

# Highly filled elastomeric matrix composites: Structure and property evolution at low temperature carbonization

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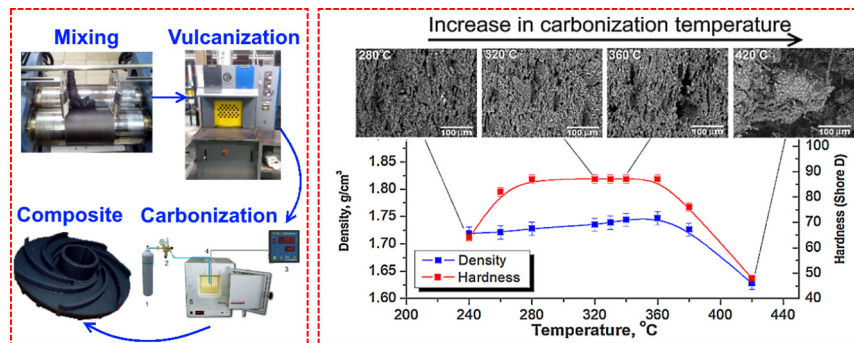
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## HIGHLIGHTS

- New inexpensive carbon composites are designed as competitors for CF-PEEK composites and Mg alloys
- Special compounding of rubber composites and further low temperature carbonization constitute the core of new approach
- Structure and properties evolution against carbonization temperature up to 420 °C is thoroughly studied
- Carbonization at 320–360 °C results in good engineering properties - strength, stiffness and maximum service temperature

## GRAPHICAL ABSTRACT



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## ABSTRACT

A new approach for the development of carbon composites via a low-temperature carbonization of elastomer compounds highly filled with various carbon fillers and dispersed SiC was systematically implemented. A new class of economically attractive carbon composites was purposely designed and relevant low-temperature carbonization approach was systematically applied for elastomer compounds highly filled with various carbon fillers and dispersed SiC. It was shown that carbonization in the range of 320–360 °C results in a combination of sound structure and optimal properties. The composites carbonized at 360 °C were thoroughly studied in terms of structure, mechanical and thermal properties. The values of the tensile and the flexural strength of the composites lie in the range of 65–85 MPa and 75–125 MPa, respectively. Positive effect of SiC fillers on the thermal expansion behavior of the carbonized composites was found. The coefficient of thermal expansion for SiC-containing composites was around  $20\text{--}35 \times 10^{-6}$  in the temperature range of 30–300 °C. Obtained combination of service properties assumes a range of applications in machine building and in the construction of high-demand mechanical parts.

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## 1. Introduction

The development of composites combining excellent mechanical, physical, thermal, and service performance is a world trend in modern materials science. The studies are widely addressed to polymer-matrix

composites based on polyphenylene sulfide, polysulfone, polyetheretherketone, and polyimide [1–4]. Full or partial carbonization of matrix polymers is a way to obtain high thermal resistant composites via the formation of bonds between thermally stable structure elements – initial reinforcing fillers and a newly formed matrix. A variety of polymers or phenolic resins having relatively high char yield may serve as precursors for carbonized matrix [5–8]. Well established methods for producing carbon materials (activated carbon) via pyrolysis in the

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complete absence of oxygen or any oxidizing agent (in an inert gas, such as nitrogen, helium or argon) in the temperature range of 400–700 °C are applied to break down the cross-linkage between carbon atoms [9–11].

We developed an approach for creating a class of new composite materials that are based on highly filled elastomeric matrices carbonized at relatively low temperatures. Principal technology was previously proposed by LLC “REAM-RTI” under the name “Karbul” for the production of products for submersible oilfield equipment. This approach targets low-cost production of high tolerance products made of heat-resistant composites that additionally provides complex shapes with almost no machining or finishing. This approach combines three principal underlying ideas: 1) application of elastomer matrices that allows high filling (potentially up to 90 wt%) easily using at standard or customized rubber mills; 2) molding or extrusion of above composites using precision molds that provides high dimensional tolerance in cured semi-products; 3) low temperature carbonization heat treatment that inherits high dimensional tolerance of cured semi-products and ultimately creates strong, heat resistant composite having carbonized matrix.

Intrinsically, carbonization of elastomers and rigid polymers assumes a series of thermochemical transformations caused by a certain sequence of holds at various temperatures. The resulting product is enriched in carbon having a re-organized structure due to the extraction of absorbed and chemically bonded water, partial destruction, cyclization of polymeric hydrocarbons, and a further release of gaseous compounds like CO, CO<sub>2</sub>, and others.

Various processes take place during carbonization in the different temperature ranges:

- Below 200 °C, softening of the binding polymer matrix and partial removal of moisture and light fractions do evolve;
- In the range of 100–300 °C, oxidative dehydropolycondensation unfolds at the interface of carbon fillers and binds the polymer matrix, and results in the removal of hydrogen;
- In the range of 270–280 °C, the primary destruction of the binding polymer matrix macromolecules (mainly in the side chains) and the formation and accumulation of free radicals begin;
- In the range of 350–500 °C both further destruction of the binding polymer matrix macromolecules and synthesis of the destruction products as well as polymerization of radicals (including those in gas phase) occur;
- At higher temperatures in the range of 500–550 °C, a semi-coke is formed due to the interaction of the radicals with the matrix residue.

Generally, two typical steps are distinctive: the exothermic depolymerization at temperatures above 280 °C with a release of gaseous products; the formation of cyclic aromatic compounds in coke residue at temperatures above 400 °C. Thermochemical reactions involving carbonyl and carboxyl groups and unsaturated carbon carbon bonds predominantly create an aromatic condensed carbon system at this step. The presence of oxygen and oxygen-enriched groups promote the formation of more dense materials as a result of carbonization [12].

The composite fillers are represented by carbon particles of various morphology such as carbon fibers, graphite, carbon black, shungite, and dispersed silicone carbide which allow obtaining a high-performance composite materials [13–19]. Additionally, we used silicon carbide (SiC) as a filler for the developed composites since SiC combines high thermal and wear resistance with high hardness [20–22].

Consistent implementation of this approach opens unprecedented opportunities for low-cost manufacturing of competitive high-temperature composites starting from cheap raw materials. The synergistic success of this approach is also caused by an application of conventional equipment and techniques of rubber industry and heat treatment. The composites developed along this approach constitute a specific class of materials filling the niche unoccupied by the competing

traditional materials up to now. The competitors belong to a number of material classes (synthetic graphite, SiC based ceramics, PEEK, PPS and PSU composites, Al and Mg alloys). In this article, we exemplify and discuss the properties of composites manufactured following the developed approach. We represent the results of the characterization of mechanical and thermal properties of carbonized elastomer matrix (CEM) composites reinforced with different carbon fillers including fibers and nanotubes.

## 2. Materials and methods

The nitrile-butadiene rubber (NBR) (BNKS-18AMN, Russia) was used as a matrix for compounding of highly filled composites. The raw compounds were fabricated using a rubber-mixing mill with a friction ratio 1: 1.25 with the temperature of leading and back rolls 30 and 35 °C, respectively. The filling degree for all the compounds was 300 parts per hundred rubber (PHR). Carbonization of the unfilled rubber and composites with lower fillers content is accompanied by significant shape changes and distortions of the experimental samples. While high filling degrees by all the used fillers reduce form alteration of the composites at carbonization providing the production of composites with the required sizes and shapes. In this paper, we used the rubber compounds having highest filling degree (300 PHR) at which it was possible to fill NBR and uniformly distribute fillers using mill mixing technique. The formulation of compounds prior the carbonization assumed the use of different carbon species reinforcing the matrix at different dimensional levels: from nanometer (carbon black) through micrometer (shungite and graphite) to millimeter (carbon fibers). The following fillers were introduced into a NBR matrix: silicon carbide (64C, Russia) with an average particle size of 3–5 μm, shungite fillers (Carbosil T-20, Russia) with an average particle size of 5 μm, chopped carbon fibers (UKN-5000, Russia) with an average length of 2 cm and average diameter of 6–7 μm, carbon black (P-234, Russia) with an average particle size of 25–30 nm (agglomerates size of 1–2 μm), and synthetic graphite powder (GMZ, Russia) with an average particle size of 40 μm. The full and uniform filling was reached as a result of 30 min mill mixing. Table 1 lists the designations and the compositions for the compounds studied.

The curing of the compounds was carried out in a plate mold (the resulting plate dimensions were 180 × 120 × 3 mm) at 170 °C for 10 min at a pressure of 3.5 MPa. The cured composites were carbonized in an argon atmosphere at a heating rate of 0.1–1.0 K/min up to 420 °C. Both elastomeric compounds and carbonized composite plates were mechanically cut to provide at least ten specimens for each composite. Density and water absorption were determined with analytical scales A&D GR-202 using hydrostatic weighing in distilled water according to ISO 1183 and ISO 62, respectively. The mechanical tests were carried out using a universal test machine Zwick/Roell Z020 equipped with 1 and 20 kN sensors and a contact strain measurement system MultiXtens. The tensile tests were conducted according to ISO 527 using dogbone samples to determine the tensile strength, Young's modulus and elongation at break. The flexural mechanical properties (flexural modulus and strength) were measured according to ISO 178 (three-point bending) for 120x10x3 mm samples with a span length of 80 mm. Charpy impact tests were carried out using an Zwick 5113 pendulum impact tester (7.5 J) according to ISO 179-1 for

**Table 1**  
The designation and composition of carbonized composite materials.

Designation	Shungite	SiC	Fillers content, PHR		
			Graphite	Carbon fibers	Carbon black
T2	300	–	–	–	–
T2-2	250	–	–	50	–
SiC-1	–	60	190	40	10
SiC-4	–	200	50	40	10

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