

PREPARATION OF REACTOPLASTIC NANO-MODIFIED POLYMER COMPOSITES. PART 5. ADVANTAGES OF USING NANO-MODIFIED STRUCTURAL CARBON-FIBER COMPOSITES (A REVIEW)*

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The characteristics of reactoplastic nano-modified polymer composites were analyzed using structural carbon-fiber prepregs as examples. The potential for application of structural carbon-fiber plastics in load-bearing elements was shown. A promising solution to the problem of surface modification of carbon-fiber plastics and polymer binders for improvement of the mechanical properties of the final product was to create a carbon-fiber-plastic combined filling in which a continuous carbon fiber was combined with a binder in which ultrafine carbon nanoparticles were uniformly distributed.

Keywords: reactoplast, polymer, technology, nanofiller, carbon fiber, composite.

The concluding part of the series (part 5) analyzes the preparation specifics for reactoplastic nano-modified (NM) polymer composites (PC) using the formation (from prepregs) of structural carbon-fiber plastics for load-bearing elements as an example.

The requirements imposed on construction materials used in load-bearing elements are high strength and rigidity, stability to dynamic loads, low mass, high durability [1, 2], thermal and corrosion resistance [3–5], and high reliability.

Carbon-fiber plastics made of thermoreactive matrices satisfy these requirements [1, 2]. NMPC with fibrous reinforcing fillers (e.g., carbon fibers) and a polymer binder (PB) containing nanoparticles are intended primarily for use in high-load and especially reliable items for the chemical, engineering, aviation, aerospace, and other industrial sectors [6, 7].

Plastics containing fiberglass, organic fibers, and carbon fibers characteristically have high compression strengths, elasticity moduli, and fatigue strength in addition to low creep, stable dimensions (due to low thermal coefficients of linear expansion), high chemical and radiation resistance, and good workability, in contrast with metals. This allows carbon-fiber plastics to be reworked on standard industrial equipment with low labor and energy costs.

Carbon-fiber plastics are used more and more in chemical and petrochemical equipment, including as materials for various types of pipelines. This is due exclusively to the high operational properties of such PC, especially if the load on the structural element or fitting is oriented in the direction of the carbon fibers. In this instance, the composites combine high specific strength, high elasticity modulus, and thermal strength.

High values of these parameters were achieved earlier mainly by increasing the characteristics of the reinforcing carbon-fiber filler. Carbon fiber is a nanocomposite in which nanocrystallites connected to each other by amorphous turbostratic carbon are oriented in a certain manner [8, 9]. Such fibers are characterized by exceptionally high strength (>700 MPa) and elasticity modulus (>60 GPa).

For Part 1, see No. 8 (2015); Part 2, No. 9 (2015); Part 3, No. 1 (2016); Part 4, No. 8 (2016).

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TABLE 1

| Physicomechanical properties | Structural carbon-fiber brand | | | | | |
|--|-------------------------------|---------|--------|--------|--------|----------|
| | KMU-11m | KMU-31n | KMU-4l | KMU-4e | KMU-5e | KMU-6-36 |
| Tensile strength $\sigma_t \cdot 10^{-1}$, MPa | 80 | 75 | 70 | 100 | 80 | 70 |
| Compression strength $\sigma_{cs} \cdot 10^{-1}$, MPa | 60 | 60 | 60 | 100 | 80 | 70 |
| Shear strength $\tau_s \cdot 10^{-1}$, MPa | 5.9 | 5.5 | 5.5 | 8.0 | 6.0 | 5.7 |
| Elasticity modulus $E \cdot 10^{-1}$, MPa | 14500 | 15000 | 14000 | 12000 | 12000 | 12500 |
| Fatigue strength $\sigma_{-1} \cdot 10^{-1}$ based on 10^7 cycles, MPa | 50 | 45 | 50 | 70 | 55 | 50 |
| Stress coefficient $K_{Ic} / 0.31$, $\text{MN} \cdot \text{m}^{3/2}$ | – | 68 | 126 | – | – | 94 |
| Maximum operating temperature, °C | 180 | 100 | 150 | 150 | 80 | 150 |

The elastic and strength parameters of a polymer matrix are typically an order of magnitude lower than those of carbon fiber. The parameters of the polymer matrices of structural carbon-fiber plastics can potentially be increased by modifying them with fullerenes C_{60} and C_{70} , their mixtures and derivatives, and fulleroid carbon nanoparticles (astralenes and carbon nanotubes (CNT)) [10–12]. For example, NTS astralene nanoparticles are added to the binder and carbon-fiber plastics during preparation of the binder used to produce the prepregs. The nanoparticles are dispersed by ultrasound (US) irradiation in the solvent used to prepare the binder to form a suspension of carbon nanoparticles [13]. The resulting suspension is mixed with the binder components and adjusted to the required concentration (of binder components and nanoparticles). Then, the carbon filler is soaked with PB containing astralene nanoparticles. The resulting prepreg is dried. Subsequent operations for preparing nano-modified carbon-fiber plastics are practically unchanged.

In 1980–1990, mainly unidirectional ribbons (width 215–280 mm) of LU-P (thickness 0.1 and 0.2 mm) and ELUR-P (thickness 0.08 and 0.1 mm) and Kulon VMN-4 and UKN-P carbon cords were used as reinforcing carbon fillers to produce high-strength and high-modulus carbon-fiber plastics [1, 2]. Carbon-fiber plastics made of carbon ribbons had tensile strengths up to 10^3 MPa; of UKN-P carbon cord, up to $1.6 \cdot 10^3$ MPa. However, their unstable properties (coefficient of variation up to 26%) were responsible for the increased scatter of the properties of carbon-fiber plastics made with cords. Oligomeric epoxide composites were used most often as polymer matrices of high-strength carbon-fiber plastics for load-bearing elements because of their availability, ease of reworking, and high adhesion and strength characteristics.

An extensive nomenclature of unidirectional carbon-fiber plastics was created (Table 1) [1].

The basic requirements imposed on construction materials are resistance to external operating factors and retention of this strength during the whole service life in addition to stable and reproducible properties (coefficient of variation of the properties should be <10% because otherwise the coefficient of safety of the construction would increase by 1.5–2 times according to calculated strength standards, which would make it impossible to decrease the construction mass).

Experience shows that the use of carbon-fiber plastics could reduce the construction mass by 25–50%; decrease the material consumption by 1.6–3.5 times; labor needs, 1.5–3 times; energy consumption, 8–10 times; and increase the service life by 1.5–3 times. Losses to corrosion are excluded [1, 2].

Carbon plastics with a combined filler. A promising solution to the problem of surface modification of carbon fibers and PB in order to improve the mechanical properties of the final item is the design of carbon-fiber plastics with a combined filler in which a continuous carbon fiber is combined with a binder in which ultradisperse carbon particles are uniformly distributed. It was found that crack migration in a composite with small disperse inclusions was associated with large energy expenditures [2]. The ultradisperse particles did not concentrate stresses (in contrast with larger particles). Incorporation of the particles did not help to order the polymer morphology. The ultradisperse particles could act as cross-linking centers of the polymer network (i.e., facilitate “healing” of network defects). The particles could agglomerate to form a three-dimensional framework in the NM PC bulk.

The high energy potential of ultradisperse carbon particles was responsible for their high modification efficiency [3]. This was due to the large fraction of atoms on the particle surface (compared with the fraction in the bulk) and the high specific surface area (up to 600 m²/g). However, this property led concurrently to aggregation of the nanoparticles.

A surfactant (SA) could disintegrate the nanoparticle aggregates. However, the formation of a SA layer could block the structural and energetic potential of an individual nanoparticle. Fullerene C₆₀ is soluble in organic solvents. However, this leads to the formation of solvates instead of stable dispersions.

Nanoparticles are difficult to distribute evenly because of not only their aggregation but also the tendency of the aggregates to settle in the liquid medium. US irradiation is an effective and available means to prevent sedimentation of carbon nanoparticles in viscous oligomers. The nanomaterial particles disintegrate at the same time. However, the US irradiation treatment must be limited in order to avoid mechanical destruction of the starting components.

In general, an improved process for producing NM carbon-fiber plastics includes: 1) preliminary finishing of the carbon fillers, e.g., with a solution of C₆₀ fullerene and its functionalized derivatives in an inert solvent; 2) disintegration of nanotubes (and/or astralenes) in the solvent using an immersed US emitter in cavitation modes; 3) preparation of an ultradisperse suspension of nanotubes (and/or astralenes) in liquid epoxide monomers and oligomers using US irradiation; 4) preparation of PB based on modified nanofillers, epoxide oligomer (EO), and hardener; 5) soaking finished carbon fillers with a prepared PB, i.e., prepreg preparation; 6) drying the prepregs at room temperature to remove the solvent; 7) cutting the prepregs and stacking them into packets according to the required reinforcement scheme; and 8) hardening of the prepreg packets using stepwise time and temperature regimes refined using the results of kinetic and rheological studies of the binders and prepregs [13].

The best results were achieved by fixing and binding the nanoparticles in the composite matrix by forming stable chemical bonds between them. The quality of the carbon-nanoparticle distribution affected the morphology of the carbon composite epoxide matrix [13].

The absolute value of elasticity modulus E of polymeric materials and the glass-transition temperature T_g are known to be determined by a combination of parameters such as the packing density of the macromolecules, the molecular mobility, the degree of intermolecular interaction, and the density of the chemical network. Changes in the structure and properties of the polymer in the boundary layers are important factors with moderate filling (substantially less than the percolation threshold) [14]. Changes in the properties caused by the filler surface can propagate up to 9 μm from the interface. Addition of CNT or fullerenes even at extremely low (<0.1 mass%) filler concentrations is expected to convert the whole polymer matrix bulk into the boundary-layer state whereas the matrix properties are changed considerably.

It was established that addition of >0.05% of carbon nanoparticles (fullerenes, nanotubes, astralenes) caused a complicated increase of the mechanical and operational properties of a material (for formation of NM carbon-fiber plastics), i.e., the compression and shear strength by 20%; impact strength, 45%; residual strength, 1.5 times; water- and fuel-resistance, 1.5–2 times; operating temperature, 30%; and service life, 1.8 times [15].

Promising structural carbon-fiber nanocomposites. VKU-18tr carbon-fiber nanocomposites [6] are prepared from ENFB-2M PB, balanced carbon cloth (Porcher Industries, art. 3692), and NTS astralene nanoparticles (0.5 mass% of the hardened matrix). The efficiency of modifying carbon-fiber plastics with astralene carbon nanoparticles is estimated by comparing their properties with those of an analog, i.e., KMU-4-2m-3692 carbon-fiber plastic based on the same components but without the astralene nanoparticles.

ENFB-2m binder is a high-strength thermally stable EO that is hardened by a latent hardener. The advantage of ENFB-2m is the hardening in a strictly determined temperature range. The shelf life of the binder and the prepreg based on it is one year at 20–25°C.

Balanced carbon cloth (Porcher Industries, art. 3692) with 2 × 2 broken twill weaving is fabricated from Tenax-E HTA5131 carbon cords (200 tex). The carbon fiber characteristics are tensile strength 4569 MPa with growth coefficient 4.49% and elasticity modulus 239 GPa with growth coefficient 1.3% [6].

Astralenes (multi-layered fulleroid carbon nanoparticles [7]) are promising nanofillers for carbon-fiber plastics and black-gray uniform powders. Astralenes are synthesized using a plasma-arc followed by physicochemical treatment. The carbon content is 99.99%; individual linear particle dimensions, 50–150 nm; bulk density, 0.6–0.8 g/cm³; pycnometer density, 2.0–2.2 g/cm³; graphene interlayer distance, 0.342 ± 0.00035 nm; pH of an aqueous suspension, 6.0–7.0; thermal

TABLE 2

| Property | Reinforcement direction | Material | | Improvement of carbon nanofiber properties, % |
|--|-------------------------|-------------------------------|------------------------------------|---|
| | | Carbon-fiber plastic VKU-18tr | Carbon-fiber plastic KMU-4-2M-3692 | |
| Tensile strength, MPa | [0°] | 780 | 750 | 4 |
| | [90°] | 600 | 550 | 8 |
| | [0°, 90°, ±45°] | 640 | 490 | 23 |
| Tensile elasticity modulus, GPa | [0°] | 65.4 | 64 | – |
| | [0°, 90°, ±45°] | 55.5 | 45 | – |
| Shear strength, MPa | [0°] | 768 | 700 | 10 |
| | [90°] | 660 | 600 | 10 |
| | [0°, 90°, ±45°] | 450 | 405 | 11 |
| Interlayer shear strength, MPa | [0°] | 46 | 42 | 10 |
| Shear strength in sheet plane, MPa | [±45°] | 93 | 82 | 13 |
| Operating temperature, °C | – | 170 | 120 | 42 |
| Tropical stability after exposure in a tropical chamber for 3 mo., percent retention of compression properties | [0°, 90°, ±45°] | 96 | 55 | 41 |

stability (temperature of extensive mass loss in air), $497 \pm 10^\circ\text{C}$; and specific electrical resistance at a pressure of 120 MPa, $<2.5 \cdot 10^{-4} \Omega \cdot \text{m}$.

Astralenes are characteristically anisotropic in shape with high surface energies and electrical conductivities and delocalized electron systems. The van-der-Waals force fields of astralenes affect all structural heterogeneities of the modified systems, including NM carbon-fiber plastics. Large easily polarized assemblies of electrons characteristic of asymmetric bulky fulleroid carbon clusters provide astralenes with the ability to find thermodynamically “comfortable” sites. These are structural defects (pores and breaks) in the NM carbon-fiber-plastic structure. The free energy associated with such sites helps to increase the thermodynamic stability of the system and the resistance to the effects of external forces or temperatures. Astralenes can act as nano-sized conducting and reinforcing elements and stop physical microcracks.

VKU-18tr NM carbon-fiber plastic is prepared by direct pressing or formation of prepregs in an autoclave with a final formation temperature of $175 \pm 5^\circ\text{C}$ and specific pressure of 0.7 MPa. The shelf life of the prepregs is six months at 20°C [6]. Table 2 lists the properties of VKU-18tr NM carbon-fiber plastic and KMU-4-2m-3692 carbon-fiber plastic [6].

Table 2 shows that several parameters of VKU-18tr NM carbon plastic are superior to those of the analog. Furthermore, NM carbon-fiber plastics are superior to the analog with respect to strength and elevated temperatures. The compression strength at 170°C of NM carbon-fiber plastic is greater by 54%; interlayer shifting, 32%; and bending, 20%.

The strength properties increase as the test temperature is increased from 10–15% at room temperature to 30–50% at 170°C .

The compression strength increases most significantly.

VKU-18tr NM carbon-fiber plastic retains higher strength characteristics as the temperature is raised. Thus, the NM carbon-fiber plastic at 170°C retains 75% of the strength at 20°C whereas KMU-4-2m-3692 carbon-fiber plastic retains only 45% of it. Also, the strength properties of KMU-4-2m-3692 carbon-fiber plastic decrease at a significantly faster rate as the temperature is raised. This is explained by the increased thermal stability of the hardened matrix if astralene nanoparticles are added to it. This increases the packing density of the molecules and the polymer matrix components and the number and strength of bonds between the nanoparticles and the polymer through van-der-Waals interactions [16].

Thus, the development of new economically efficient and technically advantageous methods for surface modification of carbon fibers and PB in order to improve the mechanical and other properties of NM carbon-fiber composites is a crucial problem for polymer materials science.

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