstract. The paper studies physical and mechanical characteristics of the basalt-composite plastic reinforcement with different anchorage layers and compares it with the glass composite reinforcement. The influence of long-term extension strain on the basalt-composite reinforcement characteristics has been found. The prospects of the composite-basalt plastic reinforcement usage have been determined. There is a brief overview of the present-day polymer composite reinforcement applications. The paper considered both advantages and disadvantages of the glass composite reinforcement and suggested using the basalt plastic reinforcement. Physico-mechanical characteristics of the basalt plastic reinforcement in comparison with other types of polymer composite reinforcement and their changes due to technological features of basalt plastic reinforcement manufacturing have been studied. The influence of technological features of basalt-composite reinforcement on its performance parameters has been found. The study revealed the action of long-term extension strain (180 days at 22ºC) — comprising 20, 40, 50, 69 % of the tensile strength at stretching of the basalt-composite reinforcement — upon the strength and tensile modulus at stretching of the 12 mm diameter basalt-composite reinforcement with the sand coating and spiral winding.

Keywords: basalt plastic; basalt-composite reinforcement; polymer reinforcement; anchorage layer

Introduction

It is impossible to imagine the modern building industry without reinforced concrete structures with comparatively low cost, high technological characteristics, durability and longevity. Their service life is determined by many factors, but the main cause of destruction is the metal reinforcement corrosion [1]. Due to the presence of an alkaline environment of concrete mixture and water starting from the moment of contact between the concrete and the metal rod, selective corrosion processes take place, negatively affecting the strength and load carrying capacity of reinforced concrete structures. The problem was solved by using the fiberglass reinforcement which is a 10–15 micron diameter alkali-resistant glass fiber. The fibre bundle was packed into a monolithic core by means of a polymer matrix (epoxy, epoxy phenol, polyether, etc.). The fiberglass reinforcement advantages were especially evident in the construction of concrete structures:

- exposed to anti-icing chlorine-containing reagents;
- in constant contact with water or exposed to moisture (geotechnical construction);
- exposed to seawater;
- exposed to aggressive media;
- exposed to high voltages and electromagnetic fields, etc.

Among the advantages of the fiberglass reinforcement over steel are low density, foundry thermal deformation coefficient, low thermal conductivity coefficient, dielectric and diamagnetic properties. The use of fiberglass composite reinforcement instead of steel allows to reduce the weight of concrete structures while simultaneously increasing their durability and strength characteristics [5]. However, such reinforcement has essential disadvantages: low elasticity modulus at tension; low fire resistance of building structures reinforced with composite reinforcement; impossibility to manufacture bent reinforcing products from fiber-reinforced polymer bar in the state of delivery; much higher cost. Some of these disadvantages can be eliminated by replacing the fiberglass polymer composite reinforcement with basalt fiber. Basalt fibers are made of basalt and their strength properties in many respects exceed those of glass fibers. At the same time, the level of main technical characteristics of basalt fibers is better than that of traditional glass fibers. Basalt-composite reinforcement improves heat-protective properties of fencing structures, provides the required durability and increases the reliability of concrete structures. However, the use of basalt-composite reinforcement in construction is hindered by the absence of experimentally substantiated values of their physical and mechanical characteristics. This paper shows the main physical and mechanical characteristics of the basalt-composite reinforcement and how they are influenced by the anchorage layer and the reinforcement diameter.

Research methodology data

Complex research of operational characteristics of the 12 mm diameter basalt-composite reinforcement with the spiral winding and sand coating. Epoxy compound ETAL-370U (TU 2257-370-18826195-99) was used as a matrix. The basalt direct roving produced by "Kamenny Vek" company (monofilament diameter of 11 microns, linear density 110 tex with sizing agent KB 41) was used as a reinforcing filler. Basalt-composite reinforcement was produced using the "Polycom-15" production line by filterless drawing of glass fiber (needletrusion) with epoxy compound impregnation and subsequent wrapping with glass fiber to form a periodic profile of reinforcement or with quartz sand coating. For comparison, both fiberglass composite and carbon composite reinforcement were used.

The tensile breaking stress and elasticity modulus, breaking compression and cross-sectional stress, the composite reinforcement-concrete bond strength were determined in accordance with the requirements of GOST 32492-2015 [2], taking into account the recommendations of works [3; 4]. Polymer reinforcement tests were carried out with the help of electrohydraulic machine Instron 3382. The basalt-composite reinforcement creep under long-term exposure to permanent tensile loads was determined using type FLA-1-11 strain gauges of "Tokyo sokki Kenkyujo Co., Ltd." with a 1 mm base glued in the middle of the reinforcement rod working area and connected to the National Instruments PXIe-1075 recording device. Strain gauges were glued in one transverse plane of the reinforcement, fixed in the tension device clamp [6], circumferentially every 90 degrees. Using the data obtained, we plotted the time dependencies of creep strain.

Experimental part

The polymer reinforcement physical and chemical characteristics are influenced mainly by the type of roving and polymer matrix. The performance properties of basalt composite reinforcement were also considered depending on the anchorage layer type.

Industrial composite reinforcement can be conceptually divided into 4 types:

type 1 — polymer reinforcement with an anchorage layer in the form of transverse protrusions formed by winding two crossed layers of continuous fiber on the forcing rod;

type 2 — polymer reinforcement with an anchorage layer in the form of crossed protrusions formed by spiral winding of one continuous fiber layer on the forcing rod;

type 3 — polymer reinforcement with an anchorage layer without transverse protrusions formed by spiral winding on the forcing rod with a continuous fiber sand coating;

type 4 — polymer reinforcement with a combined anchorage layer in the form of transverse protrusions formed by spiral winding on the forcing rod with a continuous fiber sand coating.

The nature of the reinforcing fiber (makes up to 75 % of the reinforcement mass) has the greatest influence on the polymer composite reinforcement properties, and the role of the polymer matrix is reduced to the transfer of loads to the reinforcing fibers. Table 1 shows physical and mechanical characteristics of polymer composite reinforcements with different reinforcing fibers. Polymer composite reinforcement with reinforcing carbon fiber has the maximum strength and tensile modulus under tension. In practical applications the use of such reinforcement is limited by its high cost. The glass fiber based reinforcement has the lowest strength parameters. The basalt-composite reinforcement surpasses the glass-composite one in elasticity modulus and tensile strength by 8–10 % while not inferior in other parameters.

Table 1

Physical and mechanical characteristics of 12 mm diameter polymer composite reinforcement

Characteristics	**Composite reinforcement type**		
	carbon composite	**basalt composite**	**glass composite**
Tensile strength, GPa	14.99	1.18	1.09
Tensile strain at break, %	1.00	2.22	2.23
Tensile modulus, GPa	140.9	53.2	48.8
Concrete bond strength, MPa	8.54	12.54	12.45

It has been found out that the basalt-composite reinforcement properties are also influenced by technological peculiarities of the manufacturing process. Table 2 represents physical and mechanical characteristics of the basalt-composite reinforcement depending on the type of the anchorage layer.

Table 2

Physical and mechanical characteristics of the glass-composite reinforcement with different types of the anchorage layer

Characteristics	**Anchorage layer type**			
	1	**2**	**3**	**4**
Strength, GPa,				
under compression	0.40	0.34	-	0.41
tensile	1.09	1.05	0.99	0.79
transverse	0.17	0.17	-	0.16
Concrete bond strength, MPa	16.6	16.0	12.45	15.6
Modulus of elongation, GPa	63.0	47.0	48.8	42.1
Tensile strain at break, %	1.53	2.22	2.23	1.69

Table 2 shows that the basalt-plastic reinforcement with an anchorage layer in the shape of crossed projections, formed by winding of two crossed layers of continuous fiber on a forcing rod has the maximum strength

It is important to note that basalt composite reinforcement has virtually no plastic deformations under tension. The tensile diagram of a reinforcement of that kind is straight up to its breakup (fig. 1).

Durability is one of the most important characteristics of concrete structures. Therefore, it is necessary to collect data about the influence of prolonged tensile strain on basalt-composite reinforcement physical and mechanical characteristics. The authors have studied the action of the tensile strain level on the tensile strength and elastic modulus of the 12 mm diameter basalt-composite and glass-composite reinforcement with spiral winding and sand coating. The tensile strain was 20, 40, 50, and 60 % of the tensile stress at break, and the duration is 180 days at 22°C. The results of the studies are presented in table 3.

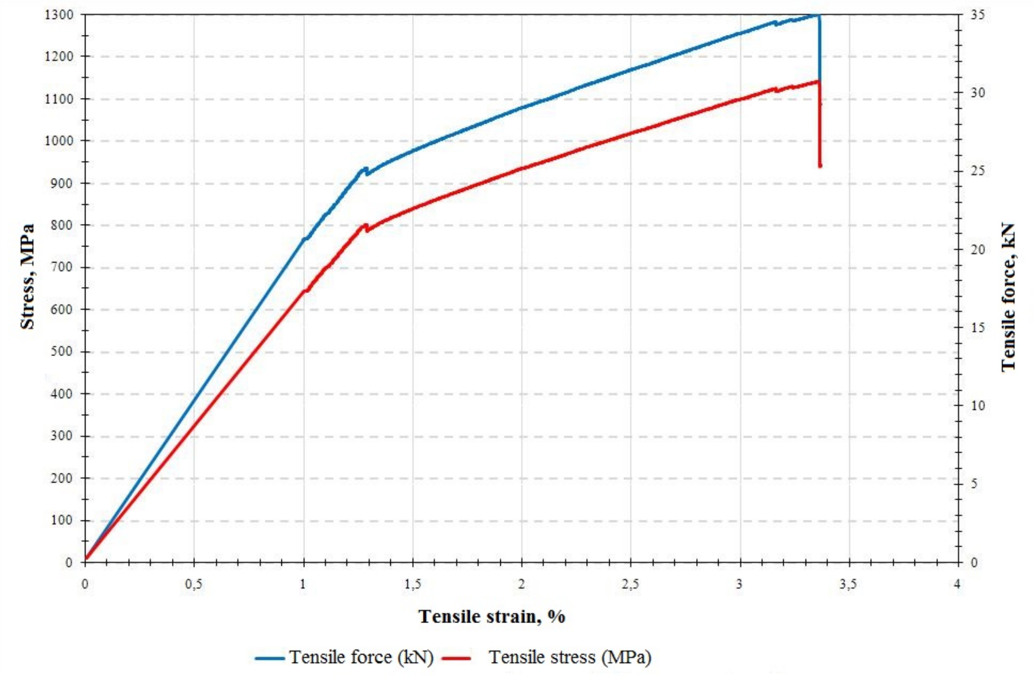


Figure 1. *The tensile diagram of the glass-composite reinforcement with spiral winding*

Table 3

Physical and mechanical characteristics of glass composite reinforcement after long-term exposure to tensile load

Characteristics	Load level, %	Basalt-composite reinforcement	Glass-composite reinforcement
Tensile stress at break after long-term long-term extension load strain, MPa	-	929.5/974.8	915.2/949.5
	40	947.7/952,5	972.0/953.1
	50	952.4/946.4	-
	60	956.6/941.2	-/954.6
Reduction of tensile stress at break after long-term long-term extension load strain, %	40	+2.0/2.3	+6.2/+0.38
	50	+2.5/2.9	-
	60	+2.9/3.4	-/+0.53
Tensile modulus after long-term long-term extension load strain, GPa	-	51.2/51.9	50.7/51.0
	40	52.4/50.8	48.4/52.1
	50	52.6/50.5	-
	60	52.9/50.2	-/52.3
Reduction of tensile modulus after long-term long-term extension load strain, %	40	+2.3/2.1	4.5/+2.2
	50	+3.7/2.7	-
	60	+4.5/3.3	-/+2.5

Note — numerator contains data for the reinforcement with spiral winding, denominator — with sand coating

It was found that tensile strength and tensile modulus of the basalt-composite reinforcement after a long-term tensile strain depends on the anchorage layer type. After long-term tensile strain exposure of up to 60 % of the initial tensile strength, the breaking stress and tensile modulus of the basalt-composite reinforcement with sandy coating decreases linearly by 3–4 %. At the same time, basalt-composite reinforcement with spiral winding shows a slight linear increase in the reinforcement strength. Such different behavior of the reinforcement with different types of anchorage layer after a long-term exposure to tensile strain can be explained by basalt fiber straightening in the anchorage layer and its fuller contribution to the resistance to the breaking force.

The nature of changes in physical and mechanical characteristics is generally the same for polymer reinforcement with different types of fibers. However, the decrease in the glass-composite reinforcement strength properties is more noticeable under prolonged loading.

Conclusions

The basalt-plastic reinforcement surpasses the glass fiber reinforcement in a number of physical and mechanical properties and has a potential to replace it in concrete structures with increased reliability. It has been established that physical and mechanical characteristics of basalt-plastic reinforcement are markedly influenced by technological features of its manufacturing. In addition to that, operational properties of the basalt-composite reinforcement have been insufficiently studied. There is a need for further research of basalt-composite reinforcement behavior under the action of corrosive media in wide temperature range.

Acknowledgement

This work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (Center NTI "Digital Materials Science: New Materials and Substances" on the basis of the Bauman Moscow State Technical University).

REFERENCES

1. Rimshin V.I., Merkulov S.I. 2015 Elements of theory of development of concrete structures with nonmetallic composite reinforcement. Industrial and civil engineering. 5. pp. 38–42.
2. GOST 32492-2015 Fiber-reinforced polymer bar for concrete reinforcement. Determination of physical-mechanical properties.
3. Benin A.V., Semenov S.G. 2014 Peculiarities of composite polymeric bars tests. Industrial and civil engineering. 9. pp. 42–46.
4. Gizdatullin A.R., Khozin V.G., Kuklin A.N., Khusnutdinov A.M. 2014 Specifics of testing and fracture behavior of fibre-reinforced polymer bars. Magazine of civil engineering. 3(47). pp. 40–47.
5. Seleznev V.A. et al. 2021 Performance characteristics of polymer composite reinforcement. Industrial and civil engineering. 1. pp. 42–50.
6. Patent RU 163607 U1 Borisov A.V., Seleznev V.A. Clamp for composite reinforcement prestressing device — 2016.

DOI: 10.15862/67MNNPK22-02

Simachev Aleksandr Dmitrievich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: asimachev@emtc.ru

Storozhuk Ivan Pavlovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: Storozhuk-ip@inbox.ru

Pavlukovich Nadezhda Gennad′evna
A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia
E-mail: npavlukovich@emtc.ru

Platonova Elena Olegovna
Bauman Moscow State Technical University, Moscow, Russia
E-mail: EPlatonova@emtc.ru

Filatova Ekaterina Vladimirovna
Bauman Moscow State Technical University, Moscow, Russia
E-mail: efilatova@emtc.ru

Shevtsov Vladislav Yur′evich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: vshevcov@emtc.ru

Tereshkov Aleksandr Gennad′evich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: atereshkov@emtc.ru

Copolysulfones with increased heat resistance

Abstract. In order to obtain polyethersulfones with an increased glass transition temperature, copolyethersulfones were synthesized based on 4,4'-dioxydiphenylsulfone, phenolphthalein, and 4,4'-dichlorodiphenylsulfone. It is shown that with an increase in the content of elementary units based on phenolphthalein, the glass transition temperature of the copolymers smoothly increases by 25°C. The resulting copolymers were studied by differential scanning calorimetry, gel permeation chromatography, and thermogravimetric analysis.

Keywords: copolyethersulfones; differential scanning calorimetry; gel permeation chromatography; thermogravimetric analysis

Introduction

Aromatic polysulfones and polyethersulfones are of great interest for the creation of a new generation of highly heat-resistant polymer composite materials with increased strength at high temperatures. They are resistant to radioactive radiation, fire resistant, have high chemical resistance (stable in alkali solutions, weak solutions of mineral acids and saturated solutions of mineral salts, aliphatic hydrocarbons, motor and diesel fuels, vegetable and petroleum oils, surfactants). The temperature of the start of thermal decomposition of these polymers is above 400°C, that is, 40–60°C higher than the processing temperature. Polysulfones and polyethersulfones are characterized by low creep, low shrinkage during molding from the melt (0.2–0.7 %), low water absorption (0.2–0.4 %), which ensures high dimensional stability of products in contact, for example, with food products [1–10].

The considering thermoplastics are used as structural materials for the manufacture of engineering products that operate for a long time under extreme conditions (at temperatures from -100 to 200°C and even up to 220°C, under load and in aggressive environments) without deterioration in physical, mechanical and electrical characteristics, as well as in the production of electrical insulating films, incl. for printed circuit boards. Polymers are used as binders in the manufacture of prepregs reinforced with carbon and other high-strength fibers. In addition, polysulfones are used for the manufacture of coatings and as additives in epoxy compositions [1; 6].

A successful combination of properties has ensured the widespread use of polysulfones in electronics, electrical engineering, instrumentation, the aerospace industry, as well as in the production of household appliances, medical instruments and equipment [1–4].

However, research on improving the heat resistance of polysulfones and polyethersulfones is still relevant both in scientific and practical terms [9–11].

It is known that the introduction of kard fragments into the structure of polyethers and complex aromatic polyesters gives them a number of specific properties. Among them is an increase in the glass transition temperature and thermal stability, which allows the use of copolymers at higher temperatures without a significant change in mechanical properties. In addition, the presence of bulky card groups in rigid-chain macromolecules improves their solubility in organic solvents, which makes it possible to process polymers from solutions [12–14].

As well-known examples, one can point to the solvent-soluble polyarylate F-2 based on phenolphthalein and terephthalic acid dichloride [12] with the general chemical structure (fig. 1).

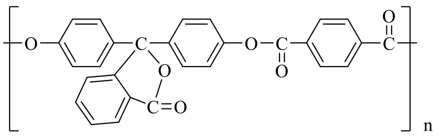


Figure 1. *Chemical structure of polyarylate F-2*

As well as chemically modified polysulfone brand PSFF-30 manufactured by JSC "NIIPM" [11] based on a mixture of bisphenol A, phenolphthalein and 4,4'-dichlorodiphenylsulfone with increased heat resistance (T_c = 210°C) of the general structure (fig. 2).

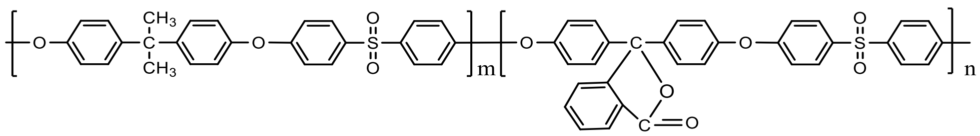


Figure 2. *Chemical structure of polysulfone PSFF-30*

In order to obtain polyethersulfones (PES) with an elevated glass transition temperature and a detailed study of their main properties, we synthesized copolyethersulfones of the PES-SF series based on a mixture of 4,4'-dioxydiphenylsulfone, phenolphthalein and 4,4'-dichlorodiphenylsulfone according to the following reaction equation (fig. 3).

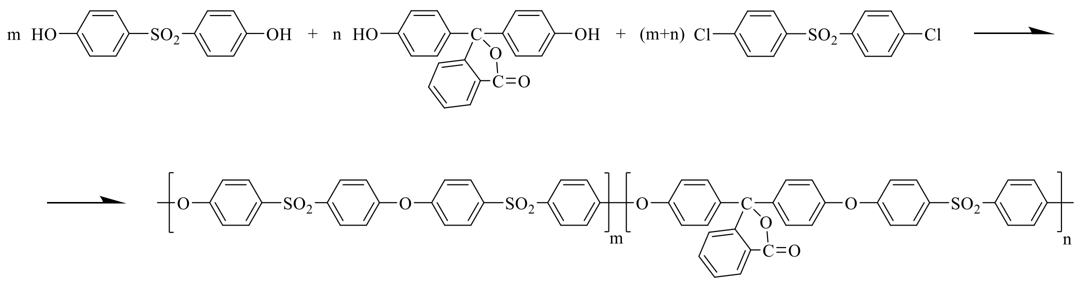


Figure 3. *Chemical reaction equation for copolyethersulfones of the PES-SF series synthesis*

Experimental procedure

To carry out the synthesis, phenolphthalein (PHPH), 4,4'-dioxydiphenylsulfone (DHDPS), calcined potassium carbonate, dimethylacetamide, and toluene were loaded into a three-necked flask equipped with an overhead mechanical stirrer, an argon inlet, a Dean-Stark trap for azeotropic water distillation, a reflux condenser, and a bubble counter. The temperature in the oil bath was gradually increased to 160°C and the toluene-water azeotrope was distilled off to obtain a suspension of dipotassium salts of phenolphthalein and 4,4'-dioxydiphenylsulfone in a mixture of dimethylacetamide and toluene. After completion of the distillation of water, it was removed from the Dean-Stark nozzle and the toluene was completely distilled from the flask. Then 4,4'-dichlorodiphenylsulfone was introduced into the flask, the bath temperature was raised to 165°C, and the polyethersulfone formation reaction was carried out for 20 hours.

Upon completion of the reaction, dimethylacetamide was added to the flask, and the polymer was precipitated in an excess of distilled water with vigorous stirring of the precipitant. The precipitate that formed was filtered off and washed from the solvent and potassium chloride to a negative test for chloride ions (using an aqueous solution of silver nitrate). After the turbidity (silver chloride crystals) ceased to appear in the wash water at room temperature, the polyethersulfone was filtered off and dried at 120°C for 3 hours.

The reduced viscosities (η_{red}) of copolymer solutions were determined in dimethylformamide at 25°C and a concentration of 0.5 g of polymer in 100 g of solvent.

Molecular weights and molecular weight distribution (MWD) were determined by gel permeation chromatography (GPC) using a Shimadzu Prominence LC-20 chromatograph equipped with a RID 20A refractive index detector and 100 angstrom PSS GRAM analytical columns. Dimethylformamide was used as a solvent, the sample concentration was from 1.1 to 2.1 mg/ml. Figure 1 shows the calibration curves were generated using six 1 mg/mL polyacrylate standards.

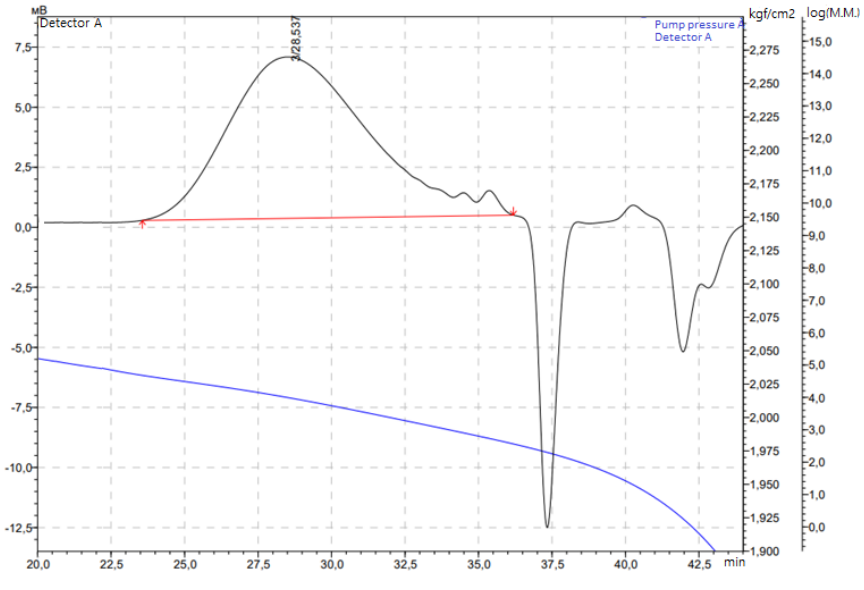


Figure 4. *Gel permeation chromatography curve of polyethersulfone PES-SF-100/0*

Results and discussion

Figure 4 shows the polyethersulfone gel chromatogram has a main maximum, which corresponds to the distribution of macromolecules by molecular weight. First, the highest molecular weight macromolecules are washed out of the liquid column, and then molecules with a lower molecular weight. A small maximum is observed on the right side of the chromatogram, which is identified as cyclic oligomers with MM = 800, the content of which in PES usually ranges from 2 to 3 wt%. The formation of cyclic oligomers is characteristic of polymers of the polycondensation type, and their amount is related to the synthesis conditions: bifunctional starting compounds, solution concentration, synthesis temperature [15].

The data on the synthesized copolyethersulfones are summarized in the table. It can be seen that there is a good correlation between the values $\overline{M}w$, $\overline{M}n$ and the values of the reduced viscosity, weight average and number average molecular weights (the higher η_{red}, the higher the MM). The molecular weight distribution of the synthesized polymers is quite narrow, from 1.61 to 2.17, which corresponds to the usual polydispersity of polycondensation-type polymers [12; 15].

Table 1

Composition of copolyethersulfones and their molecular weight characteristics

Copolymer code	Content of units, %mol		η_{red}, dl/g	$\overline{M}w$	$\overline{M}n$	$\overline{M}w/\overline{M}n$
	DHDPS	PHPH				
PES-SF-100/0	100	0	0,42	25800	16000	1,61
PES-SF-75/25	75	25	0,34	19600	11500	1,71
PES-SF-50/50	50	50	0,33	18600	11790	1,68
PES-SF-25/75	25	75	0,43	17900	8300	2,17
PES-SF-0/100	0	100	0,53	32600	15500	2,10

The glass transition temperatures of the copolymers were determined using differential scanning calorimetry (DSC) on a NETZH DSC 204 F1 Phoenix instrument [8; 9]. The rate of temperature rise was 10°C per minute, argon was used as an inert atmosphere. The test samples were compressed mini tablets weighing 12–13 mg. To obtain curves with the best kink configurations for calculation, the DSC curves were taken repeatedly 2–3 times according to the heating-cooling-heating cyclogram.

Figure 5 shows the relationship between the thermal effect and the temperature of the sample. The lower DSC curve was obtained by retesting the sample. Figure 6 shows the relationship between the glass transition temperature (T_g) of copolymers and the content of units based on phenolphthalein and 4,4'-dichlorodiphenylsulfone in their structure.

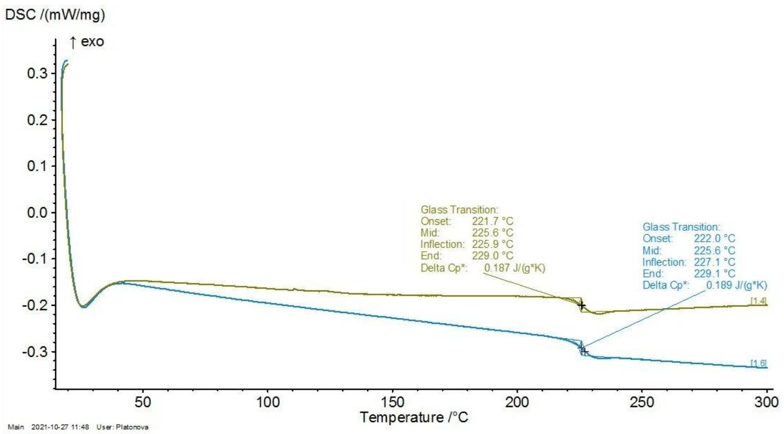


Figure 5. *DSC curves for PES-SF-75/25 copolyethersulfone*

As can be seen from the graph of the relationship between the glass transition temperature and the composition of the copolymer, with an increase in the content of units based on phenolphthalein, T_c increases from 232°C for polyethersulfone based on 4,4'-dioxydiphenylsulfone and 4,4'-dichlorodiphenylsulfone to 257°C for copolyethersulfone PES-SF-0/100. The difference in glass transition temperatures of these thermoplastics is 25°C. This is due to the fact that units based on phenolphthalein with a bulky phthalide ring are more rigid than units based on 4,4'-dioxydiphenylsulfone, which contains a SO_2 hinge group between aromatic nuclei.

To evaluate the heat resistance of the synthesized copolymers by thermomechanical analysis (TMA), tablets were prepared from polymer powders with a diameter of 4 mm and a height of 4.5 mm. Tablets were prepared by pressing at a temperature of 25°C under a pressure of 20 kgf/cm^2.

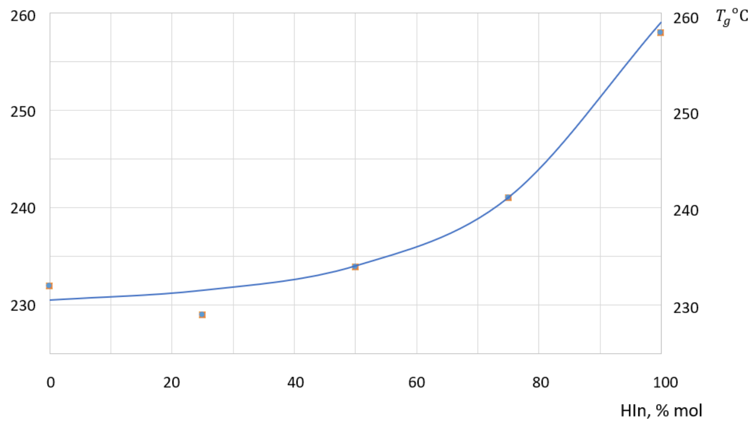


Figure 6. *Relationship between the glass transition temperature of copolyethersulfones and the content of units based on phenolphthalein and 4,4'-dichlorodiphenylsulfone in their structure*

The tests were carried out on the device "MCR 702 MultiDrive Anton Paar" according to the method developed at the Scientific and Educational Center "Composites of Russia" BMSTU, which consists in the fact that a tablet of pressed powder was placed between two plane-parallel plates of the device and a constant load of 10 N was applied. The rate of temperature rise was 3°C per minute. Figure 7 shows the typical relationship between the relative deformation of the samples and temperature is shown in.

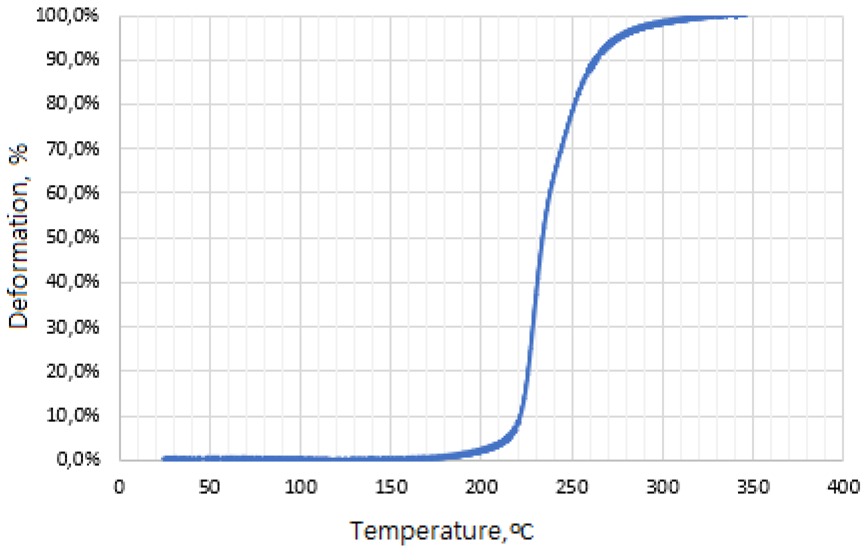


Figure 7. *Temperature dependence of the deformation of PES-SF-100/0 under a pressure of 10N*

The digital values of the glass transition temperatures of the copolymers, determined by the methods of differential scanning calorimetry and thermomechanical analysis, are shown in table 2.

Table 2

Glass transition temperatures of synthesized copolyethersulfones determined by DSC and TMA

Copolymer code	Content of units, %mol		T_g,°C	
	DHDPS	PHPH	By DSC	By TMA
PES-SF-100/0	100	0	232	223
PES-SF-75/25	75	25	226	225
PES-SF-50/50	50	50	233	234
PES-SF-25/75	25	75	241	241
PES-SF-0/100	0	100	257	-

As can be seen from a comparison of the T_g values determined by DSC and TMA, the glass transition temperatures of polymers under a small load are quite close to the glass transition temperatures found by a nonloading DSC method, which is consistent with the theoretical concepts of the behavior of polymers at elevated temperatures [1; 9–12].

The thermal stability of PES-SF melts was evaluated using the thermogravimetric analysis (TGA) method. The method makes it possible to measure the change in mass and the rate of this change for a sample, that is, to fix the integral and differential curves of its mass loss. When the sample is heated in an inert gas medium, the thermal decomposition of the polymer is studied, and when heated in air, its thermal oxidative degradation is studied. The measurements were carried out on a NETZH TG 209 F1 Libra device in an argon atmosphere at a constant heating rate of 5 degrees per minute. The temperatures of 5 % ($T_{5\%}$) and 10 % ($T_{10\%}$) weight loss were recorded. Figure 8 shows the measurement results.

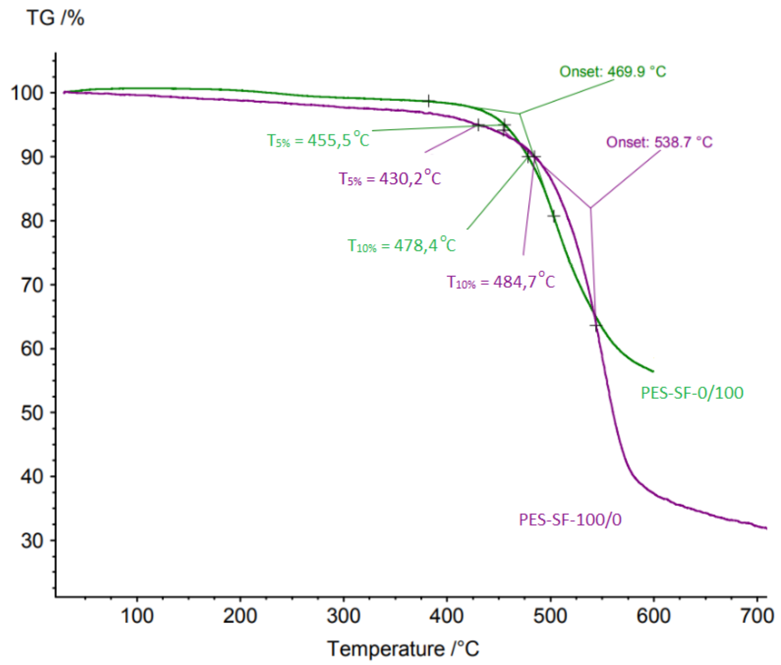


Figure 8. *Temperature dependence of weight loss of PES-SF-100/0 and PES-SF-0/100 polyethersulfones upon heating in argon*

Figure 8 shows the introduction of phenolphthalein units into polyethersulfone macromolecules based on 4,4'-dioxydiphenylsulfone and 4,4'-dichlorodiphenylsulfone does not worsen the thermal stability of the thermoplastic or even slightly increases it. In particular, the samples lose 5 % of the mass at temperatures of 430 and 455°C, and 10 % at 484.7 and 478.4°C, which allows us to hope for the possibility of processing the synthesized polymers from the melt at 340–360°C without a significant decrease in molecular weight. masses.

Conclusion

Thus, the chemical modification of polyethersulfone based on 4,4'-dioxydiphenylsulfone and 4,4'-dichlorodiphenylsulfone with phenolphthalein additives leads to a gradual increase in the glass transition temperature of copolyethersulfone. In the future, it is planned to study the solubility, mechanical strength and viscosity of the melts of the synthesized copolymers.

Acknowledgments

The work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (NTI Center "Digital Materials Science: New Materials and Substances" on the basis of Bauman Moscow State Technical University) and with the support of the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. Mikhailin Yu.A. Heat-resistant polymers and polymeric materials. St. Petersburg: 2013, CSP Profession. — 480 p.
2. Buhler K.-W. Heat and heat resistant polymers; Per. from German / Ed. Ya.S. Vygodsky. — M.: Chemistry, 1984. — 1056 p.
3. Kryzhanovsky V.K. Technical properties of plastics. St. Petersburg: TsOP Professiya, 2014. — p. 2048.
4. Storozhuk I.P., Valetsky P.M. Patterns of formation and properties of polyarylensulfone oxides. // In the book: Itogi nauki i tekhniki. Chemistry and technology of macromolecular compounds. Volume 12. — M., VINITI, 1978, pp. 127–176.
5. Storozhuk I.P., Alekseev V.M., Kalinnikov A.N., Borodulin A.S. Chemically modified polysulfones and their properties. Polymer Science — Series D. 2021, v. 14(4), pp. 580–587.
6. Kochergin Yu.S., Storozhuk I.P., Kulik T.A., Grigorenko T.I. Sulfonated epoxy resins. // Review. inf. Series: Epoxy resins and materials based on them. M., NIITEKHIM, 1990, p. 47.
7. Borodulin A.S., Kalinnikov A.N., Bazheva R.C. at all. 2018. Synthesis and properties of aromatic polyethersulfones // International Journal of Mechanical Engineering and Technology (IJMET). — v. 9(13), pp. 1109–1116.
8. Borodulin A.S., Kalinnikov A.N., Kharaev A.M., at all. 2019. Aromatic polysulfone to create polymer materials with high resistance to frost. — IOP Conf. Series: Earth and Environmental Science — v. 302, pp. 1–5.
9. Kharaev A.M., Bazheva R.Ch., Begieva M.B., Nelyub V.A., Borodulin A.S. 2019. Polyethersulfones with improved thermophysical properties. Polymer Science — Series D — v. 12(1), pp. 24–28.
10. Borodulin A.S., Kalinnikov A.N. at all. 2019. New Polymeric Binders for the Production of Composit. — Materials Today: Procttdings — v. 11, pp. 139–143.
11. Petrova G.N., Beider E.Ya., Chebotarev V.P., Lovkov S.S., Sazikov V.I. Adjustment of polysulfone properties through modification. Plastics, 2010, No. 12, pp. 23–27.
12. Vinogradova S.V., Vasnev V.A. Polycondensation processes and polymers. M: Nauka, MAIK "Nauka/Interperiodika", 2000. — 373 p.
13. Li, L.; Liu, J.; Chen, G.; Xu, L.; Mushtaq, N.; Sidra, L.R.; Wang, R.; Fang, X. Synthesis of organosoluble and transparent phenolphthalein-based cardo poly (ether sulfone imides) via aromatic nucleophilic substitution polymerization. High Perform. Polym. 2016, 28, pp. 1263–1271.
14. K.T. Shakhmurzova, Zh.I. Kurdanova, A.A. Zhansitov, A.E. Baikaziev, S.Yu. Khashirova, S.I. Pakhomov, M.Kh. Ligid Synthesis and properties of aromatic polyesters with kard fragments. // Izv. universities. Chemistry and chem. technology. 2017. V. 60. Issue. 6. — pp. 28–39.

15. Oudian J. Fundamentals of polymer chemistry. M.: Mir, 1974. — p. 614.
16. Van Crevelen D.V. Properties and chemical structure of polymers. Per. from English. ed. A.Ya. Malkin. — M.: Chemistry, 1976. — p. 416.
17. Godovsky Yu.K. Thermophysical methods for studying polymers. Moscow: Chemistry, 1986. — p. 270.
18. Bershtein V.A., Egorov V.M. Differential scanning calorimetry in the physicochemistry of polymers. L: Chemistry, 1990. — p. 256.
19. Grellman V., Seidler S. Testing of plastics. Translation from English. ed. AND I. Malkin. St. Petersburg: 2010, CSP Profession. — p. 720.
20. Askadsky A.A., Khokhlov A.R. Introduction to the physical chemistry of polymers. M: Scientific world, 2009. — p. 384.

DOI: 10.15862/67MNNPK22-03

Pavlukovich Nadezhda Gennad′evna
A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia
E-mail: npavlukovich@emtc.ru

Kireynov Aleksey Valer′evich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: alexkireinov@gmail.com

Tretyakov Il′ya Vasil′evich
N.N. Semenov Federal Research Center for Chemical Physics Russian Academy of Sciences, Moscow, Russia

Tereshkov Aleksandr Gennad′evich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: atereshkov@emtc.ru

Storozhuk Ivan Pavlovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: Storozhuk-ip@inbox.ru

Obtaining polymer composite materials using the solution technology for the manufacture of prepregs

Abstract. The results of a study of polyethersulfone PES-12 synthesized at the Scientific and Educational Center "Composites of Russia" BMSTU, the structure of which was confirmed by IR spectroscopy and gel permeation chromatography, are presented. A combined solution-powder method for manufacturing prepregs based on a unidirectional carbon fabric and synthesized PES-12 has been developed. Experiments were carried out on the manufacture of samples of carbon composites from thermoplastic prepregs by hot pressing. The resulting carbon composites were studied by electron microscopy and tomography. Regularities of changes in the internal porosity of composites depending on the temperature conditions of their pressing are revealed.

Keywords: thermoplastic prepreg; solution-powder method; carbon composites

Introduction

The development of thermoplastic prepregs and composites based on carbon fabrics and superstructural thermoplastics is an urgent scientific and applied task since these materials are increasingly used in the production of aerospace equipment, various devices, and special protection equipment, etc.

The volume of application of polymer composite materials (PCM) based on carbon fiber fillers in the domestic aviation industry is constantly increasing. Particular attention is paid to the creation of PCM with a range of operating temperatures up to 200–300°C. The increased interest in such materials both in Russia and abroad is associated with work on the creation of military and civil aviation and rocket technology of a new generation, which involves the use of PCM in heat-loaded assemblies and structural elements of the wing, fuselage, and aircraft engines [1]. Currently, research is being actively carried out aimed at expanding the scope of application of thermoplastics for the production of PCM [2–11].

To create heat-resistant PCMs, heat- and heat-resistant reinforcing fillers and superstructural polymeric binders are required. Representatives of such polymeric materials are, in particular, polyethersulfones.

The purpose of this study is to develop a technology for obtaining structural composite materials based on heat-resistant polyethersulfone and unidirectional carbon fabric.

Tasks that were solved in the course of the study:

1. Synthesis and production of heat-resistant polyethersulfone.
2. Production of thermoplastic prepregs based on synthesized polyethersulfone and unidirectional carbon fabric.
3. Selection of conditions for hot pressing of thermoplastic prepregs and study of the PCM obtained.

Experimental part

Polyethersulfone PES-12 was synthesized (synthesis scheme shown figure 1) in the laboratory of thermoplastics of the Scientific and Educational Center "Composites of Russia" on a laboratory unit for the synthesis of thermoplastic polymers (fig. 2).

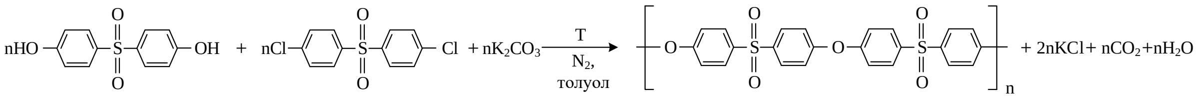


Figure 1. *Synthesis scheme of polyethersulfone PES-12*

Figure 2. *Laboratory facility for the synthesis of polymeric thermoplastics*

The composition and structure of the synthesized PES-12 thermoplastic were characterized by elemental analysis, IR spectroscopy (IR spectrometer Nicolet iS10, range 4000–650 cm^{-1} with a germanium crystal). The molecular weight distribution was determined by gel permeation chromatography (GPC) using a Shimadzu ProminenceLC-20 chromatograph equipped with the RID 20A refractive index detector. The reduced viscosity of 0.5 % solutions in N-methylpyrrolidone at 25^{o}C was determined.

The heat resistance of the resulting polymer was determined by differential scanning calorimetry (DSC) on the NETZH DSC 204 F1 Phoenix instrument. The measurements were carried out in the temperature range from 25 to 300^{o}C at a heating rate of 10 K/min in an argon atmosphere.

Thermomechanical analysis was carried out on an Anton Paar MCR 702 rheometer. The measurements were carried out in the mode of sample compression between two plane-parallel plates with a constant load of 10 N in the temperature range from 25 to 350°C at a heating rate of 3 K/min in an argon atmosphere.

The properties of the resulting thermoplastic are shown in table 1.

Table 1

Properties of synthesized polyethersulfone PES-12

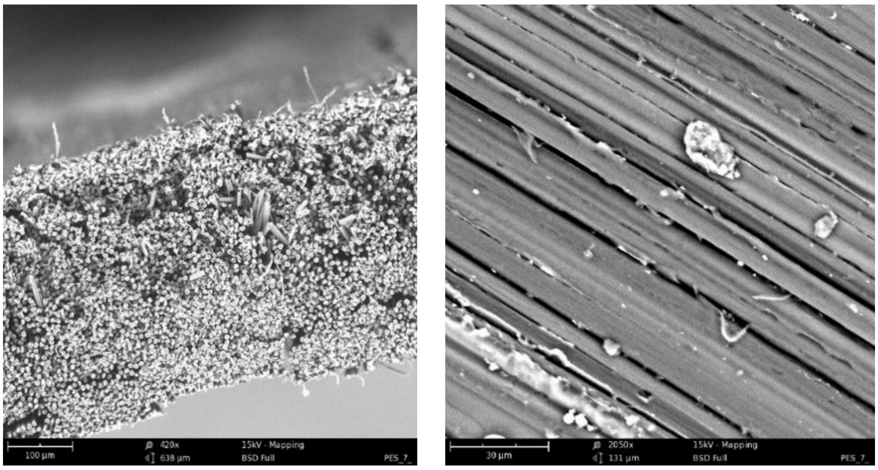
$\eta_{e.g.}$, dl/g	GPC results	$T_{glass.}$, °C	$T_{beginning\ of\ fluidity}$, °C
0.58	M_w = 74000–97000 g/mol, M_n = 24000–31000 g/mol, M_w/M_n = 3.0–3.1.	234	265–270

In addition, the objects of study were prepregs and composites consisting of a thermoplastic polymer matrix and a carbon unidirectional fabric manufactured by “G. Angeloni” (Italy), which is based on the carbon roving of the company “Torey” (Japan) brand 12KT700. To obtain electron microscopic images (SEM) of the obtained samples, a universal desktop scanning electron microscope with an integrated EMF system from Phenom ProX was used. To study the structure at the macrolevel, a high-resolution desktop X-ray microtomography of the SkyScan 1172 Bruker was used.

Results and discussion

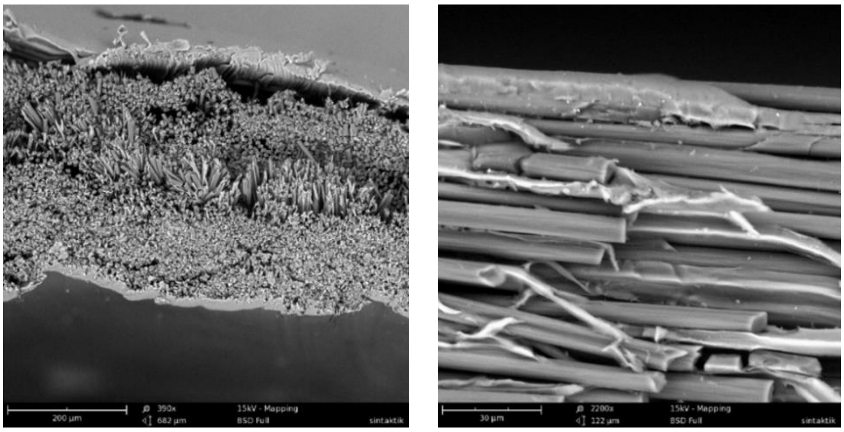
For the manufacture of thermoplastic prepregs based on carbon unidirectional fabric, a combined “solution-powder” method was used, including the following steps:

- impregnation of a carbon fabric fixed on an aluminum frame with a polymer solution of various concentrations (7, 12, or 17 % wt.) in dimethylformamide;
- ultrasonic treatment of carbon fabric in polymer solution for better impregnation of carbon fiber filaments;
- sprinkling of “wet” (sticky) prepregs with the calculated amount of polymer thermoplastic flakes to achieve the required “thermoplastic/filler” ratio in the composite = 40/60 % wt.;
- drying of prepregs in an oven at a temperature of 160°C for 48 hours to remove the residual solvent as completely as possible.



(a) (b)

Figure 3. *SEM images of a prepreg made by applying the 7 % solution of the polyethersulfone PES-12 in DMF: (a) cross-section; (b) longitudinal view of the sample*



(a) (b)

Figure 4. *SEM images of the prepreg were obtained by applying the 17 % solution of the polyethersulfone PES-12 in DMF: (a) cross-section; (b) longitudinal view of the sample*

Figures 3 and 4 show SEM images of the resulting prepregs. It can be seen that the polymer, which plays the role of an adhesive matrix, is more or less uniformly distributed among the fibers of the carbon fabric. However, it should be noted that the impregnation of carbon fabric with thermoplastic solutions does not lead to a continuous coating of elementary filaments, which is associated with the inertness of the carbon fiber surface, and the absence of polar groups, and their poor wettability by polymers.

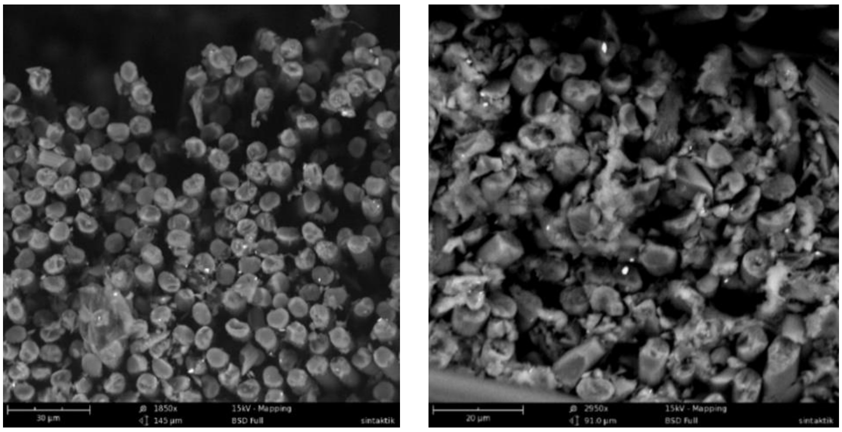
From the comparison of SEM images in figures 3 and 4, it can be seen that with an increase in the concentration of the impregnating polymer solution from 7 to 17 % wt. the amount of polymeric thermoplastic in the prepreg naturally increases.

To further obtain PCM, prepregs obtained by impregnation of 17 % PES-12 solutions were used. They were laid in a stack of 5 layers at an angle of 90^o and subjected to hot pressing at various temperatures from 250 to 350^{o}C and a pressure of 5 to 10 MPa. The conditions for obtaining PCM and their characteristics are shown in table 2.

Table 2

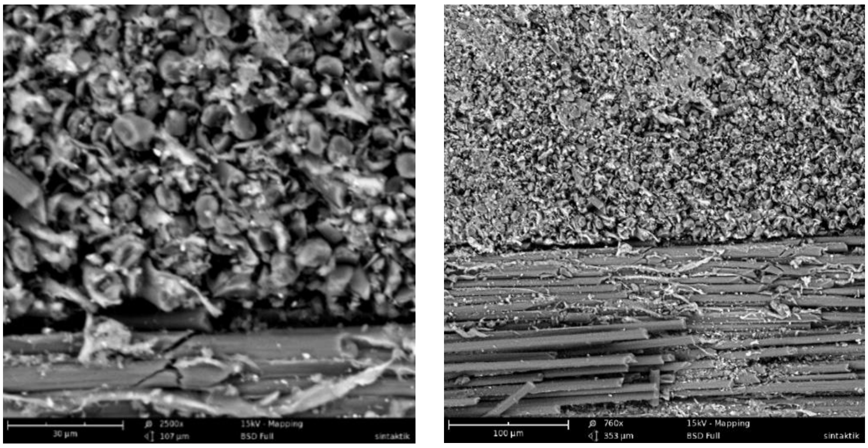
Pressing conditions and characteristics of the resulting PCM

PCM code	$T_{press.}$, ^{o}C	$P_{press.}$, MPa	$\tau_{press.}$, min	h, mm	Internal porosity, %
PCM-2	250	10	40	1.26	19.1
PCM-4	250	5	40	1.31	19.4
PCM-5	300	5	40	1.29	15.3
PCM-6	320	5	40	1.28	10.1
PCM-7	350	5	40	1.29	8.4



(a) (b)

Figure 5. *SEM images of the cross-section of PCM samples:*
(a) PCM-4 (pressing temperature 250^{o}C), (b) PCM-6 (pressing temperature 320^{o}C)



(a) (b)

Figure 6. *SEM cross-sectional images of PCM-7 samples: (a) increasing 30 µm, (b) increasing 100 µm*

On figure 5 shows SEM images of the cross-sections of PCM-4 and PCM-6 pressed at different temperatures. It can be seen that the composite sample obtained at 320^{o}C is better impregnated with the thermoplastic melt than the sample obtained at 250^{o}C. This is due to the lower viscosity of the polyethersulfone melt at higher temperatures, which allows the melt to better penetrate between the filaments.

An even more complete filling of the interfibre space with thermoplastic is observed in the PCM-7 composite obtained at a pressing temperature of 350^{o}C.

The tomographic study of composites made it possible to quantify the internal porosity of the samples, which is directly proportional to the degree of filling of the interfibre space with a thermoplastic. The value of internal porosity can be considered a quantitative parameter for assessing the quality of the PCM obtained. The smaller the value of internal porosity, the higher will be the indicators of the physicomechanical properties of the composite material.

As can be seen from the data in table 2, the value of the internal porosity of PCM depends on the pressing temperature more strongly than on pressure. PCM-2 and PCM-4 samples were pressed at the same temperature of 250^{o}C but different pressures. However, the values of their internal porosity are almost the same. At the same time, the value of internal porosity decreases by more than two times with an increase in the prepreg pressing temperature from 250^{o}C (for PCM-4) to 350^{o}C (for PCM-7).

Conclusion

1. In the laboratory of thermoplastics and composites at the Scientific and Educational Center "Composites of Russia" of BMSTU mastered the synthesis technology and developed polyethersulfone PES-12.
2. The structure of the synthesized polymer was confirmed by IR spectroscopy and gel permeation chromatography.
3. A combined solution-powder method for manufacturing prepregs based on a unidirectional carbon fabric and synthesized PES-12 has been developed.
4. Experiments were carried out on the manufacture of samples of carbon composites from thermoplastic prepregs by hot pressing using a mold.
5. The resulting carbon composites were studied by electron microscopy and tomography.

6. Regularities of changes in the internal porosity of composites depending on the temperature conditions of their pressing are revealed.
7. It has been established that the PCM pressing temperature must be at least 100°C higher than the glass transition temperature of the thermoplastic used.

Acknowledgments

The work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) based on educational institutions of higher education and scientific organizations (NTI Center “Digital Materials Science: New Materials and Substances” based on Bauman Moscow State Technical University) and with the support of the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. Kablov E.N. 2002 Aviation materials science: results and prospects Bulletin of the Russian Academy of Sciences 72(1) pp. 3–12.
2. Chukov N.A., Borodulin A.S., Kerefov T.O., Kharaev A., Kozlova E.E., Khashkhozheva R.R. 2020 Synthesis and properties of polyetheretherketones. International Journal of Pharmaceutical Research. 12. pp. 1040–1045.
3. Borodulin A.S., Kalinnikov A.N. 2020 Super engineering polyesters: Synthesis and performance characteristics. IOP Conference Series: Materials Science and Engineering 709(2). N 022038.
4. Kalinnikov A.N., Borodulin A.S., Kharaev A.M., Bazheva R.C., Balkarova S.B., Kharaeva R.A. 2019 Polyether-ketones based on 1,1-dichloro-2,2-di(3,5-dibromo-4-hydroxyphenyl) ethylene. Key Engineering Materials. 816. pp. 302–306.
5. Borodulin A., Kalinnikov A., Kharaev A., Shcherbin S. 2019 Aromatic polysulfone to create polymer materials with high resistance to frost IOP Conference Series: Earth and Environmental Science 302 (1). N 012062.
6. Borodulin A.S., Kalinnikov A.N., Bazheva R.C. at all. 2018 Synthesis and properties of aromatic polyethersulfones International Journal of Mechanical Engineering and Technology (IJMET) 9(13). P. 1109–1116.
7. Borodulin A.S., Kalinnikov A.N., Bazheva R.C. at all. 2018 Receipt and investigation of performance characteristics of super constructions polyesters International Journal of Mechanical Engineering and Technology (IJMET) 9(13). P. 1117–1127.
8. Borodulin A.S., Kalinnikov A.N., Kharaev A.M. at all. 2019 New Polymeric Binders for the Production of Composit International Conference on Modern Trends in Manufacturing Technologies and Equipment 2018 International Journal of Materials today: proceedings 11 (Issue P1) P. 107–3111
9. Nelyub V.A., Borodulin A.S. et al. 2018 Polyethersulfones with improved thermal properties Adchesives, sealants, technologies. No 7. pp. 15–20.
10. Borodulin A.S., Kalinnikov A.N. at all. 2019 New Polymeric Binders for the Production of Composit Materials Today: Procttdings 11. p. 139–143.
11. Borodulin A.S., Kharaev A.M., Kalinnikov A.N. at all. 2019 Synthesis and Perfomance Characteristics of Superstructure Polyesters Key Engineering Materials. 816. p. 307–311.

DOI: 10.15862/67MNNPK22-04

Storozhuk Ivan Pavlovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: Storozhuk-ip@inbox.ru

Orlov Maksim Andreevich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: oma@emtc.ru

Bogachev Vyacheslav Vladimirovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: VBogachev@emtc.ru

Kalinnikov Aleksandr Nikolaevich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: alexandr.kalinnikov@emtc.ru

Pavlukovich Nadezhda Gennad′evna
A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Moscow, Russia
E-mail: npavlukovich@emtc.ru

Polyurethane protective and anti-icing coating for structures for various purposes

Abstract. An effective protective and anti-icing material "Silafob" based on hydrophobic silane-containing polyurethane has been developed, which has good mechanical properties, abrasion resistance, high adhesion to metals, chemical resistance, and increased hydrophobicity. The effectiveness of the material has been tested on bench tests in high-speed dusty airflow and in the classical icing mode in Federal Autonomous Institution "Central Institute of Aviation Motors" (CIAM).

Keywords: anti-icing; silane-containing polyurethane; protective coating

Introduction

The creation of effective anti-corrosion, abrasion-resistant, and anti-icing coatings is an urgent and difficult to solve a scientific and practical problem. Corrosion and abrasive impact on structures for various purposes is a major global problem, which is fought with huge funds [1; 2]. Another, no less costly problem of mankind is the fight against icing [3; 4]. Ice fouling of structures for various purposes creates numerous problems associated with the safety of people, the safety of buildings, equipment, power lines, the safety of roads, airfields, aircraft, and ships, and significant costs for the elimination of ice deposits and emergencies [5–7]. These problems also exist in the oil and gas industry during the operation of pipelines and pipeline fittings [8–11].

As is known, polyurethanes, due to the high energy of intermolecular interactions between polar urethane groups, are among the most abrasive-resistant polymeric materials [12]. Along with this, polyurethanes have good chemical resistance, high adhesion to metals and other structural materials, and are durable, flexible, and frost-resistant. Therefore, on the basis of these polymers, various protective paintwork materials have been created and are actively used on an industrial scale. However, traditional polyurethane protective coatings are prone to ice fouling, therefore, the development of multifunctional polyurethane coatings, additionally endowed with anti-icing properties, is an actual direction of research work. Coatings based on such polyurethanes will protect structures not only from corrosion and abrasive wear but also from significant icing in the winter season, which will also contribute to the safety of equipment, extending its service life and facilitating work with it [7–11].

There are a number of traditional, so-called "active" ways to combat the formation of ice, including mechanical, in which the formed ice is destroyed as a result of a force impact on it; physical and chemical, in which special organic liquids and aqueous solutions of salts are used, which lower the freezing point of supercooled water drops or reduce the adhesive force of ice with the construction material; thermal, at which the protected surface is heated to the temperature of ice melting [5–7]. In recent decades, in connection with the development of polymer science, anti-icing polymer coatings have been actively developed and introduced around the world, which significantly reduces the adhesion of ice to the surface (passive method of protection), prevent its growth, and facilitate its removal [13–15].

The reason for the formation of ice is the sorption of water molecules on the surface of bodies and its ability to wet this or that material. At negative temperatures, water forms centers of crystallization, due to which there is active growth of ice. Therefore, in order to prevent icing, it is necessary to minimize water sorption by hydrophobizing the surface. On the other hand, it is necessary to choose a coating that would have low adhesion to the ice with long-term mechanical, chemical, light, and biological resistance. Coatings with the specified set of functional properties do not currently exist.

Along with increasing efficiency, a very important direction in the development of modern anti-icing coatings is to increase their service life under the influence of various types of erosion [16–19]. Currently, coatings with a service life of 15 years are considered good, depending on the operating conditions, systems with a durability of up to 25 years are used. Active work is being carried out to achieve the service life of coatings up to 40 years.

At present, the main types of polymer anti-icing coatings are based on the use of organosilicon and fluorine-containing polymers with low surface energy, which are known to have high hydrophobicity [20; 21]. In order to improve the performance properties and reduce the cost, various composite materials based on these polymers are being developed, including those with dispersed mineral fillers (silicon dioxide, titanium dioxide), and carbon fibers, carbon nanotubes, and other nanoadditives.

Based on new principles, superhydrophobic polymers are being developed, the properties of which are close to the properties of natural water-repellent systems present on the surface of lotus leaves, water strider legs, and butterfly wings. In total, the mechanism of repulsion of water and water drops is used by more than 200 species of plants (the lotus effect is well known) and various insects. This phenomenon is based on the use of hydrophobic substances in combination with a geometrically regular rough surface, which reduces the area of contact of the water-repellent surface with water [15; 16].

Materials according to the interaction of water with their surface are classified according to the wettability angle as follows: if the angle is less than 90^o, then the material is hydrophilic and easily wetted by water; from 90 to 150^o — the material is hydrophobic, that is, it is poorly wetted by water; above 150^o — the material is superhydrophobic, that is, water drops roll down into spheres, leaving no traces [15; 16]. The parameter of the roll angle from an inclined surface is considered by some researchers to be even more important for practical purposes than the wetting angle [19]. For good hydrophobic and superhydrophobic surfaces, the water droplet angle is between 2 and 10^o.

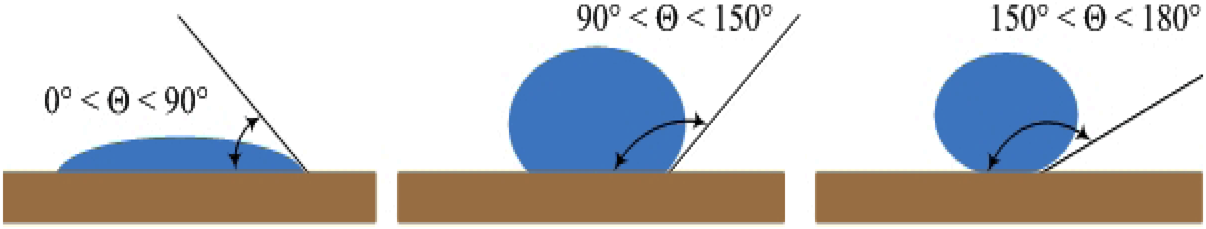


Figure 1. *Wetting angle and shape of water droplets. The maximum possible angle is 180^o*

Polydimethylsiloxane and its numerous derivatives, due to their lower cost compared to fluoroplastics, high hydrophobicity, elasticity, frost resistance, and biological inertness, are the basic materials for the development of modern passive anti-icing coatings [20; 21]. Recent works are devoted to the creation of various new compositions based on these polymers and the search for a synergistic effect when combining various mechanisms to reduce ice adhesion: achieving the maximum value of the wetting angle of the surface with water, minimizing the area of water contact by creating a pimpled surface, regulating the elastic deformation of the surface, using interfacial lubrication, filling with nanoparticles and microfibers [20].

The aim of our work was to develop a complex protective coating that combines anti-erosion, anti-corrosion, and anti-icing properties based on silane-modified polyurethane. As a result of the work, the Silafob sprayed material was obtained, strong and elastic film coatings based on which have high mechanical properties, wear resistance, hydrophobicity, adhesion to aluminum, steel, and polymer composite materials. Due to the water-repellent properties, barrier properties of the polymer in relation to oxygen and metal salts, electrical insulating properties that prevent the occurrence of electrochemical corrosion, the polyurethane coating works as a complex one, providing protection, against the erosive effects of high-speed airflow and icing in the presence of supercooled drops of water.

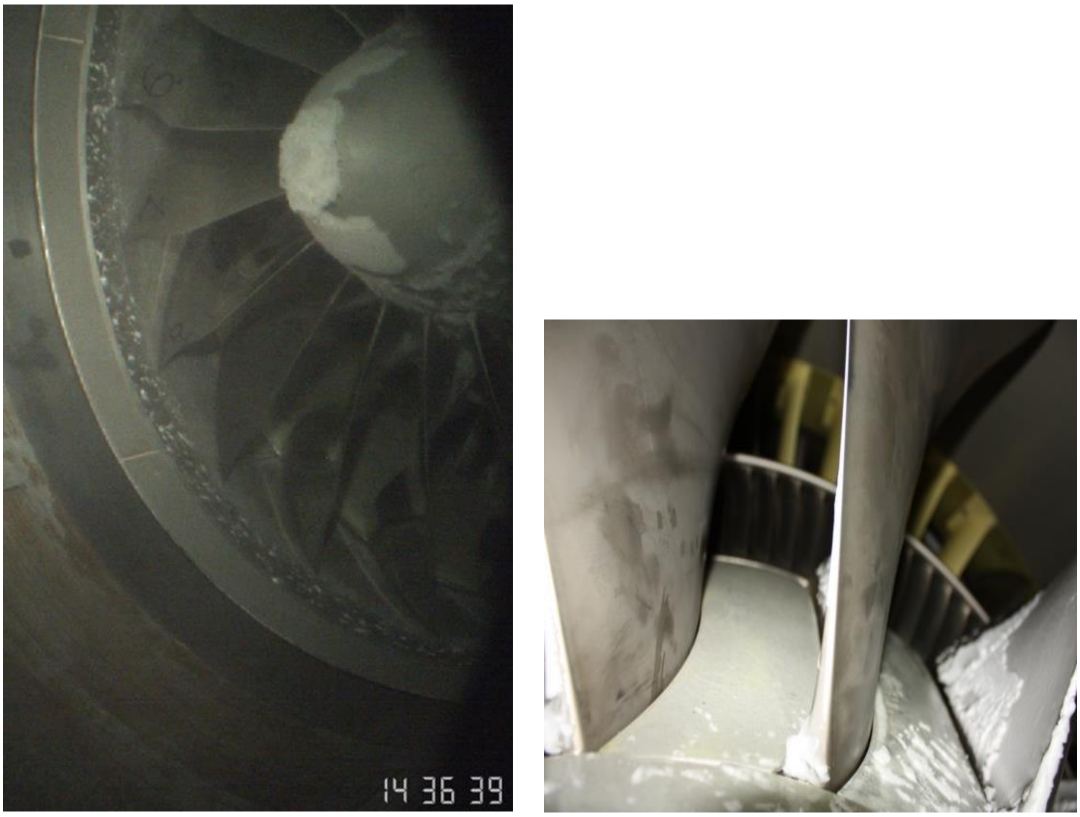
The latter is of considerable interest to the aircraft industry, where various energy-consuming and expensive anti-icing systems are used to protect aircraft from icing [20; 21]. For example, 30 % of the power of the onboard generator is spent on the thermal removal of an ice layer on the rotor blades of a helicopter, and additional fuel is consumed. The deposition of ice on the inner surface of the air intake of an aircraft engine often leads to its damage, which requires additional costs for its repair. Ground icing of aircraft in conditions of variable temperatures, accompanied by precipitation, fog, and high humidity, causes a lot of problems, requires the use of anti-icing treatment and other measures, failure to comply with this leads to catastrophic consequences.

Results and discussion

The Silafob anti-icing composition developed by us, applied to the parts of the fan of a turbofan engine, passed the bench tests of the CIAM when simulating a flight at an altitude of 6100–7600 m with intermittent icing conditions at temperatures of -20 and -30^{o}C. The airflow rate was about 400 km/h (3.3 max), the water content of the flow was from 0.2 to 1.7 g/m^3, and the fan speed was up to 3500 rpm. After the rotation stopped, it was found that a large build-up of ice formed on the fan parts (spinner fairing and blades), without anti-icing coating (fig. 2). On the surface of fan parts coated with the composition developed by Bauman Moscow State Technical University (BMSTU) there is practically no ice (fig. 3).

Figure 2. *Fan without anti-icing coating after testing*

Figure 3. *Propeller spinner coated with the Silafob after testing*



(a) (b)

Figure 4. *Platform and fan blades coated with the Silafob after testing*

Conclusion

The anti-erosion and anti-icing material "Silafob" showed good results in bench tests for the wear of coatings on metal in a dusty air stream and for freezing of a turbojet fan under conditions of classical icing in an environment of liquid supercooled water drops. It is planned to continue the work begun in order to assess the durability and effectiveness of the coating, its maintainability, and stability in various aggressive environments, and on various structures, including pipeline valves in the oil and gas industry.

Acknowledgments

The work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (NTI Center "Digital Materials Science: New Materials and Substances" on the basis of Bauman Moscow State Technical University) and with the support of the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. Angal R. Corrosion and corrosion protection: textbook: per. from English. — Dolgoprudny: Publishing House “Intellect”, 2014. — 344 p.
2. Semenova I.V. Corrosion and corrosion protection. — Moscow: Fizmatlit, 2002. — 232 p.
3. Alekseev V.R. Icing and ice processes. Questions of terminology and classification / Novosibirsk: Nauka, 1978. — 188 p.
4. Alekseev V.R. Icing. — Novosibirsk: Nauka, 1987. — 256 p.
5. Levchenko I.I. Diagnostics, reconstruction and operation of overhead power lines in icy areas. M.: Publishing house MPEI, 2007. — 494 p.
6. Merentsova G.S., Medvedev N.V. The formation of icing and the fight against them onroads and artificial structures. — Bulletin of Science and Education of the North-West of Russia, 2017, V. 3, No. 3. — p. 1–7.
7. Bogorodsky V.V., Gavrilo V.P., Nedoshivin O.A. Ice destruction. Methods, technical properties. — L., Gidrometioizdat, 1983. — 232 p.
8. Borodavkin P.P., Berezin V.L. Construction of main pipelines. — M.: Energy Press Publishing House LLC, 2011. — 480 p.
9. Mustafin F.M., Bykov L.I., Gumerov A.G., and other. Industrial pipelines and equipment. — M.: Nedra, 2004. — 662 p.
10. Mustafin F.M., Bykov L.I., Vasiliev G.G. and other. Construction technology of oil and gas pipelines. — Ufa: Oil and gas business, 2007. V. 1. — 632 p.
11. Mustafin F.M., Bykov L.I., Gumerov A.G. and other. Corrosion protection of pipelines. Vol 2. — St. Petersburg.: Nedra LLC, 2007. — 708 p.
12. Sonnenstein M.F. Polyurethanes. Composition, properties, production, application. Ref. from English. — St. Petersburg: TsOP Professiya, 2018. — 576 p.
13. Boinovich L.B., Emelianenko A.M. Hydrophobic materials and coatings; principles of creation, properties and application // Uspekhi khimii. 2008, V. 77, No 7. — p. 619–638.
14. Boinovich L.B. Superhydrophobic coatings — a new class of polyfunctional materials // Bulletin of RAS. RAS. 2013, V. 8, No 1. — p. 10–22.
15. Wang Y., Liu J., Li M., Wang Q., Q Chen. The icephobicity comparison of polysiloxane modified hydrophobic and superhydrophobic surfaces under condensing environments. — Applied Surface Science 385, p. 472–480.
16. Solovyanchik L.V., Kondrashov S.V., Nagornaya V.S., Melnikov A.A. Features of obtaining anti-icing coatings. Proceedings of VIAM, 2018, No 6(66). — p. 77–98.

17. Kuznetsova V.A., Shapovalov G.G. Development trenda in the field of erosion-resistant coatings. Proceedings of VIAM, 2018, No 11(71). — p. 74–85.
18. Zhuo Y., Xiao S., Amirfazli A., He J., Zhang Z. Polysiloxane as icephobic materials — The past, present and the future. — Chem. Eng. J., 2021, № 405. 127088.
19. He Z., Zhuo Y., He J., Zhang Z. Design and preparation of sandwich-like polydimethylsiloxane (PDMS) sponges with super-low ice adhesion, Soft Matter 14 (2018) 4846–4851.
20. Kirillov V.N., Efimov V.A., Shvedkova S.K., Nikolaev E.V. Study of the influence of climatic factors and mechanical loading on the structure and mechanical properties of PCM // Aviation materials and technologies. 2011. No 4. p. 41–45.
21. Klemenko G.P., Prikhodko Yu. M., Puzyrev L.N., Kharitonov A.M. Modeling of aircraft icing processes in agroclimatic tubes // Thermophysics and Aeromechanics. 2008. V. 15. No 4. p. 563–572.

DOI: 10.15862/67MNNPK22-05

Storozhuk Ivan Pavlovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: Storozhuk-ip@inbox.ru

Orlov Maksim Andreevich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: oma@emtc.ru

Polikarpova Irina Aleksandrovna
Bauman Moscow State Technical University, Moscow, Russia
E-mail: IPolikarpova@emtc.ru

Kalinnikov Aleksandr Nikolaevich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: alexandr.kalinnikov@emtc.ru

Pavlukovich Nadezhda Gennad′evna
A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow, Russia
E-mail: npavlukovich@emtc.ru

Polymer protective coatings for pipes and pipeline fittings in the oil and gas industry

Abstract. The main types of polymer protective coatings used for anti-corrosion and anti-icing protection of pipes and pipeline fittings in the oil and gas industry are considered. The results of tests of a self-developed polyurethane wear-resistant coating PU-633 are presented.

Keywords: polymer protective coatings; anti-corrosion; anti-icing; pipeline; polyurethane

Introduction

The oil and gas industry, like all other industries, suffers greatly from the consequences of corrosion destruction of process and transport equipment, and this is due to the increased chemical activity of the media with which oil and gas production, treatment, transportation and processing enterprises operate [1–7].

Corrosion damage and erosion-mechanical wear are the main reasons for reducing the life of equipment. Equipment failures caused by corrosion account for up to 30 % of all accidents in the oil and gas industry. Moreover, 65 % of the total number of failures for this reason is due to external corrosion, 28 % — to internal and 7 % — to other reasons [8; 9]. Types of corrosive effects of field media can be classified as follows [1; 2; 10; 11]:

- Sulfide (under the action of H_2S) corrosion cracking of metal structure elements operating under pressure.
- Local carbonate corrosion (CO_2).
- Local carbonate corrosion by sulfides (CO_2+H_2S).
- Carbonate corrosion by chlorides (CO_2+Cl–).
- Biocorrosion (biocenosis).

Modern pipelines are quite complex engineering systems, since, in addition to main pipes, they include fittings (tees, bends, couplings, transitions, etc.), shut-off and control valves (taps, gate valves, plugs, valves, gates, etc.), pumping and compressor equipment, a network of process pipelines, and much more, which must also be reliably protected from corrosion [5–7].

According to their functional purpose, pipeline fittings are divided into the following types:

- Shut-off, which provides complete blocking of the flow in the pipes. The demand for this type of fittings is the greatest and its market share in the considered products is more than 80 %.
- Regulating, with the help of which they control and regulate the flow of the working medium, its temperature, pressure, mixture composition and concentration of functional substances. Throttle valves, which also belong to control valves, are used to reduce pressure on the transported liquid. Its role is especially important at significant pressure surges.
- Shut-off and control, which combines the functions of overlapping and flow control.
- Emergency shut-off eliminates the destructive effect on the pipeline under non-standard technological conditions by blocking the protected area from the rest of the system.
- Safety. In an emergency, it opens to release excess pressure from the structure or part of the transported substance.
- Mixing, which is used to distribute flows or mix them.
- Phase dividing fittings are used to separate working media depending on their phases and states.

The tasks related to the protection of main pipes from external soil corrosion are mainly solved by using polyethylene, polyamide, polyurethane foam, polyurethane anticorrosion protection [12–16]. Heat-shrinkable polymer tapes are used to insulate welded joints of pipes, which are applied to a liquid epoxy primer, and usually, the design of the protective coating of welded joints is similar to the design of a three-layer polyethylene coating of pipes. At the same time, modern materials and technologies for protecting the inside of pipes and external surfaces of other equipment and structures with polymer coatings currently do not always meet the requirements.

Today, the most serious production problems in the industry are associated with the application of external anti-corrosion coatings on pipeline elements with a complex configuration, primarily on fittings and fittings. According to the requirements of GOST R 51164-98 "Main steel pipelines. General requirements for corrosion protection" (clause 4.6) and other specialized GOSTs, insulating coatings of fittings and welded pipe joints must correspond in their characteristics to the main coating of pipes made in the factory [17–22].

The wide possibility of modifying materials through the use of special fillers and additives makes it possible to create paintwork materials for various, including the most severe, operating conditions. In particular, coatings based on epoxy, epoxyurethane and urethane materials in the form of their solutions in organic solvents have recently been widely used for internal insulation of pipes, external painting of tanks and other metal structures. As a rule, coatings are applied using pneumatic or airless sprayers. Figure 1 shows such coatings up to 300–400 μm thick can also be applied in field (route) conditions. To apply thick coatings (1.5–2.5 mm), a multi-layer application of anticorrosive agent is required with intermediate drying of each layer and factory working conditions that provide for the protection of personnel and the environment from solvent vapors.

The accumulated domestic and foreign experience shows that for the factory protective insulation of shut-off and other valves, fittings, bends, etc. Solvent-free two-component polyurethane and epoxy-polyurethane systems are most suitable when applied using the "hot" airless spray method at an "A+B" reaction mixture temperature of 50–70^{o}C (depending on the chemical nature and composition of the mixture). These systems make it possible to apply sufficiently thick coatings, which, along with factory-made polyethylene coatings, to the greatest extent meet the technical requirements and are able to provide long-term protection of metal structures from corrosion [1–4].

Figure 1. *Spraying of anti-corrosion polyurethane field coating*

The technology for applying two-component polyurethane and epoxy-polyurethane coatings consists of the following stages: abrasive cleaning of the surface, application of an epoxy primer, drying of the primer, spraying of an external polyurethane or epoxy-urethane coating, curing of the coating. Coatings should be applied to the cleaned dry surface no later than 2–3 hours after the completion of the cleaning process at a temperature not lower than 5^{o}C and air humidity not more than 80 %. An important requirement of the technology under consideration is the deposition of layers of the same material according to the "wet on wet" scheme without intermediate drying of the applied layers, which ensures a high cohesive bond between the layers of the protective material. In the case of using a sprayed epoxy primer, the outer polyurethane coating layer is applied only after the completion of the curing process of the adhesive sublayer, after about 4–25 hours.

A good alternative to the above protective coatings is epoxy powder paints which provide heat resistant, water resistant and cathodic flake resistant coatings. However, they are more expensive, they are applied only in the factory, they have low impact resistance, especially at low temperatures, the technology of their application is more complicated and involves heating parts to temperatures of 220–240^{o}C, which requires significant energy costs.

Over the past 15 years, the following imported and domestic materials have been successfully used as external anti-corrosion coatings for pipeline valves: UP 1000 / FRUCS 1000 A epoxy urethane (Kawakami Paint, Japan); polyurethane coatings "PROTEGOL UR-Coating 32–55" ("Goldschmidt TIB Gmbh", Germany); COPON HYCOTE 165 (E. Wood, UK); PUR STOP 2000 (Ernesto Stoppani, Italy); "SIGMALINNING 7655" ("Sigma Coating BV", the Netherlands); "SCOTCHKOTE 352 HT" ("3 M", USA); epoxy-polyurethane coating "BIURS" CJSC ("Neftegazizolyatsiya", Russia); coating based on polyurea "Carboflex" (OOO Polibent, Russia) and a number of other experimental materials. To increase the resistance of coatings to cathodic peeling at elevated operating temperatures (60–80^{o}C), a liquid two-component epoxy primer, Protegol EP-Primer 6, is used [1–4; 23].

The main criteria for the selection of anticorrosive polymeric materials for introduction into production are [1–4]:

- maximum service life;
- high coating efficiency in a wide range of operational loads;
- manufacturability and safety of coating application;

- the stability of the quality of anti-corrosion materials, the availability of modern production of these materials with a strict control system for raw materials and finished products;
- the optimal ratio of price and quality of the material.

The effectiveness and durability of anti-corrosion coatings is extremely important to achieve the maximum duration of the overhaul period, since for the overhaul of the pipeline system it is necessary to decommission the equipment, which leads to enormous economic losses. Therefore, already at the design stage of the construction of new facilities of the pipeline complex, the most effective anti-corrosion protection is selected, which will last for the entire service life of the equipment (15 years or more) and will be maintained in working condition only through prompt local cosmetic repairs.

Today, for the external protection of equipment surfaces, multi-layer coatings consisting of epoxy primers and weather-resistant finishing polyurethane enamels are most in demand. This combination provides reliable and long-term anti-corrosion protection, as well as a good appearance of structures for the entire service life.

In the case of surface port facilities of oil and gas terminals located in the coastal sea zone and offshore drilling platforms, epoxy systems and tread zinc-containing epoxy and zinc ethyl silicate primers are used in combination with finishing polyurethane enamels. It should be added that polyorganosiloxane materials protect surfaces from abrasion, abrasive wear, and icing of structures [23; 24].

To protect the internal surfaces of equipment, epoxy materials are most often used, along with this, phenolic, epoxyphenolic, novolac, polyamide, polyurethane and polyethylene coatings are also used. In particular, during the construction of the Turkish Stream gas pipeline, a composition based on Rilsan PA-11 was used as an internal and external anticorrosive powder protection of pipes [16]. However, there are still a lot of unresolved problems in this area of work, since the inner surfaces of pipes and pipeline fittings are exposed to a variety of aggressive and abrasive media. In particular, it is necessary to improve the chemical resistance of materials, adhesion to steel, their barrier properties, which reduce the rate of under-film corrosion of metal, resistance to erosive wear, sticking of paraffins and mineral salts contained in carried media.

A literature analysis shows that modern protective materials for the oil and gas industry should be not only anti-corrosion, but also multifunctional, that is, combine several properties at once, such as, for example, abrasion resistance, chemical resistance, light resistance, frost resistance, heat resistance, antistatic, anti-icing effect, flame retardant functions, etc.

The aim of present work in the field of creating functional polymeric materials was the development of protective sprayed polyurethane coatings with high abrasive wear resistance, chemical resistance and resistance to swelling in hydrocarbon media.

Results and discussion

The two-component polyurethane PU-633 developed by BMSTU with a Shore hardness of 80A showed high abrasion resistance when tested in a high-speed air flow with dust particles of quartz sand, has a relatively small swelling in oil (12 % wt., Bashkir oil, 24 days at 20^{o}C), retains high strength in the swollen state, exhibits high adhesion to steel, cast iron, aluminum and a number of other materials. Spraying concentrated solutions of the polymer and its compositions with finely dispersed fillers in mixed solvent P4 makes it possible to obtain elastic coatings with a layer thickness of 100 to 300 μm. Without the addition of solvents, PU-633 can be used as a filling benzene-oil-resistant compound with heat resistance in the cured state up to +150^{o}C and frost resistance of -50^{o}C. Due to the combination of the above properties, polyurethane PU-633 can be used as a repair, anti-corrosion and abrasive-protective composition in the oil and gas industry, in particular, to protect pipeline valves with complex surface geometry.

Conclusion

The development of modern multifunctional and effective polymeric protective coatings for pipes and pipeline fittings used in the oil and gas industry is an extremely important scientific and applied task. The solution of even individual specific problems will make it possible to save significant funds now spent on the repair, re-insulation and replacement of pipes, fittings, equipment and structures in the oil and gas industries. The developed sprayed and poured polyurethane composition PU-633 is promising for use as a factory and pipeline protective material for pipeline valves in the oil and gas industry.

Acknowledgments

The work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (NTI Center "Digital Materials Science: New Materials and Substances" on the basis of Bauman Moscow State Technical University) and with the support of the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. Aginei R.V., Aleksandrov Yu.V. Topical issues of corrosion protection of long-term exploited main oil and gas pipelines. — St. Petersburg: Nedra, 2012. — 394 p.
2. Corrosion and protection of metals in the oil and gas industry. Ed. Gareeva A.G. — Ufa: Gilem, Bashk. Encycl., 2016. — 352 p.
3. Mustafin F.M., Kuznetsov M.V., Bykov L.I. Construction of pipelines. Corrosion protection. Volume 1. — Ufa: "Monograph", 2004. — 609 p.
4. Mustafin F.M., Bykov L.I., Gumerov A.G. Corrosion protection of pipelines. Volume 2. — St. Petersburg: Nedra LLC, 2007. — 708 p.
5. Borodavkin P.P., Berezin V.L. Construction of main pipelines. — M.: Energy Press Publishing House LLC, 2011. — 480 p.
6. Mustafin F.M., Bykov L.I., Gumerov A.G. etc. Industrial pipelines and equipment. — M.: Nedra, 2004. — 662 p.
7. Mustafin F.M., Bykov L.I., Vasiliev G.G. etc. Technology of construction of gas and oil pipelines. — Ufa: Oil and gas business, 2007. Vol. 1. — 632 p.
8. Safonov E.N., Nizamov K.R., Grebenkova G.L., Garifullin I.Sh. The effectiveness of the use of anti-corrosion coatings at the facilities of OAO ANK BASHNEFT. — Oil Industry, 2007, No. 4, pp. 71–73.
9. Fedin D.V., Barkhatov A.F., Vazim A.A. Comparative analysis of the economic efficiency of methods for improving the operational reliability of field pipelines. Bulletin of the Tomsk Polytechnic University, 2012, Vol. 320, No. 6. — p. 32–35.
10. Borisenkova E.A. Causes of premature failure of wedge gate valves in oil fields of the Russian Federation. — 2015, No. 7(27). — Pp. 46–48.

11. Tyusenkov A.S., Cherepashkin S.E. Causes of corrosion of oilfield tubing and technological increase in their durability // Science-intensive technologies in mechanical engineering — 2016, No. 6. — P. 11–16.

12. Pipeline transport of oil. Ed. CM. Weinstock. — M.: OOO "Nedra-Business Center", 2006. — 621 p.

13. Mazur I.I., Ivantsov O.M. Safety of pipeline systems. — M.: Nedra, 2004. — 700 p.

14. E.A. Borisenkova, E.N. Sachkova, and A.V. Ioffe, “On the mechanism of microbiological corrosion of oilfield equipment steels under operating conditions and in the laboratory”, At. // Bulletin of SamSTU, 2013, No. 3(39). — Pp. 99–104.

15. Kharisov R.A., Khabirova A.R., Mustafin F.M., Khabirov R.A. The current state of protection of pipelines from corrosion by polymer coatings. — Oil and gas business, 2005, — 26 p.

16. Ivantsova N. The use of modern materials and technologies to protect oil and gas equipment from corrosion: novelty, relevance, efficiency. Exposition Oil and Gas. — 2008. — No. 3. — Pp. 83–85.

17. GOST R 51164-98. Main steel pipelines. General requirements for corrosion protection. — M.: IPK "Standards Publishing House", 1999. — 42 p.

18. GOST 13846-89 Xmas tree and injection fittings. Typical schemes. Basic parameters and technical requirements for the design.

19. GOST 31448-2012. Steel pipes with protective outer coatings for main gas and oil pipelines. Specifications. — M.: Standartinform, 2013. — 19 p.

20. GOST 9.602-2005. Unified system of protection against corrosion and aging. Underground structures. General requirements for corrosion protection. — M.: Standartinform, 2006. — 47 p.

21. GOST R 9.905-2007. Unified system of protection against corrosion and aging. Methods of corrosion tests. General requirements. — M.: Standartinform, 2007. — 17 p.

22. GOST 34667.1-2020 (ISO 12944-1:2017). “Paint materials. Protection of steel structures against corrosion by means of paint and varnish systems. Part 1.

23. Protasov V.N. Theory and practice of using polymer coatings in equipment and facilities of the oil and gas industry. — M.: Nedra, 2017. — 373 p.

24. Heidersbach R. Corrosion protection and metallurgy of equipment for oil and gas production. Per. from English. ed. Khutoryansky F.M. — St. Petersburg: TsOP "Professiya", 2014 — 400 p.

DOI: 10.15862/67MNNPK22-06

Stoyanova Margarita Vasil′evna
Bauman Moscow State Technical University, Moscow, Russia
E-mail: MStoyanova@emtc.ru

Novikov Andrey Dmitrievich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: nad@emtc.ru

The engineering rent specifics assessment for engineering industrial companies in the field of digital materials science

Abstract. Turning to engineering industrial companies engaged in the production of new materials and digital materials science, the customer wants to get high-quality work, the result of which will be a successfully implemented project in accordance with the budget and deadlines that meets the set indicators and generates the planned profit amount. However, the cost of engineering in the Russian, as well as in the world market, is significant, and the positive effect presence from the engineering industrial companies work use is not always obvious and transparent. At first glance, it seems that the engineering industrial companies' involvement due to the high cost of its work increases the total costs of the customer company. However, modern researchers note the emergence of additional income from the customer company as a result of using the engineering industrial companies' resources, because they have special competencies that allow them to implement complex projects in the field of digital materials science.

Keywords: engineering rent; industrial company; manufacturing

Introduction

The field of digital materials science is becoming an integral part of modern industry. One of the digital materials science flagships is composite materials, which are actively spreading in all areas of technology due to the advantages they provide in comparison with metals [9]. Thus, glass-reinforced plastics compare favorably in corrosion resistance, carbon-reinforced plastics — in specific rigidity, and organoplastics — in specific strength. However, for many traditional industries, the transition to composite structures seems to be an almost impossible task, because. no competencies, testing and analytical base. To solve this problem, they turn to engineering industrial companies [11].

Engineering industrial companies (EIC) inherently implement processes related not only to the production, marketing, financial and logistics support, but also carry out pre-project work, design, preparation and production organization based on technologies and equipment developed for the customer, installation and commissioning of production and technological systems [5]. Therefore, EIC, at the moment, is understood as an enterprise that performs various engineering and economic works related to design and production based on technologies, equipment and engineering systems developed for the customer. In the context of the digital materials science field, the projects implementation made of new materials requires interdisciplinarity, a constant transition from engineering calculations to testing and vice versa, taking into account many parameters due to the relationship of product geometry, material characteristics and production technology [3]. In this regard, it is rational to transfer the composite structures designing process to engineering industrial companies. At the same time, it is important for the customer company to understand what benefits the transfer of the EIC design process will bring to it, and for this it is necessary to determine the level of engineering rent [1; 2].

Factors affecting the engineering rent emergence

The engineering rent emergence for companies in the field of digital materials science is associated with a number of factors, the main of which are:

- use of the advantages determined by the work experience availability in the field of digital materials science and competencies at each stage of the product life cycle from new materials;
- an integrated approach application, which is integral to the products design made of new materials;
- EIC has a high organizational and technological level and the possibility of its improvement;
- suppliers and contractors network presence.

It is the combined effect of these causes that creates a synergy effect that positively affects the overall positive effect of the new materials introduction in structures. However, the literature analysis showed that at the moment there is no formalized approach to the engineering rent calculation [8].

Since most projects in the field of digital materials science have a long implementation period, the time factor must be taken into account when estimating additional income. One of the most common project evaluation indicators that take into account the time factor is the amount of NPV (net present value) [8]. Taking into account the above definition of engineering rent (ER) and the specifics of its occurrence, it is rational to calculate ER as the difference between the project NPV with the involvement of EIC (NPV_{eng}) and the NPV of a project without its involvement.

$$ER = NPV_{eng} - NPV_0 \tag{1}$$

It is well known that NPV is calculated using forecasted cash flows using the following formula:

$$NPV = \sum_{i=1}^{N} \frac{NCF_i}{(1+r)^i} - \sum_{i=1}^{N} \frac{Inv_i}{(1+r)^i}, \tag{2}$$

where NCF_i — net cash flow for the i-th period;

Inv_i — investments at the i-th calculation step;

r — discount rate;

N — calculation horizon.

For the purpose of detailing and subsequent analysis, we represent formula (2) in the following form:

$$NPV = \sum_{i=1}^{N} \frac{(1-d_н)(P_i V_i - VC_i - FC_i - CI_i - O_i)}{(1+r)^i} - \sum_{i=1}^{N} \frac{Inv_i}{(1+r)^i}, \tag{3}$$

where $d_н$ — income tax rate;

P_i — customer's product made of new materials price;

V_i — product made of new materials sales volume;

VC_i — variable costs in the cost price;

FC_i — fixed costs;

CI_i — amounts paid as interest on a loan;

O_i — other expenses related to the financial result.

Practical experience and analysis of relevant literature showed that the source of engineering rent is the following factors:

- project implementation period;
- risk component [5];
- engineering and economic work quality;
- EIC business reputation.

The impact of attracting EIC on project performance indicators

Use of organizational and technological resources and engineering competencies [4] allows you to parallelize many processes and thereby reduce the pre-investment and investment stages, which in turn allows the customer company to quickly enter the operational phase and start making a profit [12]. Hence $N_{eng} < N_0$.

Thus, the positive effect of reducing the project implementation period is observed both at the investment and operating stages [10].

- At the operational stage, the fixed costs *FC* and the amounts paid in the form of interest on the loan a_i are reduced.
- At the investment stage, investment *Inv* costs are reduced.
- Also, reducing the project implementation period in the field of digital materials science reduces the discount rate, since with a shorter period, the risks are also less.

The final impact on the NPV of the project can be calculated using the formula (4):

$$NPV = \sum_{i=1}^{N} \frac{(1-d_н)(PV_i - VC_i - (1-k_{cp})FC_i - (1-k_{cp})CI_i - O_i)}{(1+(1-k_{cp})r)^i} - \sum_{i=1}^{N} \frac{(1-k_{cp})Inv_i}{(1+(1-k_{cp})r)^i}, \tag{4}$$

where k_{cp} — the project implementation period influence coefficient.

Ceteris paribus, a project with a shorter implementation period has a higher NPV value, thus, there is a component of engineering rent associated with the project implementation period $N\text{-}ER_N$.

It is also necessary to classify project risks that are taken into account when calculating NPV. In general, project risks can be divided into external and internal.

Internal risks include risks associated with [7]:

- Enterprise personnel — $R_{кадры}$ (qualified personnel shortage risk). This block of risks is associated with the qualifications of the staff and the management decisions taken, leading to an increase in variable costs *VC* and fixed costs *FC*.
- Technological processes — $R_т$ (production risk). This block of risks is associated with breakdowns, inept handling of equipment, negligence, equipment failure, etc., leading to an increase in fixed costs *FC* of the enterprise and unforeseen expenses taken into account in O (other expenses related to the financial result).
- Enterprise cash — $R_д$ (currency risk, inflation risk, credit risk). This block of risks is associated with the available and attracted funds of the enterprise, changes in exchange rates, changes in the loan rate, etc., which increases variable costs *VC*, fixed costs *FC*, amounts paid in the form of interest on a loan *Cl*, as well as other expenses, related to the financial result *O*.

External risks include risks associated with:

- suppliers — $R_п$ (supply disruption risk, fraud, transport, commercial, trade risks). This block of risks leads to an increase in fixed costs *FC* of the enterprise and unforeseen expenses taken into account in *O* (other expenses related to the financial result);
- competitors — $R_к$ (competitiveness risk). This block of risks leads to a decrease in prices *P* and sales volumes *V*;
- natural disasters — $R_{сб}$. This block of risks leads to an increase in the amount of unforeseen expenses taken into account in *O* (other expenses related to the financial result);
- buyers — $R_{пк}$ (commercial, trading risks, fraud risk) This block of risks leads to a decrease in prices *P* and sales volumes *V*.

The impact of risks is taken into account not only when forecasting cash flows in a certain period of time NCF_i, but also when calculating the discount rate r. Since the risk component is taken into account in its calculation ($r_{ang} < r_0$). Thus, it is necessary to separately highlight the risk of an increase in the discount rate $R_{диск}$.

The total impact of the above risks on the project NPV can be calculated using the following formula:

$$NPV = \sum_{i=1}^{N} \frac{(1-d_н)(R_к R_{пок} P_i V_i - R_{кадры} R_д VC_i - R_{кадры} R_m R_д R_п FC_i - R_д CI_i - R_m R_д R_п R_{сб} O_i)}{(1+R_{диск} r)^i} - \\ -\sum_{i=1}^{N} \frac{Inv_i}{(1+R_{диск} r)^i} \quad (5)$$

Thus, for each element of formula (5), one can single out its own risk coefficient.

$$NPV = \sum_{i=1}^{N} \frac{(1-d_н)((1-RR_2)(1-RR_3)P_i V_i - (1-RR_4)VC_i - (1+RR_5)FC_i - (1+RR_6)CI_i - (1+RR_7)O_i)}{(1+(1-RR_1)r)^i} - \\ -\sum_{i=1}^{N} \frac{Inv_i}{(1+(1-RR)_1 r)^i}, \quad (6)$$

where RR_1 — discount rate increase risk factor; RR_2 — price reduction risk ratio; RR_3 — reduction risk ratio; RR_4 — risk factor for increasing variable production costs; RR_5 — risk factor for increasing fixed production costs; RR_6 — loan repayment risk ratio; RR_7 — fixed cost risk factor.

EIC, having broad competencies and accumulated experience, also has databases on possible risks, the likelihood of their occurrence and the magnitude of potential damage. Thus, the risks impact on the project implementation in the field of digital materials science with the involvement of EIC is much less than on a project without its participation. Consequently, there is a component of engineering rent associated with a reduction in project risks ER_{RR}.

In the process of implementing a project in the field of digital materials science, EIC, having accumulated knowledge and competencies, selects the best technologies and equipment in terms of technical and economic characteristics, quality and costs.

Thus, a positive effect from the choice of engineering solutions is observed both at the investment and operating stages.

- At the operational stage, prices *P* and sales volumes *V* increase, while variable *VC* and fixed costs *FC* decrease.
- At the investment stage, investment costs are reduced *Inv*.

The final impact on the NPV of the project can be calculated using the formula (7):

$$NPV = \sum_{i=1}^{N} \frac{(1-d_н)((1+k_{тех})P_iV_i - (1-k_{тех})VC_i - (1-k_{тех})FC_i - CI_i - O_i)}{(1+r)^i} - \sum_{i=1}^{N} \frac{(1-k_{тех})Inv_i}{(1+r)^i}, \quad (7)$$

where $k_{тех}$ — engineering solutions level influence coefficient on the elements of the project NPV.

Thus, there is a component of engineering rent associated with the level of engineering solutions $ER_{тех}$.

The presence of an EIC image, positive business reputation and connections in banks can help to obtain project financing on more favorable terms.

- The amounts paid as interest on credit CI decrease, the discount rate r decreases;
- Increase in sales V.

The final impact on the NPV of the project can be calculated using the formula (8):

$$NPV = \sum_{i=1}^{N} \frac{(1-d_н)((1+k_{им})P_iV_i - VC_i - FC_i - (1-k_{им})CI_i - O_i)}{(1+(1-k_{им})r)^i} - \sum_{i=1}^{N} \frac{Inv_i}{(1+r)^i}, \quad (8)$$

where $k_{ким}$ — coefficient of the company's image on the project NPV elements.

Thus, there is a component of engineering rent associated with the image and business reputation of EIC — $ER_{ким}$.

The influence of all 4 factors on the project NPV is reflected in the formula (9).

$$NPV_{eng} = \sum_{i=1}^{N} \frac{(1-d_н)((1+k_{тех})(1-RR_2)(1-RR_3)P_iV_i - (1-k_{тех})((1+RR_4)VC_i - (1+RR_5)FC_i)}{(1+(1-k_{им})(1+RR_1)r)^i} - \\ - \frac{(1-d_н)(1-k_{им})(1+RR_6)CI_i - (1+RR_7)O_i)}{(1+(1-k_{им})(1+RR_1)r)^i} - \sum_{i=1}^{N} \frac{(1-k_{тех})Inv_i}{(1+(1+RR_1)r)^i} \to \max \quad (9)$$

while fulfilling the restrictions: $0 \le i \le N$

Assessment of the engineering rent influence degree on npv

When analyzing the engineering rent influence on the project NPV in the field of digital materials science, it is important to highlight critical indicators, namely: the project implementation period, project implementation risks, engineering economic work quality and EIC business reputation.

Assessing the terms of the project implementation, the EIC involvement allows to reduce them due to the competent level of the EIC. This effect is achieved, firstly, due to a certain engineering experience of the EIC, which allows to reduce the number of possible combinations of material layers, reinforcement angles, etc., as well as the availability of specific equipment and software for the EIC, designed to work with new materials. In addition, the organizational structure of the EIC is more flexible, which reduces the time for transferring a project from one department to another, and also allows for parallel development, when one department is busy, for example, in determining the structural layout of a future product, and the other is focused on the material.

In the case of the risk component, there is a certain reduction in risks, because EIC has practically no risks associated with personnel and technological processes (due to the narrow specialization of EIC). The external risks associated with suppliers are also significantly lower (EIC has well-established supply chains for the necessary raw materials and equipment).

The presence of special qualifications, highly qualified personnel and an established supply chain logically affects the quality of the engineering economic work, and, as a result, the EIC business reputation.

Schematically, the impact of all four benefits of attracting EIC on the project NPV is reflected in accordance with figure 1.

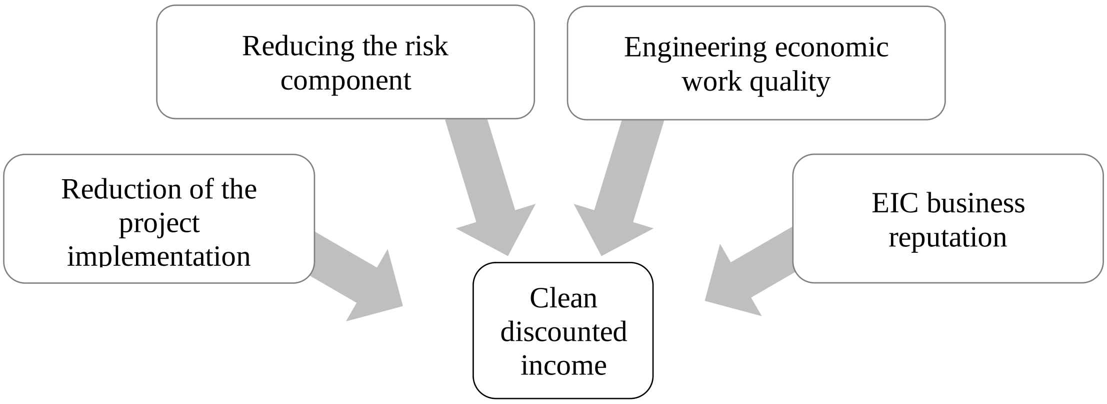


Figure 1. *Impact of EIC benefits on NPV*

Conclusion

Engineering industrial companies' involvement for the development of products and structures made of new materials. Due to the fact that EIC is organizationally much more “flexible”, it becomes possible to develop products in parallel and, as a result, the development and implementation time of the product is reduced. Also, due to the narrow specialization of the EIC, the risks in the implementation of the project are reduced due to the fact that highly qualified personnel are involved in the design and manufacture (which reduces the risk of incorrect management decisions, as well as the human factor in the product made of new materials manufacture and the appropriate equipment use). In addition, EIC has established a supply chain for specific raw materials and equipment, which reduces the external project implementation risks. EIC has much more competence to select the best technologies and equipment in terms of technical and economic characteristics, quality and costs, and the positive reputation of EIC allows creating a favorable financial environment around the project. Thus, the designing process transfer and implementing to the EIC can significantly increase the products made of new materials introduction economic effect.

Acknowledgments

The work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (NTI Center "Digital Materials Science: New Materials and Substances" on the basis of Bauman Moscow State Technical University) and with the support of the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. Brom A.E., Stoyanova M.V. 2016. Engineering rent in the engineering industry: specifics, problems, evaluation opportunities. Bulletin of the Moscow Region State University. Series: Economics 4. pp. 48–55.

2. Brom A.E., Stoyanova M.V., Yazev M.V., Korolev S.A. 2020. Assessment of technological resources for the production of composite products based on mathematical methods IOP Conference Series: Materials Science and Engineering 934(1). 012003.
3. Gorlacheva A.G., Gudkov I.N. 2016. Knowledge management: experience of empirical research. Machine builder. 3. pp. 13–15.
4. Efremov V.S., Khanykov I.A. 2003. The key competence of the organization as an object of strategic analysis. Management in Russia and abroad. 2. pp. 8–33.
5. Kharlanov A.S., Bazhdanova Y.V., Kemkhashvili T.A., Sapozhnikova N.G. 2022. The Case Experience of Integrating the SDGs into Corporate Strategies for Financial Risk Management Based on Social Responsibility (with the Example of Russian TNCs) Risks 10, 12. pp. 19.
6. Litvinov K.S. 2010. Modern market of engineering services Russian Foreign. Economic Bulletin. 5. pp. 68–73.
7. Nazarenko M.A., Sychev R.S., Blinov E.V., Karetina C.R. 2022. Organization Risk Management of the Machine-building Complex International Transaction. Journal of Engineering, Management, & Applied Sciences & Technologies. 13(2). pp. 1–10.
8. Osika L.K. 2010. Modern engineering: definition and subject area. Professional magazine. 4. pp. 11–21.
9. Stoyanova M.V., Novikov A.D., Morozov S.A. and Brom A.E. 2021. Digital material science for industrial companies. Journal of Physics: Conference Series. 1990(1). pp. 5.
10. Stoyanova M.V. 2017. Formation of the competence level of engineering companies in the machine-building Economics: Yesterday, Today, Tomorrow. 7(11). pp. 81–87.
11. Tsisarskiy A.D. 2016. Training of specialists in the areas of "system engineering" and "project management for the rocket and space industry". Controlling. 59. Pp. 28–33.
12. Vasiljeva M.V., Ponkratov V.V., Vatutina L.A., Volkova M.V., Ivleva M.I., Romanenko E.V., Kuznetsov N.V., Semenova N.N., Kireeva E.F., Goncharov D.K., Elyakova I.D. 2022 Crude Oil Market Functioning and Sustainable Development Goals: Case of OPEC plus plus. Participating Countries Sustainability. 14(8). pp. 23.

DOI: 10.15862/67MNNPK22-07

Stoyanova Margarita Vasil′evna
Bauman Moscow State Technical University, Moscow, Russia
E-mail: MStoyanova@emtc.ru

Novikov Andrey Dmitrievich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: nad@emtc.ru

On the issue of new materials use in satellite communication systems economic efficiency assessing

Abstract. Of all the existing space technologies, satellite communication systems are the only commercial type of technology today. Based on the features of the spacecraft in near-Earth orbits movement, it is rational to place communication satellites in geostationary orbit. However, the launching 1 kg of payload to such a height (35,786 km) cost is extremely high, which makes launching vehicles extremely expensive. At first glance, the use of new materials will reduce costs, however, it is necessary to take into account the developing, manufacturing and testing such structures cost. The paper considers the peculiarity of using such new materials in satellite communication systems evaluating economic efficiency.

Keywords: satellite; geostationary orbit; composite reflector

Introduction

Satellite communication systems perform an important function of providing a radio signal on the Earth surface. They consist of spacecraft (SC) that act as a repeater. Depending on the orbit used, the number of devices required to provide a continuous signal on the entire Earth surface also changes. For example, Starlink satellites operate at an altitude of 550 to 560 km, and at least 60 devices are needed for satellites operating at this altitude to provide communications to the entire planet (at the same time, to increase the system throughput, SpaceX plans to launch several tens of thousands devices). The minimum number of satellites (fig. 1) can be achieved using the geostationary orbit. Geostationary orbit (GSO) is a special case of geosynchronous orbit, which is located at an altitude of 35,786 km and provides a vehicle conditionally fixed placement relative to the Earth's surface.

Figure 1. *Communication satellite Yamal-402*

Only 3 satellites in geostationary orbit provide radio communications on all planet surfaces except for the polar regions. But, in turn, there are significant differences in the cost of launching vehicles into low and high orbits. Thus, the approximate cost of launching 1 kg of payload into low orbit is estimated at 2,500 US dollars, while into geostationary orbit — 25,000 US dollars [1]. Also, one of the disadvantages of systems using GSO is the radio signal delay caused by the distance that the signal needs to travel from the source on Earth to the spacecraft, between the spacecraft, and back to Earth. To ensure communication between spacecraft, inter-satellite communication systems are used. The solution to the problem of signal delay can be an increase in the operating frequencies of inter-satellite communications, because. the frequency of the spacecraft "to Earth" is limited by the planet atmospheric features. To date, devices operating in the frequency range from 40 to 75 GHz are known. Operation at such frequencies is associated with strict requirements for permissible deviations in the shape of the reflecting surface during operation. So, for the frequencies indicated earlier, the permissible deviations of the reflector shape under the orbital flight factors influence should not exceed the values of $\Lambda/16$, and sometimes $\Lambda/50$, where Λ is the radio emission wavelength, i.e. must not exceed 0.1 mm [2]. It is possible to achieve high dimensional stability when using rigid reflectors made of polymer composite materials (PCM), such as carbon fiber reinforced plastics. At the same time, it is necessary to increase the structure weight efficiency, which is characterized by linear density, i.e. the mass ratio of the reflector structure to the aperture area. For modern onboard antennas, this parameter is 3.0–3.5 kg/m^2. The simultaneous achievement of an even lower linear density and high dimensional stability is a complex scientific and technical task, in which the structural and power scheme is linked to the characteristics of PCM. CFRP have low linear thermal expansion coefficient, relatively low density, high rigidity, strength and thermal conductivity [3]. However, they are characterized by a high cost of both the structure itself and the design process, so it is necessary to evaluate the economic efficiency of carbon fiber structures introduction in various engineering branches.

Features of the space reflector made of carbon fiber designing process

Reflectors made of carbon fiber are actively used in various companies' spacecraft (such as Intelsat, Inmarsat, Lockheed Martin, Thales Alenia Space, etc.). However, they all have different configurations. Known reflectors made by three-layer technology, with different configurations of rib reinforcement, with truss reinforcement, mesh reflective surface. At the same time, there is no data that would establish the relationship between the configuration of the reflector and its main characteristics (rigidity and linear density). Therefore, when designing such a structure, it is necessary to consider a wide range of possible structural and power schemes. Another problem associated with the use of carbon fiber is the lack of these materials characteristics. Moreover, their characteristics can vary widely depending on the shape and dimensions of the structure, the composition and structure of the components, and manufacturing techniques. Composite materials correspond to the trinity "design-technology-material", and when determining the design parameters, it is impossible to abstract from one of the three components, each of which, at the same time, is connected to each other [4]. Despite a fairly large number of works devoted to the development of reflectors made of composites, a number of problems have not yet been solved to ensure an integrated approach in determining the parameters of such structures made of PCM. The dependence of PCM characteristics on the production technology is not fully taken into account, the thermophysical characteristics of thin-walled carbon fiber reinforced plastics structures (less than 1 mm thick) along the reinforcement plane are not studied. To design products from polymer composite materials, it is necessary to experimentally determine its characteristics. Tests of composite materials based on fibrous fillers are characterized by a number of features. For example, when loading samples, various types of destruction are observed. The anisotropy of the composite structure, as well as the absence of PCM plastic deformations during the destruction, cause significant difficulties in obtaining mechanical characteristics even under uniaxial loading [6]. Also, the fibrous structure affects the thermal and optical characteristics of the material [5; 7].

One of the criteria for choosing a test method is the theoretical ability to obtain the required characteristics. However, the robustness of a test method, or relative immunity to minor changes in the prototype and test procedure, is just as important as the theoretical perfection of the method. Often, in order to determine certain characteristics of a composite, it is necessary either to re-make fixtures for existing research equipment, or to develop unique test facilities, which significantly increases the complexity and cost of designing.

Taking into account the complexity, multi-stage and interdisciplinarity of the reflector design process, the complex technique presented in figure 2 is of particular interest.

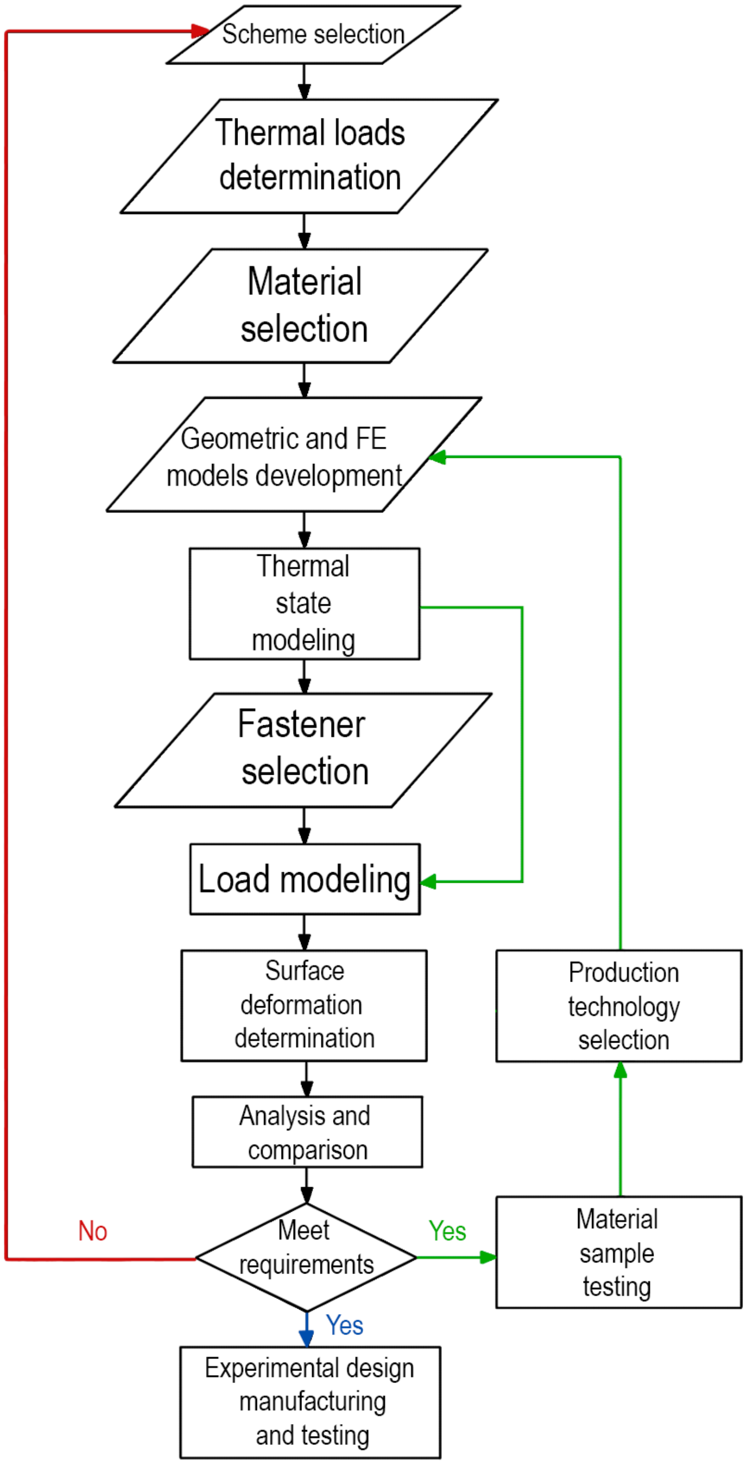


Figure 2. *Technique for designing a reflective space antenna reflector*

Figure 1 shows that the composite reflector designing process can begin from the very first stage, the choice of a structural power scheme, if the design being developed does not meet the requirements of the technical specifications, and this may not be due to an error of an engineer or designer, but due to due to insufficient data on the composite structure, technological features or characteristics anisotropy [8].

Composite reflectors production

No less difficulties arise when choosing a technology for the reflector production. As mentioned above, due to the unique specific characteristics, the main structural material for the production of onboard antenna reflectors has become a composite based on polymer binders and carbon fibers. To improve the production manufacturability, carbon fibers are woven into fabrics, the various weaves of which are shown in figure 2.

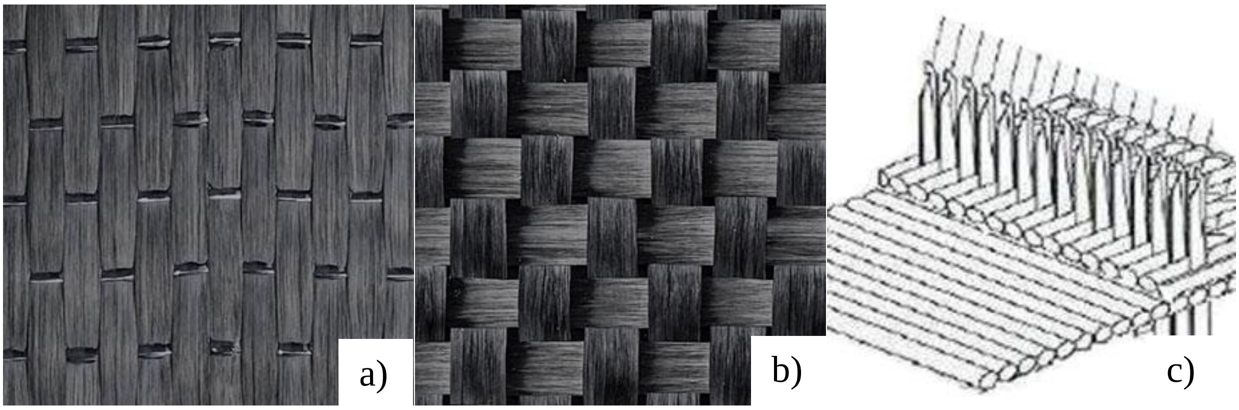


Figure 2. *Types of carbon fabrics: (a) unidirectional; (b) bidirectional; (c) multiaxial*

The use of equal-strength fabrics allows achieving the required characteristics of the future design. Bidirectional fabrics differ in the type of source material (tow) and the method of weaving (fig. 3). To reduce the distortion of the reflected signal and temperature deformations, a flattened fabric was used in the reflector design (fig. 3b). A distinctive feature of these fabrics is a thickness of 0.1 mm (whereas the thickness of traditional fabrics is 0.2–0.4 mm). In such fabrics, the bundle bends in the weaving places are smaller, which reduces contact stresses and, as tests have shown, improves mechanical characteristics. However, the cost of such fabrics is higher, because an additional technological operation is added to their production process [9].

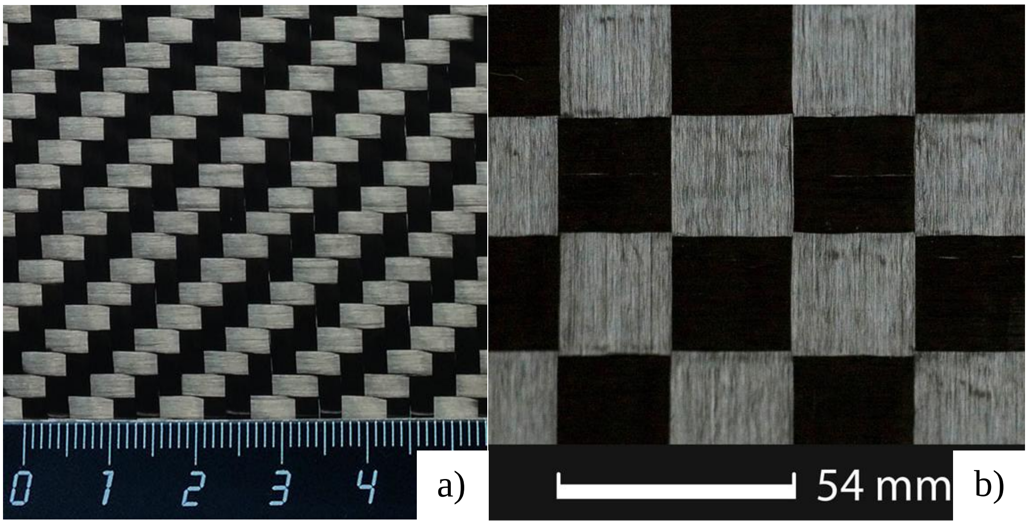


Figure 3. *Equal-strength fabrics based on (a) conventional tourniquet; (b) flattened tourniquet*

There are several methods for the carbon fiber production. Each of the existing methods for manufacturing structures made of polymer composite materials based on epoxy binder and carbon fibers has both its own advantages and disadvantages. One of the most cost-effective technologies — contact molding. This technology is distinguished by manual reinforcing material laying out, followed by the application of a polymer binder. The disadvantage of this method is the binder high percentage, low productivity, low surface quality and accuracy and high product porosity.

Molding using an elastic diaphragm, in particular vacuum infusion technology, can significantly improve the quality of manufactured products.

Unlike contact molding, in the vacuum infusion method, the impregnation and polymerization process takes place in a sealed circuit under atmospheric pressure. A vacuum is created in the circuit using a sealing cord and a vacuum film acting as an elastic diaphragm. The product front surface quality and accuracy largely depends on the shaping tooling (matrix) roughness. In most polymer binders, the curing process is accompanied by the heat release, the magnitude of which depends on the binder density. Due to various factors, of the binder density in different parts of the product may differ, which leads to temperature differences, the internal stresses occurrence and warping of the structure at the molding stage. The warpage amount also, in turn, depends on the technology, so, for example, when using the method RTM (Resin Transfer Molding), where molding takes place between two metal matrices pressed by a hydraulic press with a force of up to 100 tons, the manifestation of this effect will be pronounced. A similar effect occurs in the production of structures using autoclave molding technology. When using vacuum infusion, the warpage effect is less pronounced, because. flexible punch allows you to equalize internal stresses in the workpiece [10].

One of the most important technological aspects is shaping tooling. The future reflector characteristics depend on the quality and accuracy of the shaping tooling (matrix). For the manufacture of dimensionally stable structures, the tooling material must also have low CLTE values, so that during hot curing and binder polymerization, the matrix does not change its linear dimensions, deviating the reflector profile [11]. These requirements are met by FeNi36 metal alloy, known under the Invar trademark, and carbon fiber. Both tooling options are distinguished by a very high cost, however, in comparison with Invar tooling, carbon fiber tooling turns out to be more technologically advanced, because lower costs for its production, and it is also more mobile, which eliminates the need for specialized equipment for the transportation of the matrix in the production shop.

Conclusion

Despite the fact that the one composite reflector cost is significantly higher than that of a traditional metal reflector, the use of the former provides significant savings at the stage of putting a communication satellite into geostationary orbit. So, the metal reflectors mass with diameters of 1.2 meters varies from 5 to 10 kg, while carbon fiber — from 2 to 3 kg. The 1 kg of payload putting cost into the working orbit of a communications satellite is 25,000 US dollars. Several reflectors are installed on board the communication satellite, from 4 to 10. Thus, despite the high cost of carbon fiber reflectors, they provide a 3-fold advantage in terms of costs for putting spacecraft into working orbit.

Acknowledgments

The work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (NTI Center "Digital Materials Science: New Materials and Substances" on the basis of Bauman Moscow State Technical University) and with the support of the Ministry of Science and Higher Education of the Russian Federation.

REFERENCES

1. Yakovlev A.V., Vnukov A.A., Balandina T.N., Balandina E.A., Tarletsky I.S. 2018. Description of scenarios of transition of material from an operable to inperable state using an operable to inperable stage using an equation of fold catastrophe theory. Bulletin of SibSAU. 17(3). pp. 782–789.
2. Reznik S.V. and Novikov A.D. 2018. Comparative analysis of the honeycomb and thin-shell space antenna reflectors MATEC Web of Conferences. 92. p. 5.
3. Stoyanova M.V., Novikov A.D. and Borodulin A.S. 2020. Evaluation construction made of polymer composite materials by molding using reusable flexible punches production profitability IOP Conf. Ser.: Mater. Sci. Eng. 934. P. 11.
4. Borodulin A., Kalinnikov A., Tereshkov A. 2019. New polymeric binders for the production of composites. Materials Today: Procceding. 11. pp. 139–143.
5. Kharaev A.M., Bazheva R.C., Begieva M.B., Nelyub V.A., Borodulin A.S. 2019 Polyethersulfones with improved thermophysical properties. Journal of Polymer Science — Series D. 12(1). pp. 24–28.
6. Kotomin S.V., Obidin I.M., Pavluchkova E.A. 2022. Adhesive Bond Strength Calculation of Reinforcing Fibers with Polymers by the "Loop" Method Mechanics of Composite Materials. 58(1). pp. 141–150.
7. Nelyub V.A. 2013. Technologies of production of components of electric transmission line supports from epoxy binders by the winding method Polymer Science — Series D 6(1) pp. 44–47.
8. Nelyub V.A. 2018 Adhesive-strength evaluation via the pull-out method in a binder-elementary-filament system at various treatments of filaments. Journal of Polymer Science — Series D. 11(3). pp. 263–266.
9. Borodulin A.S. 2015 Simulation of impregnation kinetics of fabric fillers in the production of fiberglass articles Glass physics and chemistry. 41(6). pp. 660–664.
10. Nelyub V.A., Fedorov S.Y., Malysheva G.V., Berlin A.A. 2021 Properties of Carbon Fibers after Applying Metal Coatings on Them by Magnetron Sputtering Technology Fibre Chem. 53. pp. 252–257.
11. Kuznetsov S.V. 2022 Appearing ZGV point in the first flexural branch of Lamb waves in multilayered plates Composite Structires. 290. pp. 9.

DOI: 10.15862/67MNNPK22-08

Tereshkov Aleksandr Gennad′evich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: atereshkov@emtc.ru

Polysulfones and fabric composite materials based on them

Abstract. This article discusses the current state of the issue in the field of fabric polymer composite materials with a thermoplastic matrix, in particular, based on industrial aromatic polysulfones. The greatest attention is paid to the development of technology for the production and study of the properties of fabric carbon composites. The main characteristics and features of various types of polysulfones and composites based on them are considered.

Keywords: thermoplastics; carbon plastics; thermoplastic prepregs; molding technology; polysulfone; polyethersulfone

Introduction

Aromatic polysulfones are structural thermoplastic polymers that are widely used in aerospace engineering, various branches of mechanical engineering, instrumentation, electronics, for the manufacture of a wide range of components for medical and food equipment, and membrane technology [1–5].

The family of industrial aromatic polysulfones, obtained by the reaction of nucleophilic substitution of chlorine atoms in 4,4'-dichlorodiphenylsulfone with alkaline salts of bisphenols, includes polysulfone (PSU) based on 2,2-bis(4-hydroxyphenyl)propane (bisphenol A), polyethersulfone (PES) based on 4,4'-dioxydiphenylsulfone (bisphenol C) and polyphenylenesulfone (PPSU) based on 4,4'-dioxydiphenyl.

Main characteristics of structural thermoplastic polymers

The advantages of structural thermoplastic polymers include [6–10]:

- high strength properties at low density, which makes it possible to replace metal in the structures of machines and mechanisms;
- resistance to aggressive environments (acids, alkalis, organic solvents, etc.), which ensures the possibility of long-term operation of products without the use of protective coatings;
- relatively low material consumption of products made from them, which allows to reduce the weight of the final product;
- high manufacturability, which consists in the possibility of manufacturing large-sized products of complex shape for a period of time 5–10 times less than would be required for the manufacture of similar products from metals and alloys;
- the ability to control over a wide range of thermal and electrical conductivity, radio and optical transparency, depending on the purpose of the product and the type of reinforcing fibers used;
- low capital costs for organizing the production of products from reinforced plastics;
- operability in a wide range of ambient temperatures and operating mechanical, electrical and radiation stresses.

The tightening of requirements for structural thermoplastic materials led to the use in their composition, in addition to glass fibers, first of carbon and basalt fibers, and later of organic fibers. This was required by the creation of modern space-rocket and aviation technology, the need to reduce its mass and simultaneously increase strength and endurance, as well as provide special technical properties [11–14].

Structural polymers unreinforced and reinforced with dispersed particles have long been used for the manufacture of products in all industries and are used everywhere [15–17].

At present, interest in the use of structural thermoplastics for the production of reinforced continuous fibers and fabric polymer composite materials (PCM) has grown significantly. Thermoplastics can replace thermosets as binders for fabric PCMs, which will significantly expand the scope and possibilities of such materials. Previously, thermoplastics were not used to create fabric PCMs due to technological limitations, but research in this direction is currently being actively conducted [18–21].

Industrial aromatic polysulfones

Polysulfone (PSU)

Polycondensation product of 4,4'-dichlorodiphenylsulfone and bisphenol A.

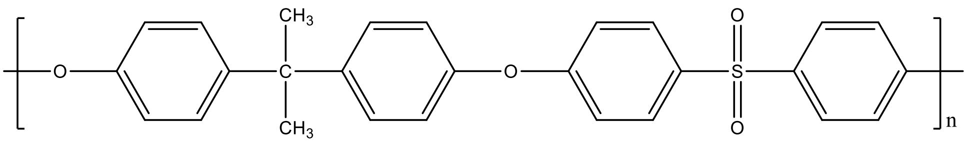


Figure 1. *Structural formula of polysulfone*

Heat-resistant, strong, transparent polymer of amorphous structure. Polysulfone has high impact resistance, density — 1240 kg/m^3. Temperature of glass transition (T_{GT}) equal to 190°C. The temperature of the start of destruction is 420°C. The maximum operating temperature is 160°C. Frost-resistant down to minus 100°C. Chemically resistant, oil and petrol resistant, water resistant, resistant to acids and alkalis, withstands steam sterilization. It has good dielectric properties. Processed by injection molding, extrusion (310 to 340°C). It is used in electrical engineering, medicine. Brands and manufacturers: PSN (NIIPM named after G.S. Petrov), Ultrason PSU (BASF), Udel, Mindel (Solvay Advanced Polymers) [10].

Polyethersulfone (PES)

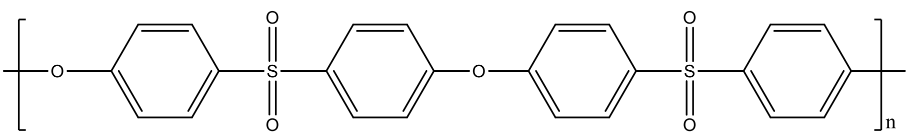


Figure 2. *Structural formula of polyethersulfone*

A domestic laboratory technology for the production of polyethersulfone (PES) by high-temperature polycondensation in solution has been developed.

Polyethersulfone has an amorphous structure, T_{GT} = 230°C. Has high temperature of long operation (200°C). Polyethersulfone has high impact resistance, density — 1370 kg/m^3. The temperature of the start of destruction is 420°C. Frost-resistant down to minus 100°C. Chemically resistant, oil and petrol resistant, water resistant, resistant to acids and alkalis, withstands steam sterilization. It has good dielectric properties. It is processed by injection molding, extrusion (from 310 to 340°C) [10].

It has a wide application in electrical, electronics and instrumentation: instrumentation, oil level indicators, high-frequency insulators, junction box covers, transparent panels, flanges, insulators, switch parts, valve bodies, sensor bodies, sockets, indicator parts and much more.

For the medical industry: parts of dialysis systems, surgical instruments, sterilization trays, valve bodies, dishes for microwave ovens, filtration membranes (for highly sensitive analyzes and obtaining ultra-pure reagent water), and other parts (parts) of medical equipment that are subject to sterilization and disinfection.

Due to such features of PES as a high degree of protein adsorption, stability at pH 1-14, it is used for the manufacture of membranes (sterile filtration of small volumes of liquids: cultural liquids, pharmaceuticals, cosmetics, diagnostics, buffers, biological solutions, infusion solutions, etc.).

In the food industry, PES is used for the manufacture of membrane and depth filter cartridges (filtration of water, alcoholic beverages, etc.), for the manufacture of dishes resistant to microwave radiation.

The addition of dispersed fillers makes it possible to change the characteristics of PES: increasing fire resistance (antiperene), reducing density, reducing moisture absorption, etc.

Polyphenylenesulfone (PPSU)

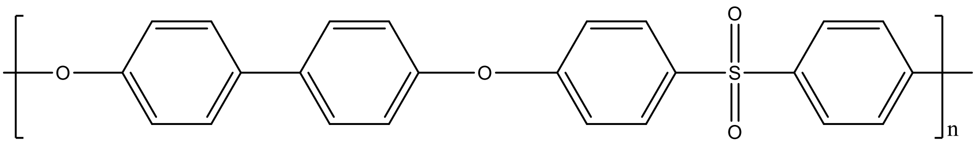


Figure 3. *Structural formula of polyphenylenesulfone*

Amorphous polymer, has excellent hardness and stiffness, impact strength and chemical resistance. In addition to high mechanical strength and stability of characteristics over a wide temperature range, polyphenylene sulfone has an increased viscosity, therefore, it has an increased resistance to shock loads. The dispersion coefficient is low and the material does not absorb moisture well. With a small thickness and polishing, the thermoplastic becomes transparent and is easily processed mechanically.

Resistant to fuels and lubricants, fats, alcohols and weak acidic and alkaline solutions. Resistance to benzene and aromatic hydrocarbons is limited. When exposed to substances with a strong dissolving effect, the formation of cracks is possible. Of particular value to PPSU polymer is its resistance to hydrolysis and hot steam.

The material has good electrical insulating properties, is resistant to high-frequency electromagnetic radiation (including X-ray), but at the same time it has good permeability for radiation in the microwave range.

Fire resistance — high, when ignited, the flame self-extinguishes.

Density — 1290 kg/m^3. T_{GT} = 218^{o}C. The maximum operating temperature is 190^{o}C.

Dispersion-reinforced thermoplastics

In the production of plastic products, dispersed reinforced thermoplastic polymers are used. Thermoplastics without additives are practically not used. Modification of thermoplastics is carried out to improve operational and technological characteristics [22]:

- fire resistance (flame retardants);
- heat resistance;

- mechanical strength;
- wear resistance;
- chemical resistance;
- reduction of moisture absorption;
- frost resistance;
- decrease in melt viscosity.

In addition, various dispersed fillers are used for coloration [22]. Examples of the use of pure and dispersion-reinforced polysulfones are shown in figure 4.

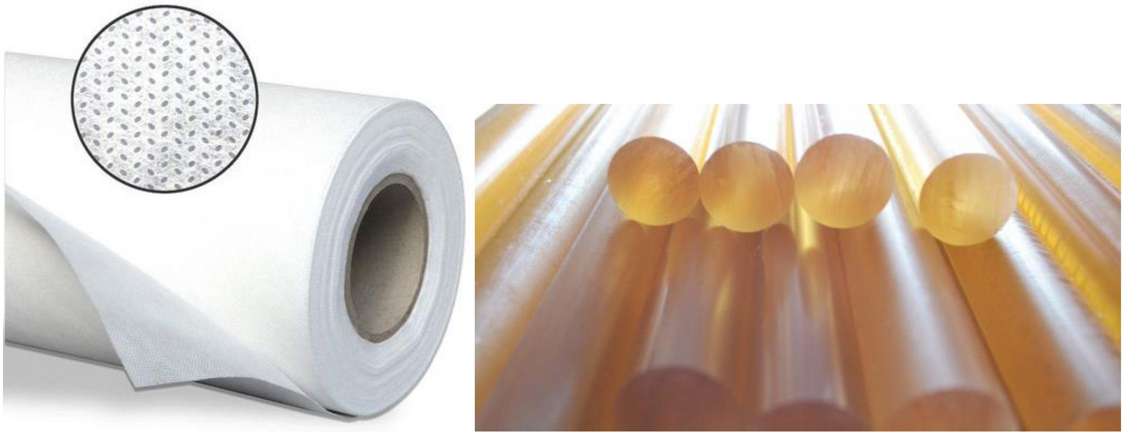


Figure 4. *Filtration membranes [23] and raw materials for electrical products [24] from polyethersulfone*

Products from dispersed reinforced thermoplastics are made using injection molding or pressing technologies, where the thermoplastic in the molten state is fed into the mold from the screw injection molding machine, as shown in figure 5.

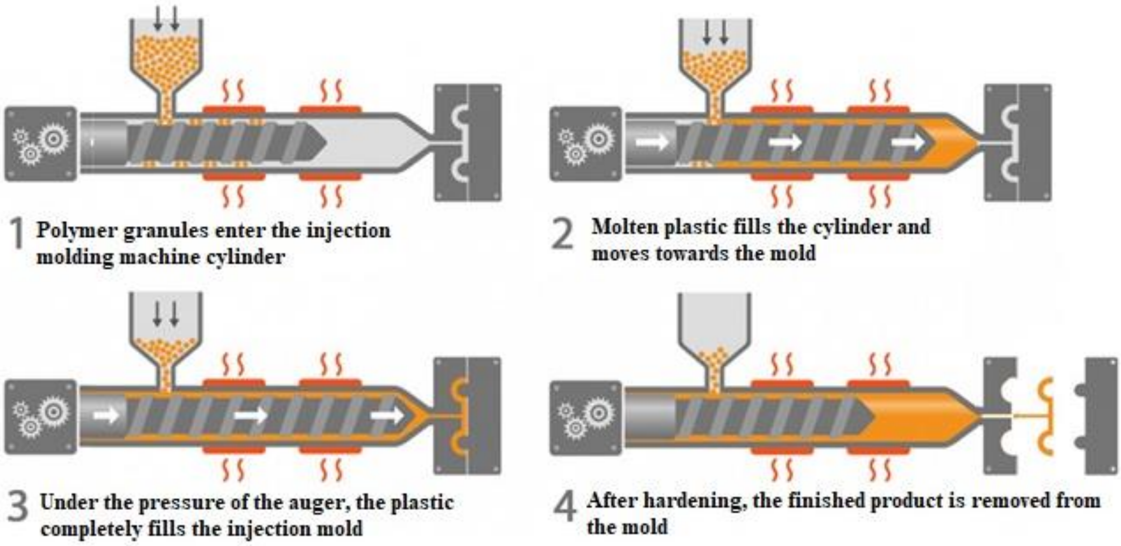


Figure 5. *Technology for the production of products from pure, dispersion-reinforced and short-fiber-reinforced thermoplastics*

Thermoplastics reinforced with short fibers

Reinforcement with short fibers improves the mechanical characteristics of PES. At the same time, the technological process of manufacturing products from PES practically does not change —

a screw injection molding machine is also used, only PES granules with short fibers are used. Thanks to the reinforcement with short fibers, the scope of PES significantly expands — these are parts of pumping equipment and pipeline fittings, cases of various devices (household and other appliances), car bodies, etc.

Figure 6. *Products from PCM on a thermoplastic binder with short fibers*

Production of fabric PCM on a thermoplastic binder

Of greatest interest is the use of PES as a binder in the production of PCM reinforced with continuous fibers. In the manufacture of PCM based on PES, the same technologies are used as in the manufacture of PCM based on any other thermoplastic binder, only the temperature regimes differ.

Let's consider options for production technologies of PCM on thermoplastic binders.

The production of products from PCM on a thermoplastic binder reinforced with continuous fibers is not yet as widespread as the production of such PCM on thermoset binders. At the moment, the following companies have technologies for the production of thermoplastic PCMs with continuous fibers: Solvay (Cytec), Arkema (Elium, Rilsan), Arris composites, Stelia Aerospace, BÜFA Thermoplastic Composites, etc.

There are several technologies for the manufacture of thermoplastic PCM with continuous fibers:

1. Impregnation of dry filler with a concentrated solution of thermoplastic, with the addition of thermoplastic powder, and subsequent pressing.
2. Impregnation with a thermoplastic melt followed by pressing.
3. Film technology — layer-by-layer laying of filler and thermoplastic film with subsequent pressing of the package.
4. Layer-by-layer automated laying out of the prepreg using additive technologies (possible subsequent pressing).

The above technologies are applicable both for the manufacture of semi-finished products (prepregs) and finished products.

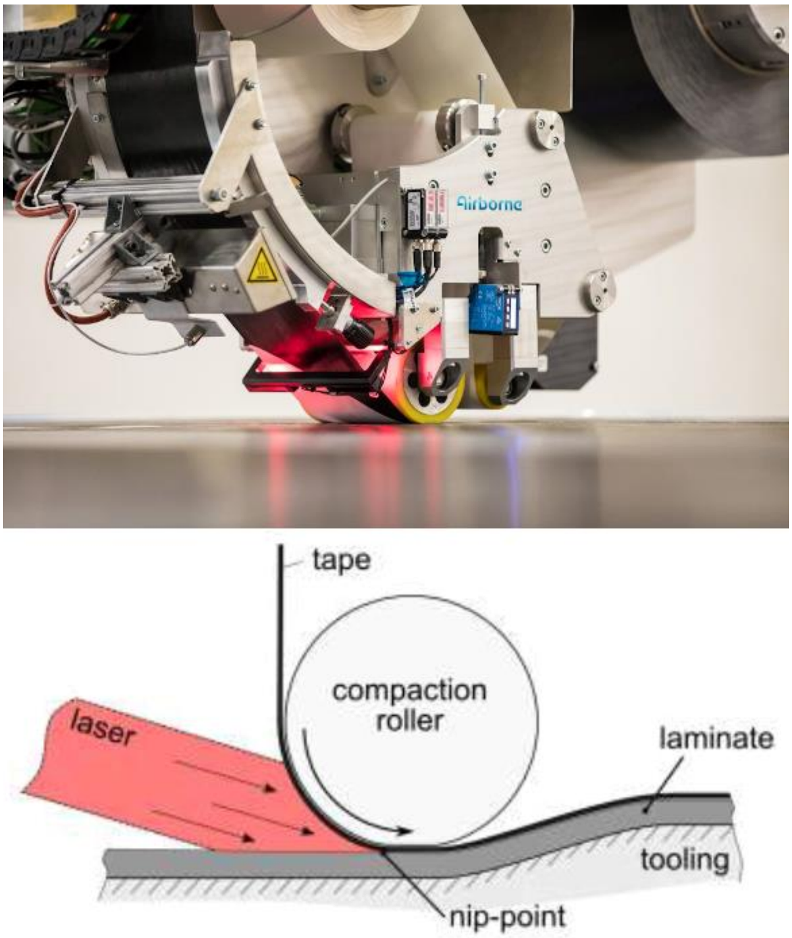


Figure 7. *Layering technology [25]*

Let's consider some developers and manufacturers of products and materials based on thermoplastics and continuous fibers.

Researchers at the Fraunhofer IPT Institute in Aachen Germany (industrial partner — AZL) have created a fully automated Tapelege system patented by the institute [26]. During the molding process, unidirectionally reinforced thermoplastic tapes are layered by additive manufacturing in accordance with the desired load direction. The preform is then heated and molded to the final contour. The process was initially tested on 16 mm thick PA12 and carbon fiber sheets, followed by a PEEK and carbon fiber prepreg.

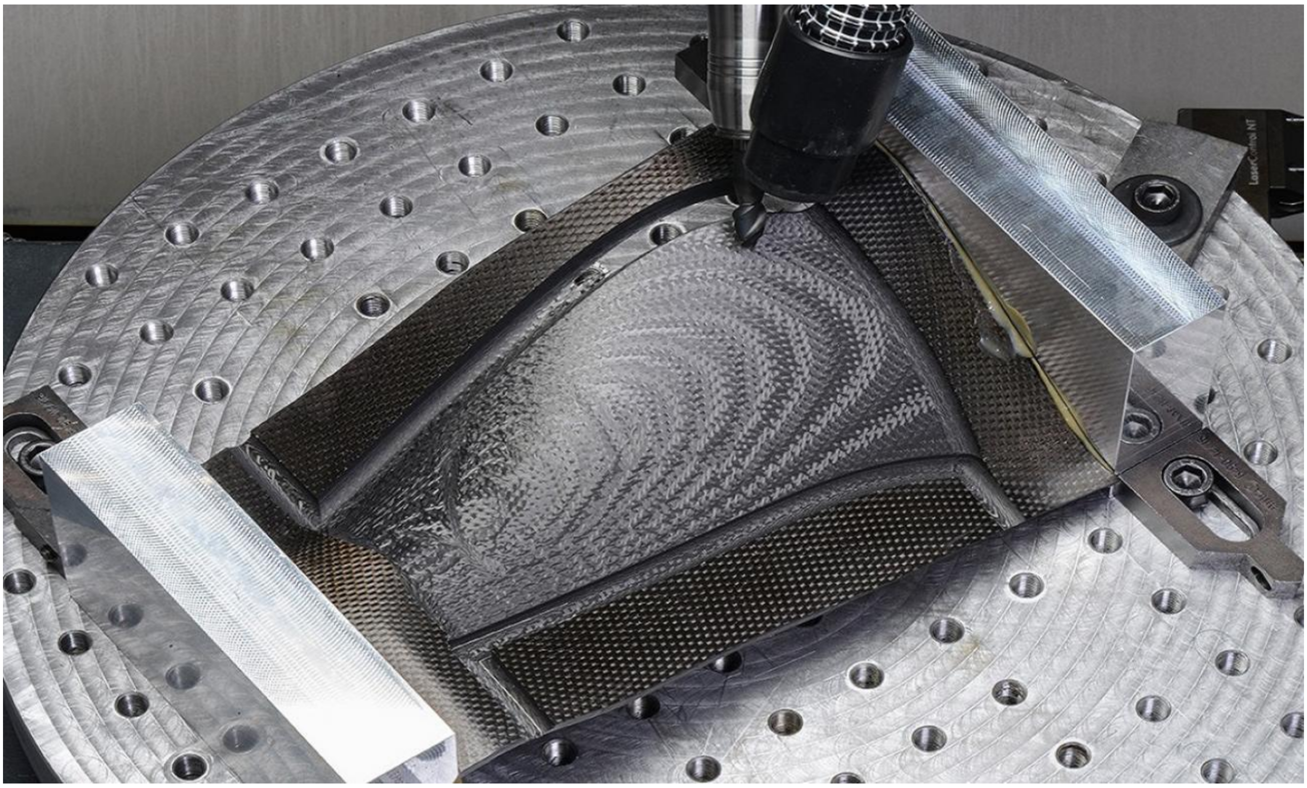


Figure 8. *Tapelege system*

Arkema uses the technology of automated laying of a prepreg impregnated with a PEEK solution (Elium binder) [27]. It also manufactures products from PCM with chopped Rilsan thermoplastic fibers (polyamide 66).

Figure 9. *Rilsan Elium carbon reinforced plastic (CFRP) by Arkema*

The Solvay company, which bought the well-known PCM manufacturer Cytec, produces semi-finished products and products from AS4 fiber-reinforced polyetheretherketone (PEEK) [28]. It uses technologies of automated layout, preform pressing and preform molding in an autoclave.

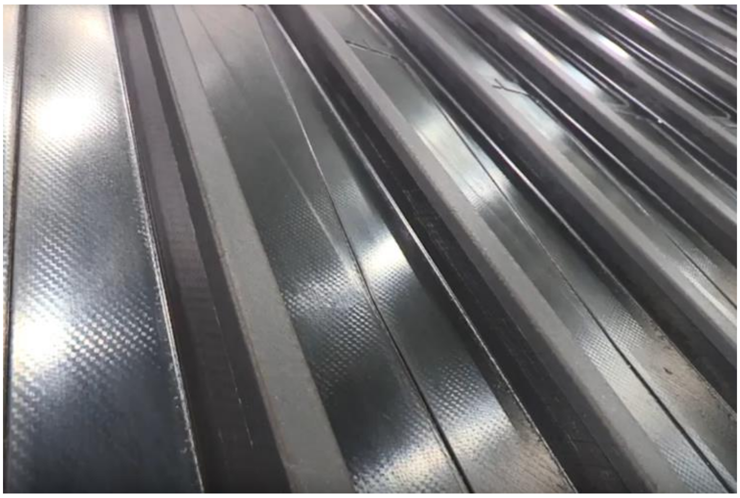


Figure 10. *Cytec PEEK PCM Products*

Arris composites manufactures truss structures using additive technologies using a continuous carbon fiber coated with a PEEK layer [29].

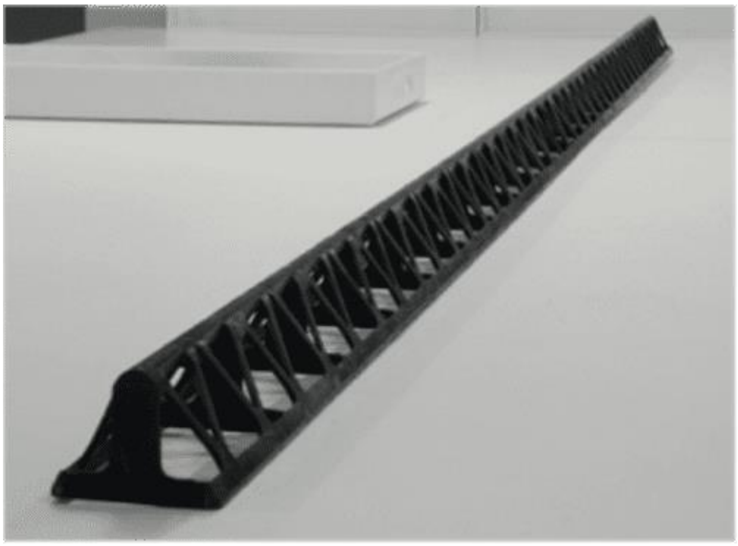


Figure 11. *Arris composites product*

Stelia Aerospace manufactures aviation stringer panels using automated laying and welding (stringers are welded). Polyetherketoneketone (PEKK) is used as a binder [30].

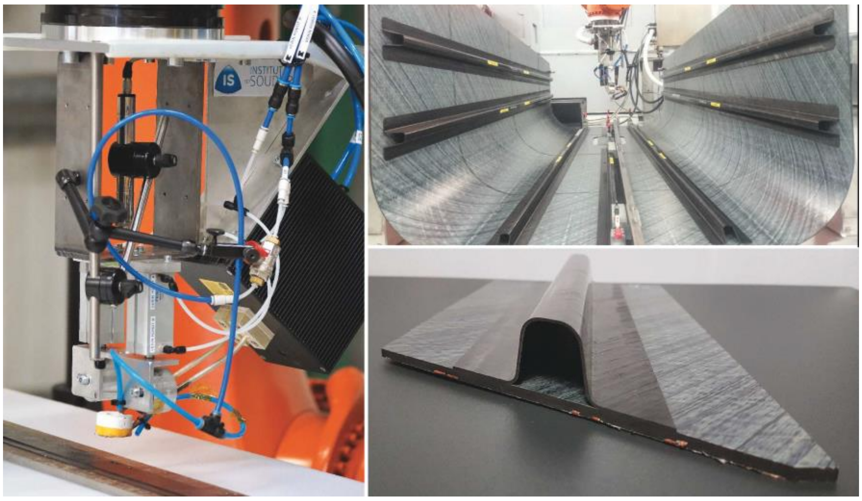


Figure 12. *Stelia Aerospace technologies: automated laying, welding*

Teijin produces TENAX TPUD prepreg, based on carbon fiber and PEEK. When forming products from this prepreg, it is necessary to add additional volumes of the binder, either in the form of a powder or in the form of a melt [31].

Figure 13. *Thermoplastic unidirectional prepreg TENAX TPUD*

BÜFA Thermoplastic Composites produces unidirectional prepregs on various thermoplastics: PEKK, Polypropylene, Polyamide 66, Polyethylene terephthalate, Polycarbonate [32].

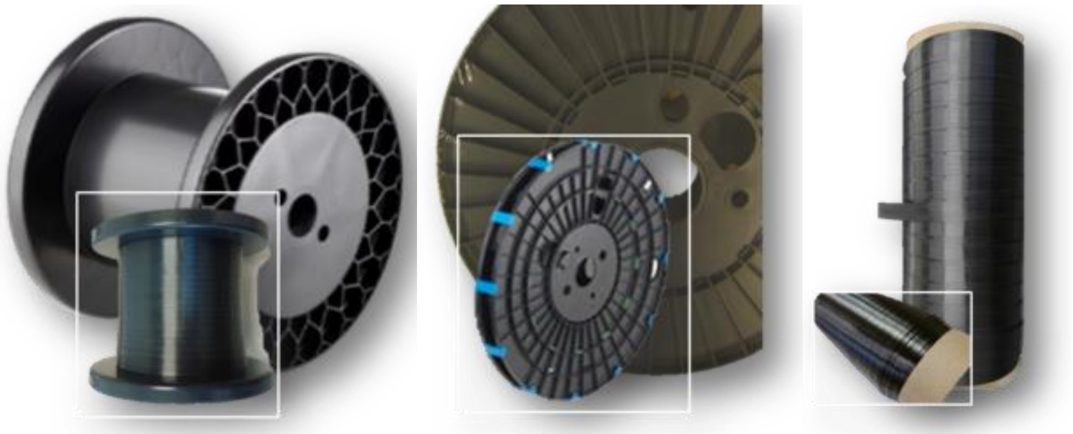


Figure 14. *BÜFA thermoplastic prepregs*

SGL Carbon manufactures unidirectional prepregs (SIGRAFIL) on various thermoplastics: Polyetherketonketone, Polypropylene, Polyamide 6, Polyethersulfone, Polycarbonate, Polyphenylene sulfide [33].

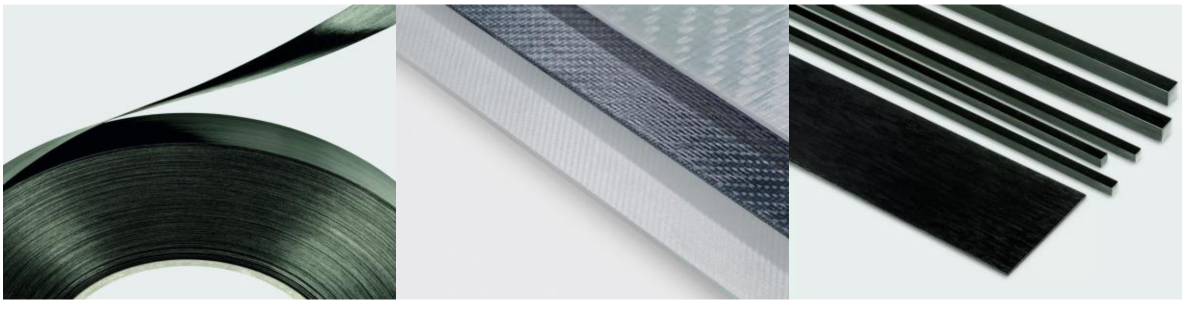


Figure 15. *SIGRAFIL thermoplastic prepregs*

There are still a sufficient number of companies and research organizations involved in the development and production of PCM on thermoplastic binders. All of them use the technologies and materials described earlier.

Conclusion

Analysis of sources in international and Russian databases showed that research and development on the creation of semi-finished products and products of fabric PCM based on PES are carried out in a limited volume and there are no offers of such products on the market. At the same time, research and production of fabric PCMs based on other thermoplastic binders (mainly PEEK and PA66) are becoming widespread in world practice. However, there are no such developments and, moreover, finished products in Russia. Under these conditions, a group in BMSTU is developing a technology for the manufacture of prepregs and products from previously synthesized PES reinforced with continuous fibers and fabrics.

Acknowledgement

This work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (Center NTI "Digital Materials Science: New Materials and Substances" on the basis of the Bauman Moscow State Technical University).

REFERENCES

1. Storozhuk I.P., Alekseev V.M., Kalinnikov A.N., Borodulin A.S. 2021. Chemically Modified Polysulfones and Their Properties Polymer Science — Series D14(4). pp. 580–587.
2. Deberdeev T.R., Akhmetshina A.I., Karimova L.K., Ignat’eva E.K., Galikhmanov N.R., Grishin S.V., Berlin A.A., Deberdeev R.Y. 2020. Aromatic Polysulfones: Strategies of Synthesis, Properties, and Application Polymer Science — Series D 13(3). pp. 320–328.
3. Mittal V. 2015. Advances in synthesis and properties of engineering polymers. Manufacturing of Nanocomposites with Engineering Plastics. pp. 1–13.
4. Dizman C., Tasdelen M.A., Yagci Y. 2013. Recent advances in the preparation of functionalized polysulfones. Polymer International 62(7). pp. 991–1007.
5. Guo R., McGrath J.E. 2012. Aromatic Polyethers, Polyetherketones, Polysulfides, and Polysulfones. Polymer Science: A Comprehensive Reference, 10 Volume. Set 5. pp. 377–430.
6. Bachinger A., Rössler J., Asp L.E. 2016. Electrocoating of carbon fibres at ambient conditions. Compos Part B Eng. 91. pp. 94–102.
7. Chukov D.I., Stepashkin A.A., Maksimkin A.V., Tcherdyntsev V.V., Kaloshkin S.D., Kuskov K.V. et al. 2015 Investigation of structure, mechanical and tribological properties of short carbon fiber reinforced UHMWPE-matrix composites. Compos Part B Eng. 76. pp. 79–88.
8. Han S.H., Oh H.J., Kim S.S. 2014 Evaluation of fiber surface treatment on the interfacial behavior of carbon fiber-reinforced polypropylene composites. Compos Part B Eng. 60. pp. 98–105.

9. Stepashkin A.A., Chukov D.I., Senatov F.S., Salimon A.I., Korsunsky A.M., Kaloshkin S.D. 2018 3D-printed PEEK-carbon fiber (CF) composites: structure and thermal. Compos Sci Technol. 164. pp. 319–326.

10. Lishevich I.V. 2015 Sozdanie antifriktsionnih teplostoikikh ugleplastikov dlya visokoskorostnikh podshipnikov nasosov I parovykh turbin [Tekst]: dis. na soisk. uchen. step. kand. tekhn. hauk (05.16.09) Federalnoe gosudarstvennoe unitarnoe predpriyatie «Tsentralnii nauchno-issledovatelskii institut konstruktsionnykh materialov «Prometey» — Sanct-Reterburg 157 p.

11. Bachmann J., Hidalgo C., Bricout S. 2017 Environmental analysis of innovative sustainable composites with potential use in aviation sector — A life cycle assessment review. Science China Technological Sciences. 60(9). pp. 1301–1317.

12. Abbas S., Li F., Qiu J. 2018 A review on SHM techniques and current challenges for characteristic investigation of damage in composite material components of aviation industry. Materials Performance and Characterization. 7(1). pp. 224–258.

13. Arani A.G., Farazin A., Mohammadimehr M. 2021 The effect of nanoparticles on enhancement of the specific mechanical properties of the composite structures: A review research. Advances in Nano Research. 10(4). pp. 327–337.

14. Evdokimov A.A., Donetskii K.I., Sidorina A.I., Gunyaeva A.G. 2019 Manufacture of Three-Dimensional Reinforced Fabric Preforms for Making Aviation Products in Russia and Abroad — a Review Fibre Chemistry. 51(2). pp. 105–108.

15. Saleem M.Z., Akbar M. 2022 Review of the Performance of High-Voltage Composite Insulators Polymers. 14(3). No 431.

16. Iqbal Kh.Z, Habib U, Binti M.Z, Razak B.R.A, Amira S.B.A.N. 2022 Mechanical and thermal properties of sepiolite strengthened thermoplastic polymer nanocomposites: A comprehensive review. Alexandria Engineering Journal. 61(2). pp. 975–990.

17. Yousfi M., Samuel C., Soulestin J., Lacrampe M.F. 2022 Rheological Considerations in Processing Self-Reinforced Thermoplastic Polymer Nanocomposites: A Review Polymers. 14(3) № 637.

18. Carrillo-Escalante H.J, Álvarez-Castillo A., Valadez-González A., Herrera-Franco P.J. 2016. Effect of fiber-matrix adhesion on the frac-ture behavior of a carbon fiber reinforced thermoplastic-modified epoxy matrix. Carbon Letters. 19. pp. 47–56.

19. Chukov D., Nematulloev S., Zadorozhnyy M., Tcherdyntsev V., Stepashkin A., Zherebtsov D. 2019 Structure, Mechanical and Thermal Properties of Poly-phenylene Sulfide and Polysulfone Impregnated Carbon Fiber Composites Polymers. 11. Pp. 684.

20. Yao S.S., Jin F.L., Rhee K.Y., Hui D., Park S.J. 2018 Recent advances in carbon-fiber-reinforced thermoplastic composites: a review Compos Part B Eng. 142. pp. 50.

21. Kerber M.L., Vinogradov V.M., Golovkin G.S. 2011 Polimernie kompozicionnie materialy: structura, svoistva, tekhnologiya: Uch. pos. Sanct-Peterburg: Professiya 560 p.

22. https://www.directindustry.com.ru/prod/sanin-filtertechnik-gmbh/product-173849-2036693.html.

23. https://polimer1.ru/catalog/vysokoeffektivnye-polimery/poliefirsulfon-tecason-e-pes.

24. https://www.airborne.com/automation-solutions-advanced-composites/automated-laminating-cell/.

25. https://azl-aachen-gmbh.de/newslight-18-ipt/.

26. https://www.arkema.com/global/en/innovation/lightweight-materials-and-design/thermoplastic-composites/.
27. https://www.solvay.com/en/chemical-categories/our-composite-materials-solutions/thermoplastic-composites.
28. https://arriscomposites.com/manufacturing-technology/
29. https://www.compositesworld.com/articles/welding-thermoplastic-composites.
30. https://www.teijincarbon.com/ru/produkcija/kompozity-tenaxr/termoplastiki-tenaxr?r=1&cHash=b6372963d5f0eb5f53a7a53edfc453d8.
31. https://thermoplasticcomposites.de/en/semi-finished-products/ud-tapes/overview/.
32. https://www.sglcarbon.com/en/markets-solutions/material/sigrafil-continuous-carbon-fiber-tows/.

DOI: 10.15862/67MNNPK22-09

Seleznev Vyacheslav Aleksandrovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: vseleznev@emtc.ru

Chukov Nikolay Aleksandrovich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: nchukov@emtc.ru

Dorofeev Konstantin Sergeevich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: kdorofeev@emtc.ru

Digital system for designing matrixes of self-regulating heating cables

Abstract. The paper describes a digital system for designing matrixes of self-regulating heating cables, consisting of the following subsystems: prediction of the electrically conductive properties of the matrix, prediction of the deformation-strength properties of the matrix, mathematical modeling of the relationship "composition-technology-properties", multifactorial modeling of the structure, 3D modeling of the composite semiconductor matrix, formation Database. The functionality of each subsystem is considered and their necessity is substantiated in the design of polymer composite materials with a positive thermal coefficient of electrical resistance. The possibility of both creating new semiconductor composite materials and selecting known compositions to meet specified technical requirements is substantiated.

Keywords: electrically conductive composite material; self-regulating heating cable; digital technology; polymer composite material

Introduction

One of the urgent problems of our time is the efficient use of energy resources. One of the methods for solving this problem is the creation of heating systems based on self-regulating heating cables. They are widely used in anti-icing complexes, for heating industrial equipment, heating oil and gas pipelines, underfloor heating systems, etc. [1]. The main component of self-regulating heating cables is their semiconductor matrix, which is able to change its electrical conductivity depending on the ambient temperature. These matrices are composite materials with a positive temperature coefficient of electrical resistance. A positive temperature coefficient of electrical resistance is achieved both due to the precise selection of the composition of the composite (the percolation nature of the dependences of the electrical characteristics is required [2]), and the features of the technological process for obtaining the matrix of a self-regulating heating cable (to stabilize the characteristics and increase the service life, chemical or radiation crosslinking of the polymer is often used). matrices [3]). The complexity of obtaining suitable composite materials is poorly reflected by manufacturers of self-regulating cables: RAYCHEM (USA), HEATTRACE (Great Britain), ISOPAD (Germany), THERMON (USA) [4].

The need to expand the range and import substitution of matrices of self-regulating heating cables leads to the development of digital technologies for the design of semiconductor composite materials. At BMSTU was developed an information-computing complex that allows for a comprehensive solution of problems related to modelling the structure and designing the properties of semiconductor matrices. The main purpose of creating this complex was to design electrically conductive composite materials suitable for use as matrices for self-regulating heating cables, to determine the parameters of their processing, and to determine the most important performance characteristics of heating cables from the designed materials.

The use of an information-computing complex will allow developing new self-regulating cables with specified characteristics, reducing the time of such developments and the period of their introduction into production.

This software package consists of separate subsystems that have the ability to work autonomously, and provides the ability to design an electrically conductive composite material, technology for its production and processing, and predict the performance characteristics of a self-regulating heating cable matrix based on this composite. Digital technology consists of the following subsystems with the ability to work autonomously:

- prediction of electrically conductive properties of the matrix;
- prediction of the deformation-strength properties of the matrix;
- mathematical modeling of the relationship "composition-technology-properties";
- multifactor modeling of the structure;
- 3D modeling of a composite semiconductor matrix;
- formation of the database.

The interaction of digital technology subsystems is shown in figure 1.

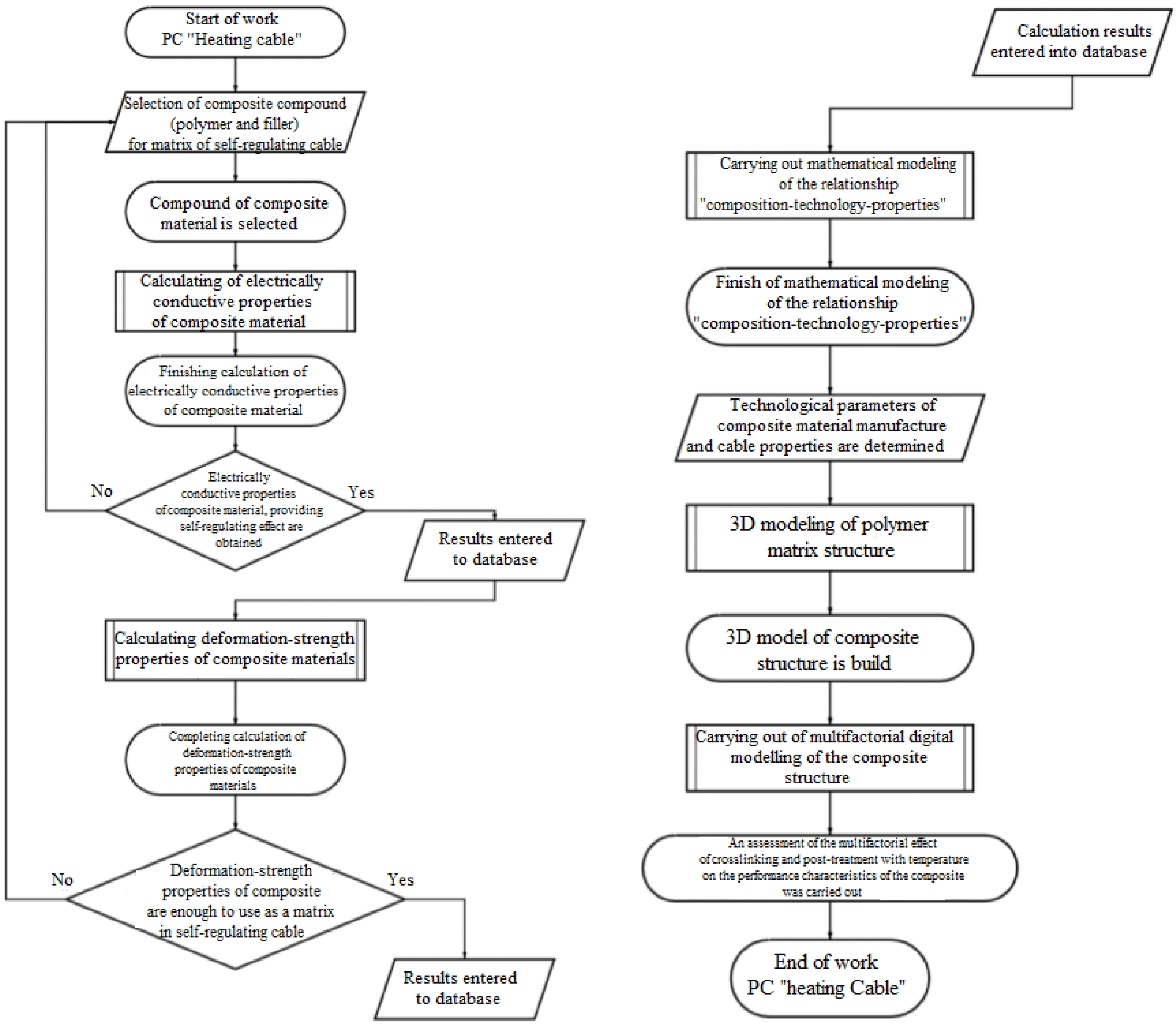


Figure 1. *General block diagram of the digital system for designing matrixes of self-regulating heating cables*

Subsystems development

Subsystem "prediction of electrically conductive properties of the matrix" [5].

To obtain self-regulation properties (changes in electrical resistance and power), a semiconducting polymer matrix must have a positive temperature coefficient of electrical resistance. In practice, this is achieved by introducing conductive carbon fillers into the polymer matrix. This stage in the development of the formulation of semiconducting matrices makes it possible to evaluate the electrical conductivity of the future product with a quantitative variation of the components.

The subsystem for predicting the electrically conductive properties of the matrix provides the calculation of the following parameters of the polymer composite material:

- the magnitude of the electron quantum jump;
- theoretical concentration of percolation;
- true concentration of percolation;
- graph of the conductivity of the composite depending on the content of the filler in the range from 0 to the concentration of percolation;
- graph of the conductivity of the composite depending on the temperature;
- output of the following parameters of the composite at the true concentration of percolation in tabular form;
- true concentration of percolation in mass fractions;
- electrical conductivity of the composite at percolation concentration;
- electrical conductivity of the composite at the maximum content of the filler;
- conductivity of the composite at room temperature;
- conductivity of the composite at the melting temperature;
- coefficient of positive thermal resistance.

The main characteristic determined in this subsystem is the true concentration of percolation, since it is this characteristic that determines the ability of the composite material to have a positive temperature coefficient of resistance. This parameter is calculated by the continual percolation model of rigid prolate ellipsoids of revolution with permeable shells. The mathematical model takes into account the magnitude of the electron quantum jump in the absence of direct contact between electrically conductive particles. Empirical coefficients are applied to the obtained theoretical percolation concentration, taking into account the type and characteristics of the polymer matrix, the shape of the filler particles, the interaction between the filler and polymer particles, the technology of processing the composite, etc. In addition to the percolation concentration in the considered subsystem, the main electrical characteristics of composites for matrices of self-regulating heating cables and their changes depending on the temperature and the content of the electrically conductive filler are determined. The main result of the work of this subsystem is the conclusion about the possibility of using the considered composite with the given parameters as a matrix of a self-regulating heating cable.

Subsystem "Forecasting the deformation-strength properties of the matrix" [6].

The subsystem "Forecasting the deformation-strength properties of the matrix" predicts the deformation-strength properties of the semiconductor matrix when the quantitative ratio of its constituent components changes. The increased content of the electrically conductive additive in the matrix structure leads to a decrease in its deformation-strength properties and a decrease in the manufacturability of the material. Thus, having determined the electrical conductive properties of the matrix at the first stage of formula development, at the next stage it is necessary to evaluate the deformation-strength properties of the resulting material.

In addition to the electrical characteristics, a number of requirements are imposed on the matrices in terms of physical and mechanical characteristics, mainly to the ultimate strength and relative elongation at break. In addition to these characteristics, the subsystem "Forecasting the deformation and strength properties of the matrix" calculates the following parameters:

- dependence of the density of the composite on the content of the filler;
- dependence of the tensile yield strength of the composite on the filler content;
- dependence of the elastic modulus of the composite in tension on the content of the filler;
- dependence of elongation at break on the filler content;
- dependence of specific heat capacity on the filler content;
- dependence of the thermal conductivity coefficient on the content of the filler;
- dependence of the coefficient of linear thermal expansion on the content of the filler;
- dependence of thermal diffusivity on the filler content;
- dependence of the coefficient of volumetric thermal expansion on the content of the filler;
- dependence of the viscosity of the composite material on the content of the filler;
- dependence of the matrix polymer viscosity on temperature.

In addition, this subsystem presents the following characteristics for a composite with a filler content in the region of percolation concentration:

- density;
- tensile yield strength;
- tensile modulus;
- elongation at break;
- specific heat capacity;
- coefficient of thermal conductivity;
- coefficient of linear thermal expansion;
- thermal diffusivity;
- coefficient of volumetric thermal expansion.

As a result of the work of the subsystem "Forecasting the deformation-strength properties of the matrix", it can be concluded that the physical and mechanical characteristics of the composite under consideration correspond to the requirements for materials used in self-regulating heating cables.

Subsystem "Mathematical modeling of the relationship "composition-technology-properties" [7].

The subsystem "Mathematical modeling of the relationship "composition-technology-properties" makes it possible to evaluate the characteristics of a composite material that affect the process of its processing and helps to calculate the main parameters of the technological process of extrusion of a matrix of a self-regulating heating cable, as well as to establish a connection between the technology of manufacturing a matrix and its main operational characteristics.

This subsystem allows you to calculate the following technological characteristics of the composite:

- melt flow index of PCM for matrices of self-regulating heating cables;
- minimum temperature of PCM processing.

Depending on the characteristics of the composite and the conditions of its processing, the subsystem calculates the following performance characteristics of the self-regulating heating cable matrix:

- the maximum possible length of the cable section, m;
- rated power of the cable, W;
- recommended core diameter of the self-regulating heating cable matrix, mm;
- relative rigidity of the section of the temperature characteristic of the heating cable in the following temperature sections:
  1. 25–65^{o}C;
  2. 65–85^{o}C;
  3. 85–105^{o}C.

As a result of the work of the subsystem "Mathematical modeling of the relationship "composition — technology — properties", it is possible to make a decision on the speed of rotation of the screws and the temperature of the material cylinder in the heating zones of the extruder. At the same stage, the area of possible application of self-adjusting matrices based on the considered composite becomes clear. The most effective operating range, power and mounting limitations of semiconductor matrices are determined.

<u>Subsystem "Multifactor structure modeling" [8].</u>

This subsystem solves the problem of modifying the formulation and manufacturing technology of the self-regulating heating cable matrix in order to obtain optimal operating parameters. The "Multifactor Structure Modeling" module provides the calculation of the following characteristics of polymer composite materials with fillers of various sizes:

- total true concentration of percalation;
- mass content of nanosized and microsized electrically conductive fillers;
- conductivity of the composite at room temperature;
- conductivity of the composite at the melting temperature;
- coefficient of positive thermal resistance;
- tensile modulus of the composite;
- relative elongation at break.

In addition, this module takes into account the effect of annealing, chemical or radiation crosslinking on the specified parameters.

The results of the work of the subsystem "Multifactor modeling of the structure" determine the effects of processing the matrix after its formation, as well as the influence of this processing on the operational properties of the self-regulating cable. As a general rule, annealing and/or radiation crosslinking of the semiconductor composite matrix will affect the service life and stability of the parameters of the self-regulating heating cable.

Subsystem "3D modeling of a composite semiconductor matrix".

This subsystem is necessary to create virtual 3D models of the structure of the resulting composite semiconductor matrix. This module is necessary to visualize the statistical calculation of the distribution of the conductive filler in the dielectric matrix, a visual representation of the distribution of conductive tracks in the composite material depending on the properties of the polymer matrix. An example of the subsystem operation is shown in figure 2.

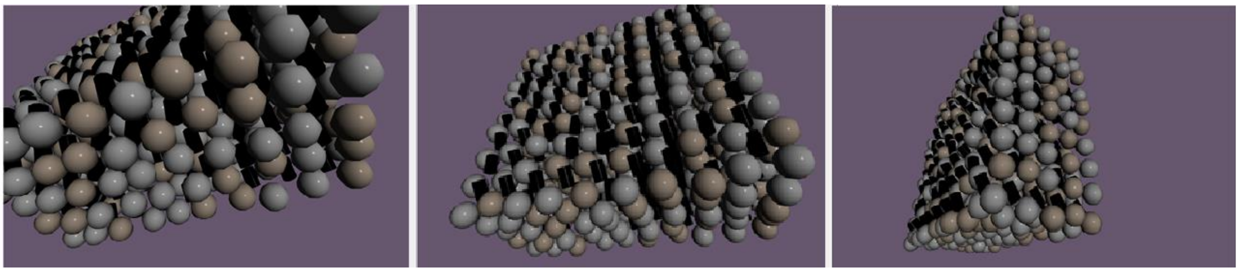


Figure 2. *Rotation of a 3D model of a composite material when working in the subsystem "3D modeling of a composite semiconductor matrix"*

Subsystem "Database formation".

The subsystem includes data on the components and the compositions of semiconductor matrices obtained on their basis, including information on the component composition, the qualitative characteristics of the constituent elements, the calculated properties of the developed materials, as well as data on experimental confirmation of the indicators and characteristics of products developed using a digital system computer simulation.

Conclusion

In 2022, a pilot version of the digital technology will be launched, the performance of which will be confirmed and verified based on a comparison of predictive and real (determined as a result of tests) values of the characteristics of experimental and industrial samples of semiconductor materials produced. This work is carried out jointly with cable industry enterprises, which are highly interested in the results of this project.

The digital system for the design of self-regulating heating cable matrices covers the production cycle of self-regulating heating cable matrices from the selection of semiconductor composite material components to determining the performance characteristics of self-regulating heating cables. Its use allows both the design of new self-regulating systems of direct electric heating and the selection of ready-made compositions for specified technical requirements. The interconnection of subsystems allows a quick restructuring of the technological process to alternative raw materials without losing the quality of the heating cable being produced. The implementation of digital technology for designing matrices of self-regulating heating cables and electrically conductive composite materials for them corresponds to the strategic directions for the development of polymer composite materials for the period up to 2030 [9–11]. In addition, the described digital technology allows organizing the production of import-substituting electrically conductive composite materials for low- and medium-temperature self-regulating cables.

Acknowledgement

This work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (Center NTI "Digital Materials Science: New Materials and Substances" on the basis of the Bauman Moscow State Technical University).

REFERENCES

1. Nakhabin A.V. 2014. Issledovaniye opyta zarubezhnykh stran v voprosakh sberezheniya energoresursov i modernizatsii ZHKKH s pomoshch'yu vnedreniya innovatsiy. Aktual'nyye problemy gumanitarnykh i yestestvennykh nauk. № 2–1.
2. Lipatov Yu.S., Mamunya Ye.P., Gladyreva N.A., Lebedev Ye.V. 1983. Vliyaniye raspredeleniya sazhi na elektroprovodnost' smesey polimerov. Vysokomol. soyed. Ser. A. 25(7). Pp. 1483–1489.
3. Markov A.V., Sorokina E.A. 2013. Effect of silane-crosslinking on electrical properties and heat resistance of carbon black-filled polyethylene composites. Plasticheskie massy. 10. Pp. 21–24.
4. Sparber — Anti-icing system. Roof without icicles. Cable heating systems [Electronic resource]. — Access mode: http://www.mukhin.ru/stroysovet/kco/03.html.
5. Nelyub V.A., Borodulin A.S., Seleznev V.A., Chukov N.A., Stremyakov A.V. Certificate of state registration of the computer program "Software module for predicting the electrically conductive properties of semi-conductive polymer composite materials with a positive resistance effect" RU 2021681492.
6. Nelyub V.A., Borodulin A.S., Seleznev V.A., Chukov N.A., Stremyakov A.V. Certificate of state registration of the computer program "Software module for determining the deformation-strength properties of semi-conductive polymer composite materials with a positive resistance effect" RU 2021681758.
7. Nelyub V.A., Borodulin A.S., Seleznev V.A., Chukov N.A., Stremyakov A.V. Certificate of state registration of the computer program "Software module for predicting the operational characteristics of semiconducting polymer composite matrices depending on the materials used and their manufacturing technologies" RU 2021681545.
8. Nelyub V.A., Borodulin A.S., Seleznev V.A., Chukov N.A., Stremyakov A.V. Certificate of state registration of the computer program "Software module for modeling the operational characteristics of semiconducting polymer composite matrices depending on the technology of their manufacture and post-processing" RU 2021681493.
9. Kablov E.N. 2012. Strategic directions for the development of materials and technologies for their processing for the period up to 2030. Aviation materials and technologies. 5. pp. 24–30.
10. Grashchenkov D.V., Chursova L.V. 2012. Strategy for the development of composite and functional materials. Aviation materials and technologies. № S. pp. 231–242.
11. Decree of the Government of the Russian Federation of April 18, 2016 N 317 On the implementation of the National Technology Initiative https://docs.cntd.ru/document/420349846.

DOI: 10.15862/67MNNPK22-10

Vdovin Dmitriy Sergeevich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: Vdovin.dims@gmail.com

Borodulin Aleksey Sergeevich
Bauman Moscow State Technical University, Moscow, Russia
E-mail: asb@emtc.ru

Experience in evaluating the properties of fiberglass using a neural network and non-destructive testing method

Abstract. A technique for constructing and training a neural network to diagnose the quality of polymer composite materials based on non-destructive testing data is proposed. As an object of research, glass-reinforced plastic made by vacuum infusion technology using an epoxy phenol binder is considered. The quality of the manufactured samples was determined by the method of non-destructive testing, and the received signals were used as input data for training the neural network. A technique for constructing, training, and monitoring the accuracy of the neural network has been developed. The results of studies of the accuracy of the neural network operation depending on the method of presenting the initial data are given.

Keywords: polymer composite materials; neural networks; nondestructive testing methods

Introduction

The areas of application of glass and carbon fiber reinforced plastics as structural materials are constantly expanding. They have a complex of unique characteristics, which provides products made from them with high reliability [1–3]. The main advantages of carbon fiber and glass fiber reinforced plastics include high specific characteristics of strength and rigidity, low density, low values of thermal expansion coefficients, etc. These materials have a high damping capacity [4–6], which makes it possible to manufacture structures with high vibration strength indicators from them.

Contact molding technologies for products made of carbon and fiberglass have been used in industry for a long time and are constantly being improved [7–9]. Traditionally, two-stage processes were used, where at the first stage a prepreg was obtained, and at the second stage, a part was molded from the prepreg [1; 2]. The use of prepregs has become widespread in the aviation industry and in the production of rocket and space technology, which is associated with high mechanical characteristics of finished products [1; 2].

However, the prepreg technology has disadvantages, the main of the finished ones are high labor intensity and cost, and therefore they are gradually being replaced by infusion technologies, for example, vacuum infusion, which allows combining the processes of impregnation of the reinforcing material and molding of products in a single technological cycle [7]. The cost of products manufactured by infusion technologies is significantly lower than by prepreg, which was the main reason for their widest distribution.

Currently, new types of binders have been developed [10–13], including self-healing properties [14–16].

To assess the quality of parts manufactured using vacuum infusion technology, various non-destructive testing methods, including acoustic ones, are used [17–19]. Detection of internal defects in composite materials by non-destructive methods is an important requirement, both for quality control at the production stage and for monitoring their durability during operation when performing maintenance operations. Non-destructive testing makes it possible to determine structural defects at different scale levels, however, the data obtained from such an analysis are difficult to interpret, since they are valid only for one area of the material under study.

In the last decade, neural networks have become increasingly widespread, which, unlike other systems, can learn. It is known [20; 21] that a neural network can replace manual labor associated with the analysis of initial data, which will eventually lead to automation and significantly speed up the processing of results obtained by non-destructive testing methods. In addition, in the process of such processing, the neural network can independently determine typical defects, which will improve the technological modes when molding specific parts.

The purpose of this work is to create, train and control the accuracy of a neural network using the example of evaluating the properties of fiberglass.

Objects and methods of research

As an object of study, a fiberglass panel consisting of 6 layers of TS 8/3 quarts fabric was used. An epoxy phenol material was used as a polymer matrix.

In the work, 34 samples were used, the manufacture of which was carried out using vacuum infusion technology. All of them were investigated by the method of acoustic non-destructive testing (reverberation-through). The essence of the non-destructive testing method used is that emitting and receiving ultrasonic transducers are installed on the tested product, which is located at a fixed distance from each other. With the help of a generator, a piezoelectric element is excited, which emits ultrasonic pulses of longitudinal waves. These pulses reach the receiver after multiple reflections from the walls of the controlled sample, after which they are amplified and processed. Traditionally, such signals have the form of a continuous curve (fig. 1a), characterized by discrete values of amplitudes and frequencies. For the convenience of loading data into the neural network and obtaining the best results, the values were cleared of “noise” and converted into scalograms (fig. 1b) by using the Morle continuous wavelet transform.

a) b)

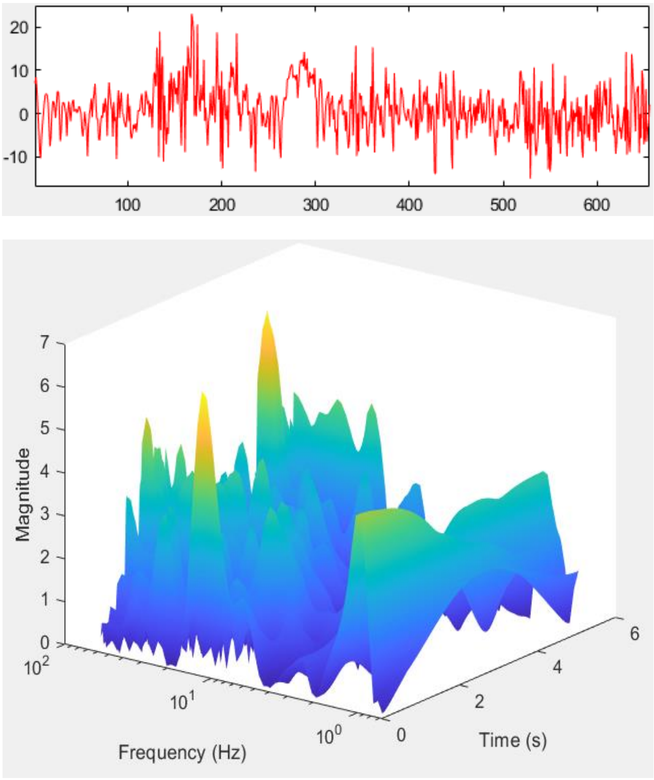


Figure 1. *The signal obtained by the method of non-destructive testing, before (a) and after the wavelet transform (b)*

After receiving the results of non-destructive testing, all the studied samples were subjected to a tensile test to determine the modulus of elasticity of each studied sample. Based on the test results, all samples were divided into three groups depending on their elasticity modulus:

- 1 group — samples with an elastic modulus from 25 GPa to 28 GPa;
- 2 group — samples with an elastic modulus from 21 GPa to 24 GPa;
- 3 group — samples with an elastic modulus from 17 GPa to 20 GPa.

Thus, as input parameters for training the neural network, the values of the amplitudes and frequencies of the signals converted into images-scalograms were used, and the output parameters were groups of fiberglass samples that differ in the values of the modulus of elasticity.

Results and discussion

The task set for the neural network is to classify the scalogram images obtained during the wavelet analysis of the signal. The classification should divide the scalogram images into three groups depending on the magnitude of the studied characteristics. In future work, it is planned to use as output data, not groups created by a range of characteristics, but specific characteristics of materials. However, at the moment it is not possible to do this, since there is no database on materials.

The work used the MatLab software with the Deep Network Designer tool.

The process of creating a new neural network (based on the existing one) consists of 3 main stages:

1. Choosing a “pre-trained network” and changing its architecture by the task.
2. Network training.
3. Determining the accuracy of predictions.

In the first step, based on the available data for this study, the SqueezeNet network was chosen: the network that requires the least data to function has a satisfactory classification accuracy of 65 % and is also suitable for classifying our data types: image format (jpg).

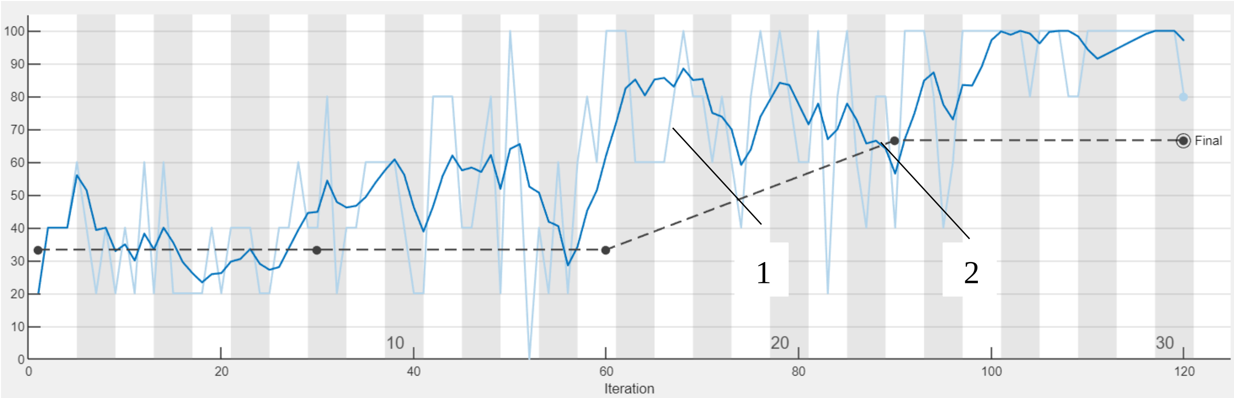
In the second stage, which was called neural network training, we divided all the data into two subgroups:

- training sample — data that will be used directly in the course of network training;
- validation sample — data that will be used to analyze the accuracy of the network.

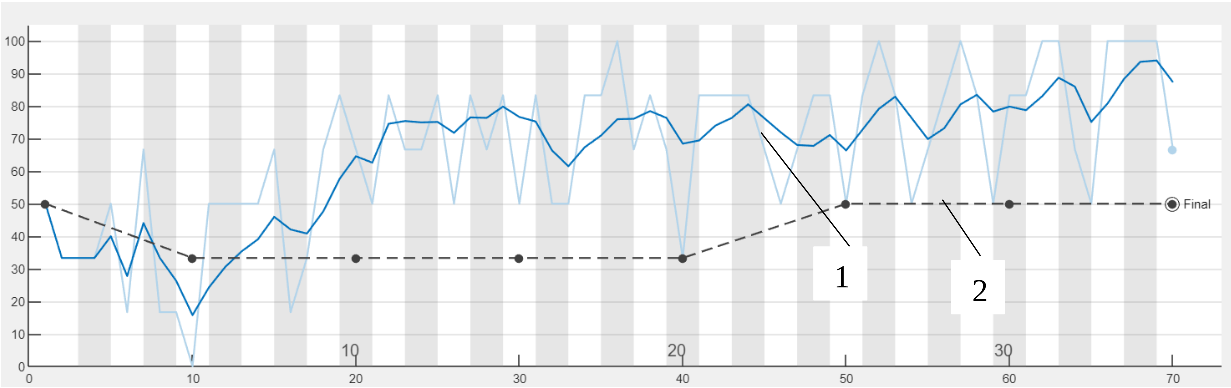
The third stage — determination of the prediction accuracy, was determined by comparing the training accuracy of the variational sample with the values of the training sample. To achieve the best results, it is necessary to select the neural network training parameters: Number of epochs, batch size, InitialLearnRate, and optimization method, and then retrain.

If satisfactory results are obtained, the network can be further used to classify new data. If we get results that do not meet the requirements, we can either resort to training more layers of the neural network or make small modifications to the network architecture. If you repeatedly get unsatisfactory results, you should choose another network.

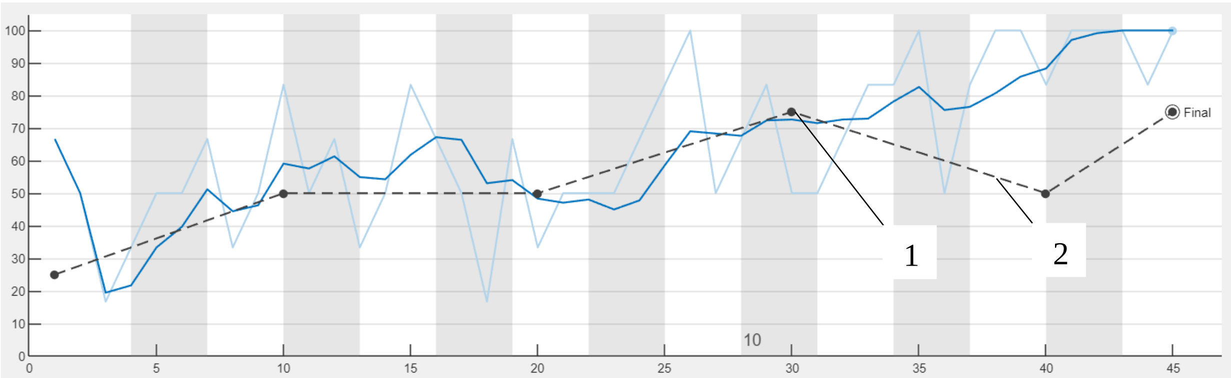
It is convenient to present the results obtained in graphical form (fig. 2), where the ordinate axis indicates the prediction accuracy, and the abscissa axis indicates the number of learning stages. The values corresponding to the accuracy of the network on the training set are marked with the number 1, and similar values for the validation set are marked with the number 2.



a)



b)



c)

Figure 2. *The results of training the neural network during the first (a) second (b) and third (c) experiments (see table) with training (1) and validation (2) samples*

During the training of the neural network, 20 experiments were carried out, the best of which are listed in the table, which corresponds to figure 3 (a-c). The values of the validation sample varied from 20 to 75 %.

Table 1

Initial data for the neural network at all stages of its training

No experiment	Neural network training parameters			
	number of epochs	batch sizes	initial learn rate	optimization method
1 (fig. 2z)	30	4	0.01	adam
2 (fig. 2b)	35	6	0.01	sgdm
3 (fig. 2c)	15	6	0.001	adam

The analysis of the obtained results (see fig. 2c) shows that we managed to increase the prediction accuracy up to 75 %, which is a satisfactory indicator of the network operation now, and therefore, we managed to prove the existence of cause-and-effect relationships between the characteristics of amplitudes and frequencies and specific properties of polymer composite materials (in the examples under consideration, such property was the modulus of elasticity).

Conclusion

In the example of glass-reinforced plastic samples, a method for training neural networks is considered, the main purpose of which is to diagnose the quality of polymer composite materials based on non-destructive testing data.

As an object of research, glass-reinforced plastic made by vacuum infusion technology using an epoxy-phenol binder is considered.

The study of fiberglass samples was carried out by the method of acoustic non-destructive testing (reverberation-through). The results of the conducted research were used as input data for building and training a neural network.

A technique for constructing, training, and controlling the accuracy of the neural network has been developed, which included three stages. In the first stage, a ready-made neural network was chosen from the MatLab database, which allows the processing of images in the (jpg) format. In the second stage, all data previously obtained as a result of experimental studies were divided into two groups, which were called “training” and “validation” samples. This data has been uploaded to the network. In the third stage, the accuracy was assessed by comparing the training accuracy of the variational sample with the values.

It has been established that the estimation accuracy is 75 %, which is a satisfactory indicator of network operation, and, therefore, the results obtained can be scaled by increasing the number of samples studied and using other non-destructive testing methods.

Acknowledgement

This work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (Center NTI "Digital Materials Science: New Materials and Substances" on the basis of the Bauman Moscow State Technical University).

REFERENCES

1. Technology for the production of products and integral structures from composite materials in mechanical engineering // Scientific editors A.G. Bratukhin, V.S. Bogolyubov, O.S. Sirotkin. — M.: Gothic, 2003. 516 p.
2. Mikhailin Yu.A. Fibrous polymeric composite materials in engineering. St. Petersburg: Publishing House Scientific foundations and technologies. 2013. 720 p.
3. Nelyub V.A. Technologies of production of components of electric transmission line supports from epoxy binders by the winding method // Polymer Science — Series D 2013. 6(1). pp. 44–47.
4. Kobets L.P., Borodulin A.S., Malysheva G.V. Study of microcapillary impregnation of carbon fiber by epoxy binder // Fibre Chemistry, 2016, 48(4), pp. 311–315.
5. Nelyub V.A., Malysheva G.V., Komarov I.A. New technologies for producing multifunctional reinforced carbon plastics // Materials Science Forum. 2021. 1037 MSF.
6. Yanyan C., Nelyub V.A., Malysheva G.V. An investigation of the kinetics of the heating process for parts made of carbon fiber in the process for parts made of carbon fiber in the process of curing // Polymer Science-Series D, 2019, 12(3). pp. 296–299.

7. Maung P.P., Htet T.L., Malysheva G.V. Simulation and optimization of vacuum assisted resin infusion process for large-sized structures made of carbon fiber-reinforced plastic // IOP Conference Series: Materials Science and Engineering, 2020, 709(2), 022041.
8. Chen' Y, Gorodetskii M.A., Nelyub V.A., Malysheva G.V. Algorithm for the Optimization of the Technological Conditions of Forming Epoxy-Matrix-Based Composites Russian Metallurgy (Metally). 2019 (13). pp. 1369–1372.
9. Belov P.A., Borodulin A.S., Kobets L.P., Malysheva G.V. Kinetics of fiber impregnation by a binder. Gradient generalization of Navier-Stokes-Darcy equations // Polymer Science-Series D. 2016, 9(2). pp. 205–208.
10. Borodulin A.S., Nelyub V., Shaov A.K., Kalinnikov A.N., Kharaev A.M., Khasbulatova Z.S., Bazheva R.C., Borukaev T.A. Study of low-molecular weight polyether ketones in relation to high-density polyethylene // International Journal of Pharmaceutical Research. 2020. 12(3). pp. 2323–2328.
11. Borodulin A., Kalinnikov A., Kharaev A., Shcherbin S. Aromatic polysulfone to create polymer materials with high resistance to frost / IOP Conference Series: Earth and Environmental Science. 2019. 302(1). N 012062.
12. Kalinnikov A.N., Borodulin A.S., Kharaev A.M, Bazheva R.C., Balkarova S.B., Kharaeva R.A. Polyether-ketones based on 1,1-dichloro-2,2-di(3,5-dibromo-4-hydroxyphenyl) ethylene / Key Engineering Materials. 2019. 816. pp. 302–306.
13. Shaov A.K., Kharaev A.M., Borodulin A.S., Nelyub V., Kalinnikov A.N., Khasbulatova Z.S., Chamalovna B.R., Borukaev T.A. Polyethylene modification and stabilisation with lowmolecular weight polyetheretherketones International // Journal of Pharmaceutical Research. 2020. 12(3). pp. 2316–2321.
14. Platonova E.O., Vlasov E., Pavlov A.A., Kireynov A., Nelyub V.A., Polezhaev A.V. Self-healing polyurethane based on a difuranic monomer from biorenewable source // Journal of Applied Polymer Science 2019. 136(33), N 47869.
15. Bessonov I.V., Polezhaev A.V., Kuznetsova M.N., Nelub V.A., Buyanov I.A., Chudnov I.V., Borodulin A.S. Rheological and thermal analysis of low-viscosity epoxy-furan composites // Polymer Science — Series D. 2013. 6(4). pp. 308–311.
16. Bessonov I.V., Kopitsyna M.N., Nelyub V.A. Synthesis of furfurylideneacetones and their application as active diluents for epoxy resins fabrication // Russian Journal of General Chemistry. 2014. 84(12). pp. 2439–2444.
17. Nondestructive testing: Handbook: In 7 vol. Under the general ed. V.V. Klyuev. Vol. 3: Ultrasonic control / I.N. Ermolov, Yu.V. Lange. — Moscow: Mashinostroenie, 2004. 864.
18. Slyadnev A.M., Soldatov A.I. Acoustic nondestructive testing of multilayer structures made of PCM in the production and operation of the aviation equipment // Control. Diagnostics. 2019. No 10. p. 36–49.
19. Murashev V.V., Yakovleva S.I. Nondestructive testing of filler and permanent joints of propeller blade parts made of polymer composite material // Proceedings of VIAM. 2018. No 10. p. 83–92.
20. Yuanyuan Wang Shuhong Chai, Hung Duc Nguyen Experimental and numerical study of autopilot using Extended Kalman Filter trained neural networks for surface vessels // International Journal of Naval Architecture and Ocean Engineering. 2020. 12. pp. 314–324.
21. H. Hwang, J. Oh, K.H. Lee, J.H. Cha, E. Choi, Y. Yoon, J.H. Hwang, Synergistic approach to quantifying information on a crack-based network in loess/water material composites using deep learning and network science // Comput. Mater. Sci. 2019. 16. pp. 240–250.

DOI: 10.15862/67MNNPK22-11

Chehn′ Yanyan
Bauman Moscow State Technical University, Moscow, Russia

Malysheva Galina Vladlenovna
Bauman Moscow State Technical University, Moscow, Russia
E-mail: malyin@mail.ru

Technique for optimizing the curing mode of glass-reinforced plastic parts based on an epoxy binder

Abstract. The technological process of curing samples of glass-reinforced plastics made by vacuum infusion technology based on an epoxy binder is considered. As optimization parameters, two heating stages (before and after gelation) and five criteria were used, which were used as average values of temperature gradients during the curing process, maximum temperatures, average values of the gradient of the degree of cure, maximum values of the degree of cure and the total duration of the curing process. The results of the calculation of the optimal values of the rate of the heating process, performed by the ideal point method, are presented.

Keywords: polymer composite materials; epoxy matrix; curing; multicriteria optimization

Introduction

Modern polymer composite materials are used as structural materials in the manufacture of a wide variety of parts and products, the operation of which occurs under the simultaneous influence of a large number of factors [1; 2]. The main areas of their application were originally rocket and space production and the aircraft industry. Gradually, as the cost of materials decreased, polymer composites began to be used in mechanical engineering and construction, and other industries [3–6]. Currently, they are already used in all sectors of the national economy as the main structural materials.

The reliability and cost of parts made from polymer composite materials are associated with the quality of molding processes [7–10]. Depending on the geometric features of the parts, different forming technologies are used in their manufacture: pultrusion, vacuum infusion technology, pressure impregnation technology, winding, and others, however, the final operation, regardless of the forming technology used, is curing.

Glass fabrics are widely used as reinforcing materials, and epoxy materials are used as binders [11–17]. The process of their curing, in terms of resources expended (large energy consumption and duration), is one of the most expensive technological operations, especially if large-sized parts and products are made of fiberglass. Cost reduction (without loss of quality) is one of the priority areas of development.

Much attention is paid to the problem of studying the kinetics of the curing process [3; 18; 19], especially if the issues of developing a technology for molding multilayer, large-sized products of complex geometric shapes, in which the curing processes proceed unevenly, which leads to the occurrence of residual stresses and, as a consequence, to decrease in the strength of the composite structure. The main factor influencing the occurrence of thermal stresses is the uneven distribution of heat released during the curing process, and this is the main reason for the occurrence of temperature gradients and local overheating of the cured structure.

The purpose of this work is to develop a universal methodology for optimizing the technology of curing glass-reinforced plastics.

Objects and methods

As an epoxy binder, a composition based on epoxy resin ED-20 and isomethyltetrahydrophthalic anhydride as a hardener was used. The reinforcing material was fiberglass with a density of 2660 kg/m^3, its heat capacity and thermal conductivity were 1260 J/(kg·K) and 0.1 W/(m·K), respectively.

The curing mode is shown in figure 1. It is conditionally divided into four stages: heating before the start of the gelation process, holding at the gelation temperature until it is completed, heating to the desired curing temperature, which for the selected materials was 180°C, and holding at the desired curing temperature. The values of the temperature and time of gelation, depending on the rate of the heating process, were determined by the authors according to the method given in [18] and are indicated in table 1.

The site before gelation is indicated by number one. The area after the completion of the gelation process is indicated by number three. These two sections are used in the work as optimization parameters.

Heating, in these two areas, was carried out heating at different rates, changing it from 0.5°C/min to 5°C/min. In total, 25 variants of various technological regimes were considered (tab. 2).

Table 1

Temperature and gel time values

Heating rate, °C/min	Temperature gel time, °C	Gel time start, min
0.5	111	172
1	124	99
2	138	57
3	146	40
5	158	27

Table 2

List of options when optimizing the technological mode of curing

Heating rate in section III, °C/min (see fig. 1)	Variant numbers				
	heating rate in section I, °C/min (see fig. 1)				
	0.5	1	2	3	5
0.5	1	6	11	16	21
1	2	7	12	17	22
2	3	8	13	18	23
3	4	9	14	19	24
5	5	10	15	20	25

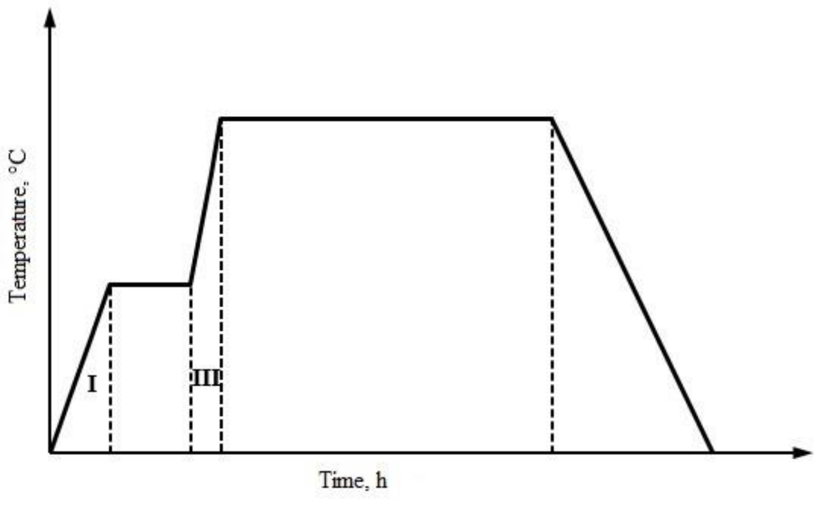
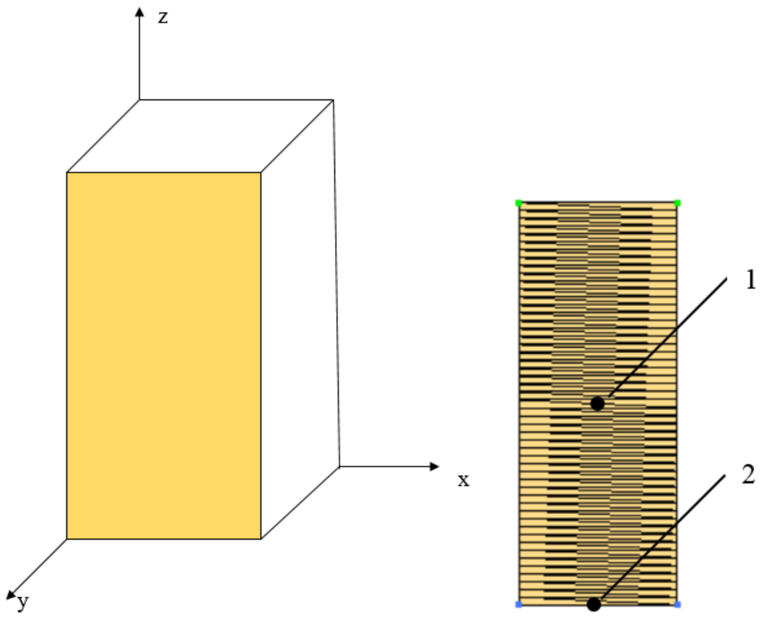


Figure 1. *Scheme of the technological process of curing, indicating the areas where heating is carried out*

To simulate the degree of curing of a fiberglass sample, the Arrhenius equation and the Kamal model were used, which made it possible to determine the kinetic parameters that were used further in the work when modeling heat transfer processes. The ESI PAM-RTM program was used to evaluate the kinetics of the heating and curing process. The temperature field of fiberglass was modeled considering the process of heat release during their curing at different heating rates. All calculations were carried out for a fiberglass sample 25x10x25 mm in size (fig. 2). The values of temperatures and the degree of curing were determined at two points: the center (point 1, see fig. 2b) and the surface (point 2, see fig. 2b).



a) b)

Figure 2. *Three-dimensional (1) and two-dimensional (b) models of fiberglass, built in the ESI PAM-RTM program, indicate the center of the sample (1) and its surface (2)*

Results and discussion

The optimization parameters are:

- V_1 heating rate in the 1st section (5 values, see table 2).
- V_2 heating rate in the 2nd section (5 values, see table 2).

Optimization criteria:

1. the average value of the temperature difference for the two considered sections (points 1 and 2, see fig. 2b) of sample $K_1(V_1,V_2) \to min$;
2. the maximum value of the temperature difference for the two considered sections (points 1 and 2, see fig. 2,b) of sample $K_2(V_1,V_2) \to min$;
3. the average value of the difference in the degree of curing for the two considered sections (points 1 and 2, see fig. 2b) of sample $K_3(V_1,V_2) \to min$;
4. the maximum value of the difference in the degree of curing for the two considered sections (points 1 and 2, see fig. 2b) of sample $K_4(V_1,V_2) \to min$;
5. the duration of the process $K_5(V_1, V_2) \to min$.

Five values of each of the optimization parameters V_1 and V_2 correspond to 25 alternative options for the technological process (see table 2), so in the 5-dimensional space of criteria there are 25 points Ai corresponding to all possible alternatives:

$$Ai(K_1\ (V_1,V_2);\ K_2\ (V_1,V_2),\ \dots\ ,\ K_5\ (V_1,V_2\ )),\ i = 1,2,\ \dots\ ,\ 25.$$

The choice of the optimal option is carried out in 2 stages:

- formation of a set of non-dominated alternatives (Pareto set);
- from the Pareto set, the optimal variant is selected using an additional criterion of the minimum distance to the ideal center (fig. 3):

$$min\{Ri\} = \sqrt{\sum}(Kj\ i - Kj)\ 2,\ 5\ j = 1\ i = 1,2,\ \dots\ ,\ 25.$$

Table 3 shows the simulation results for all selected parameters and optimization criteria.

Table 3

Results of modeling a fiberglass sample

No. option, see table 2	Optimization criteria				
	ΔT_a, °C K_1	ΔT_{max}, °C K_2	$\Delta\alpha$, % K_3	$\Delta\alpha_{max}$, % K_4	t, min K_5
1	4.2	7.1	1.1	6.2	396.7
2	4.8	9.8	1.3	5.6	332.8
3	5.5	10.7	1.7	5.7	286.0
4	5.9	18.2	1.8	11.0	287.5
5	6.4	37.1	1.9	17.6	288.3
6	7.0	14.2	2.2	12.5	273.0
7	8.2	14.2	2.7	11.7	222.2
8	8.1	-14.5	2.6	11.5	188.0
9	8.6	-15.5	2.5	11.4	181.0
10	9.1	-17.2	2.5	11.2	185.7
11	10.7	27.4	4.0	25.0	194.2
12	13.0	27.4	4.7	23.8	156.8
13	14.0	27.4	5.1	23.6	128.2
14	14.0	27.4	5.0	23.4	124.8
15	13.7	27.4	4.4	23.1	130.8
16	13.2	40.2	5.5	35.7	156.8
17	16.2	40.2	6.2	34.4	124.5
18	17.1	40.2	6.6	34.1	109.2
19	16.7	40.2	6.1	33.9	113.8
20	16.9	40.2	5.8	33.6	115.2
21	16.2	57.9	8.4	40.9	116.2
22	18.7	57.9	8.3	40.2	102.0
23	19.3	57.9	8.0	42.5	105.1
24	20.3	57.9	7.9	46.5	105.0
25	21.3	57.9	7.7	51.6	104.8

As a result of the calculations, it was found that for some modeling options, for example, options 2–5, the maximum temperature gradient occurs at the moment when the temperature on the surface is higher than the temperature in the center of the sample. The maximum temperature gradient occurs in the third section of the regime (see fig. 1).

For options 8, 9, and 10, the maximum values of temperature gradients are achieved provided that the temperature in the center is higher than the temperature on the surface of the sample.

For the remaining options, the maximum temperature gradient occurs in the first section, where the temperature on the surface is higher than the temperature in the center of the sample. The exothermic effects that occur during the curing process in the second and third sections equalize the temperature field of the sample

For options 14 and 15, although the heating rate in the first section is the same (2°C/min), the heating rate in the third section for option No. 15 (5°C/min) is higher than the rate for option No. 14 (3°C/min), however, the average value of the temperature gradient for option No.15 is lower than that for option No. 14.

To optimize the heating mode, calculations were carried out using the ideal point method and the value of R_i was determined (tab. 4).

Table 4

The values of the distance to the ideal point are obtained from the data in table 3

No. option according to table 2	1	2	3	4	5	6	7	8	9
R_i	294.7	230.9	184.0	185.9	189.1	171.3	120.6	86.6	79.7
No variant	10	11	12	13	14	15	16	17	18
R_i	84.6	96.5	61.8	38.9	36.6	40.4	71.3	50.7	46.1
No variant	19	20	21	22	23	24	25	-	-
R_i	46.7	46.9	64.8	63.2	64.6	67.2	70.5	–	–

As a result of calculations, it was found that the lowest R_A value was obtained for mode No. 14, R = 36.6, in which heating in section 1 is carried out at a rate of 2°C/min, and in section 3 at a rate of 3°C/min.

Conclusion

The technological process of curing samples of glass-reinforced plastics made by vacuum infusion technology based on an epoxy binder is considered, which consists of several stages: heating to the gelation temperature, holding at this temperature, heating to the curing temperature, holding at this temperature, and cooling.

Two stages of heating (before and after gelation) were used as optimization parameters. Five criteria were used as optimization criteria: average values of temperature gradients during the curing process, maximum temperature values, average values of the gradient of the degree of cure, maximum values of the degree of cure, and the total duration of the curing process.

The paper presents the results of calculating the optimal values of the rate of the heating process, performed by the ideal point method. As a result of the research, it was found that the lowest RA value was obtained for mode No. 14, R = 36.6, in which heating in section 1 is carried out at a rate of 2°C/min, and in section 3 at a rate of 3°C/min.

Acknowledgement

This work was carried out within the framework of the program of state support for the centers of the National Technology Initiative (NTI) on the basis of educational institutions of higher education and scientific organizations (Center NTI "Digital Materials Science: New Materials and Substances" on the basis of the Bauman Moscow State Technical University).

REFERENCES

1. Nelyub V.A, Frantsev M.E., Borodulin A.S. Technology for the production of small-tonnage ships from composite materials. M.: Publishing house BMSTU, 2021. — 219 p.
2. Maung P.P., Malysheva G.V. Elaboration of the technology of producing space antenna reflector // Polymer Science — Series D. 2017. 10(4). Pp. 364–367.
3. Baurova N.I., Zorin V.A. Technological heredity in the production of machine parts from polymer composite materials: monograph. M.: MADI. 2018. 220 p.
4. Baurova N.I. The use of polymer composite materials in the production and repair of machines: textbook / N.I. Baurova, V.A. Zorin. — M.: MADI, 2016. — 264 p.

5. Technology for the production of products and integral structures from composite materials in mechanical engineering // Scientific editors A.G. Bratukhin, V.S. Bogolubov, O.S. Sirotkin. — M.: Gotika, 2003. 516 p.

6. Nelyub V.A. Technologies of production of components electric transmission line supports from epoxy binders by the winding method // Polymer Science — Series D. 2013. 6(1). Pp. 44–47.

7. Nelyub V.A., Boroodulin A.S. Properties of epoxy materials used for production of glass-reinforced plastics by winding method // Polymer Science — Series D. 2018. 11(2). pp. 14–153.

8. Kobets L.P., Borodulin A.S., Malysheva G.V. Study of microcapillary impregnation of carbon fiber by epoxy binder // Fibre Chemistry, 2016, 48(4), pp. 311–315.

9. Maung P.P., Htet T.L., Malysheva G.V. Simulation and optimization of vacuum assisted resin infusion process for large-sized structures made of carbon fiber-reinforced plastic // IOP Conference Series: Materials Science and Engineering, 2020, 709(2), 022041.

10. Borodulin A.S. 2013 Plasticizers for epoxy adhesives and binders Polymer Science — Series D 6(1) pp. 59–62.

11. Nelyub V.A., Gorberg B.L., Grishin M.V., Berlin A.A., Malysheva G.V. Properties and technology of applying metal coatings to carbon tape // Fibre Chemistry. 2019, 50(6). pp. 524–527.

12. Sokolov G.S., Shakirov K.M., Nelyub V.A. New effective lubricants for continuous basalt fibers // Journal of Physics: Conference Series, 2021, 1990(1), 012043.

13. Konoplin A.Y., Baurova N.I. Hardness of the near-weld zone during contact spot welding of steels using an adhesive-weld technology // Russian Metallutgy (Metally). 2016. 13. P. 1308–1311.

14. Zorin V.A., Baurova N.I., Pegachkov A.A. Assessment of products risks of mechanical engineering by result of diagnosing // Periodicals of Engineering and Natural Sciences. 2019. 7(1). P. 287–293.

15. Baurova N.I. Surface structure of fractured carbon-fiber composites before and after climatic aging // Fibre Chemistry. 2014, 46(4). pp. 241–244.

16. Belov P.A., Borodulin A.S., Kobets L.P., Malysheva G.V. Kinetics of fiber impregnation by a binder. Gradient generalization of Navier-Stokes-Darcy equations // Polymer Science-Series D. 2016, 9(2). pp. 205–208.

17. Marycheva A.N., Guzeva T.A., Pe P.M., Tun L.K., Malysheva G.V. Reinforcing fillers for polymer composite based on organic unwoven materials // Polymer Science-Series D, 2019, 12(2). pp. 170–173.

18. Yangyang C., Malysheva G. Method for determining the rational ragimes of curing products from polymer composite materials // Materials Today: proceedings. 2019. 11. pp. 128–133.

19. Yanyan C., Nelyub V.A., Malysheva G.V. An investigation of the kinetics of the heating process for parts made of carbon fiber in the process for parts made of carbon fiber in the process of curing // Polymer Science-Series D, 2019, 12(3). pp. 296–299.

IV Международный форум
«Ключевые тренды в композитах: наука и технологии 2021»
(Москва, 2–3 декабря 2021 г.)

Материалы конференции публикуются в авторской редакции
Сетевое издание

Ответственный за выпуск — Алимова Н.К.

Вёрстка — Ватаман Е.С.

Научное издание

Системные требования:
операционная система Windows XP или новее, macOS 10.12 или новее, Linux.
Программное обеспечение для чтения файлов PDF.

Объем данных 3,9 Мб

Принято к публикации «14» декабря 2022 года

Режим доступа: https://izd-mn.com/PDF/67MNNPK22.pdf
свободный. — Загл. с экрана. — Яз. рус., англ.

ООО «Издательство «Мир науки»

«Publishing company «World of science», LLC

Адрес:

Юридический адрес — 127055, г. Москва, пер. Порядковый, д. 21, офис 401.

Почтовый адрес — 127055, г. Москва, пер. Порядковый, д. 21, офис 401.

https://izd-mn.com/

ДАННОЕ ИЗДАНИЕ ПРЕДНАЗНАЧЕНО ИСКЛЮЧИТЕЛЬНО ДЛЯ ПУБЛИКАЦИИ НА ЭЛЕКТРОННЫХ НОСИТЕЛЯХ