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Effect of carbon fibers on thermal properties and mechanical strength of ceramizable composites based on silicone rubber

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Abstract Ceramizable (ceramifiable) silicone composites are one of the most important elastic technical materials produced industrially. These composites are commonly used to increase flame retardancy of electrical cables and to ensure integrity of electricity network during fire by their ability to create a continuous ceramic structure. In this paper, ceramizable silicone composites filled with different contents of carbon fibers were tested. The research was focused on the characterization of ceramic structure created during heat treatment of the composites and thermal properties of the composites. For this purpose, morphology (SEM) and compression strength of the ceramic structures were studied. To describe process of ceramic structures creation, TG/DSC analysis was done. These tests have demonstrated that, the increase in carbon fibers amount improves the mechanical properties of ceramic structure regardless of heat treatment conditions.

Keywords Polymer composites · Ceramization · Ceramification · Silicone rubber · Carbon fibers

Introduction

Ceramization process has been already quite widely described in the literature. This process is characterized by creation of stiff, durable and porous ceramic structure from highly filled polymer composite during heat treatment. The created structure can block propagation of flames and decrease rate of flammable, caloric fuel production, created during thermooxidative destruction of polymer matrix, by preventing burning material from deeper penetration of oxygen. Because of high flammability of unfilled elastomer materials, composites destined for wire covers should contain effective flame retardants [1, 2]. One of the most efficient ways to assure required level of fire safety of cables is incorporation of large amount of filler mix promoting ceramization, which provide outstanding mechanical properties of mineral residue created during firing [3–9].

Creation of the ceramic structure can take place in several ways: (1) formation of a continuous and porous structure involving amorphous fluxing agent, which softens in elevated temperature and sticks thermally stable mineral particles together [10], (2) creation of silica connections between particles of mineral filler during thermooxidative degradation of silicone matrix [11, 12] and (3) creation of silicon oxycarbide (SiOC) ceramic phase due to deposition, crosslinking and volatilization of siloxane macromolecules on the surface of reinforcing silica particles dispersed in silicone matrix in the presence of platinum complex [13].

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In our previous research, we used B_2O_3 as a fluxing agent, ceramic, crystalline powder, which is characterized by melting point temperature (T_m) of 450 °C [14]. Low T_m value of B_2O_3 makes it effective fluxing agent, but its acidic and hydrophilic character can cause problems during compounding and processing of composites. Marosi et al. showed that also boro-siloxanes can be used as efficient fluxing agent even for organic polymers [15]. However, in present work, we decided to use glassy oxide frit containing large amount of Na_2O, which decreases its softening point temperature significantly. The use of this kind of frit makes compounding and processing of the ceramizable silicone composite much securer [16]. Mechanisms 2 and 3 are not as relevant as mechanism 1 from the point of view of ceramic structure strength, but their impact favors silicone rubber in role of continuous phase for ceramizable composites.

Selection of the appropriate fillers for ceramizable composite is extremely important, because chosen fillers, after polymer matrix degradation, serve as backbone of the ceramic structure. Mineral fillers can also increase flame retardancy of the composites by their endothermic decomposition, release of chemically bound water and formation of a layer of oxide that protects bulk of the composite against further thermal degradation [17]. Also

Table 1 Composition of the silicone composites studied

Components	Content/phr
Silicone pre-mix, Polsil MV-007 (30 phr of silica)	100
Mica	30
Fluxing agent	25
Carbon fibers	0, 1, 3, 5, 7
2,4-dichlorobenzoyl peroxide	2

size of filler particles influences mechanical strength of ceramic phase. Reduction in the average particle size allows for better dispersion of filler and increases the surface area of filler where silica or SiOC ceramic can be deposited. The size of filler particles also most often influences flame retardancy of polymer composites, smaller particles act in solid phase performing creation of more barrier char, increasing flame resistance [18]. On the other hand, with particle size decreasing, their ability to aggregation and agglomeration increases what can cause completely opposite effect, if the affinity between polymer matrix and the filler surface is poor [19].

Carbon fibers are becoming more and more popular. For example, recently Airbus, one of the biggest aircraft manufacturers, focused on application of carbon-fiber-
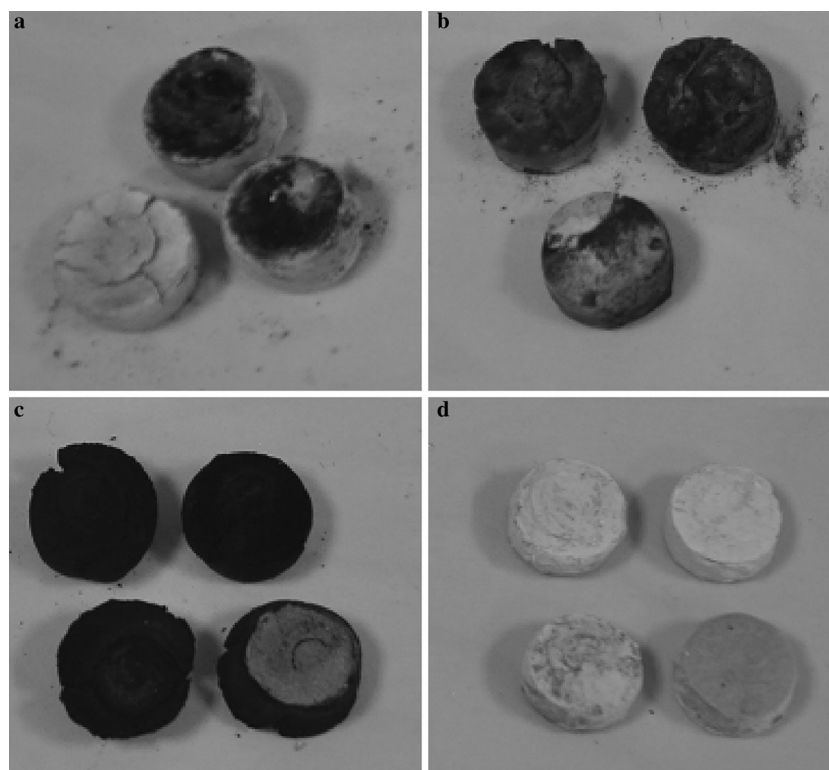

Fig. 1 Effect of heat treatment conditions on morphology and stability of dimensions of the silicone composite filled with 5 phr of carbon fibers. (**a** 600 °C/rapid, **b** 800 °C/rapid, **c** 1000 °C/rapid, **d** 950 °C/slow)

Table 2 Compression strength of the ceramized silicone composites studied

Carbon fibers content/phr	The average maximum force/N		
	800 °C	1000 °C	s950 °C
0	28.8 ± 7.6	46.7 ± 28.8	43.7 ± 18.6
1	90.1 ± 19.0	50.1 ± 16.0	44.1 ± 28.7
3	92.4 ± 48.4	126.5 ± 55.2	96.3 ± 49.0
5	144.3 ± 32.8	187.9 ± 90.3	147.2 ± 62.6
7	181.3 ± 23.6	175.3 ± 96.7	146.4 ± 61.4

s950 °C, slow heating; 800 °C, 1000 °C, rapid heating

reinforced thermoplasts in aircraft technology because of their excellent mechanical properties and ability to full recycling [20]. Carbon fibers exhibit tensile strength of 2800–5000 MPa [21]. Among others, carbon fibers are applied to production of high-quality laminates based on epoxy resin, which are widely used in building industry [22]. In medical field, carbon fibers are used as polymer reinforcement for composites utilized for orthopedic rails manufacturing [23].

In this paper, the influence of carbon fibers addition on properties of ceramizable silicone-based composites is presented. Thermal stability and ability to ceramic structure creation of composites filled with different amount of carbon fibers was examined, taking into account their micromorphology and mechanical strength.

Experimental

Materials

As an elastomer base, high-temperature vulcanizable silicone rubber (HTV) containing 0.07 % mol/mol of vinyl groups, produced by "Polish Silicones" Ltd., and reinforced by 30 phr (parts per hundred weight parts of rubber) of "Aerosil 200" (Evonik Industries) fumed silica was used. Mica phlogopite "PW30" [containing 40–42 % SiO_2, 20–26 % MgO, 10–11 % K_2O, 9–11 % Al_2O_3, 3–11 % Fe_2O_3 and 1–3 % other compounds (Minelco Minerals)] was used as a filler to enhance properties of ceramic structure. Glass frit FR-2050 (Reimbold und Strick; having a softening point temperature at 515 °C) was used as a fluxing agent in composite. This glass frit is a mix of oxides consisting of 27.1 % Na_2O, 6.8 % CaO, 1.7 % Al_2O_3, 64.4 % SiO_2. Carbon fibers (T-101T, Kreca), with elasticity modulus of 30 GPa, were used to improve mechanical properties of composites. 2,4-dichlorobenzoyl peroxide (50 % paste) was used as a curing agent.
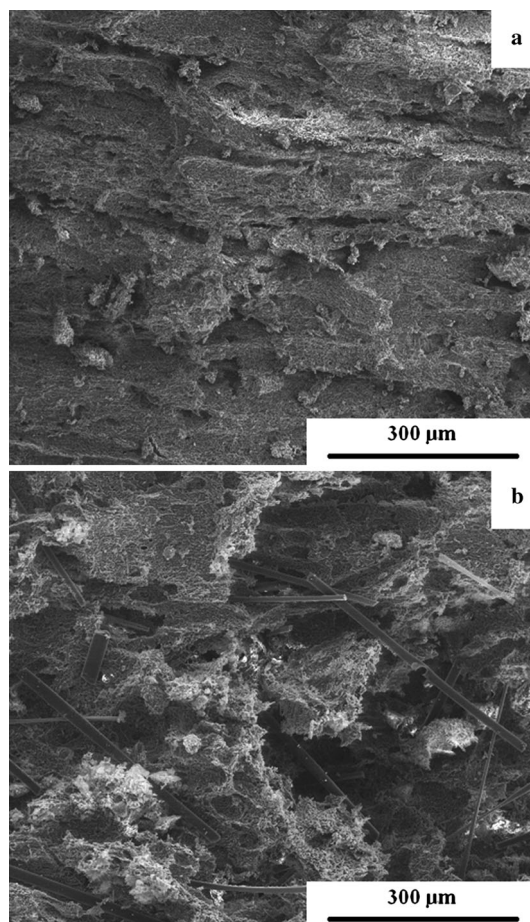

Fig. 2 Cross-section micromorphology (SEM) of silicone composite filled with 7 phr of carbon fibers, treated thermally in different conditions (**a** 950 °C/slow, **b** 1000 °C/rapid)

Preparation of the samples

Composite mixes (Table 1) were prepared by Brabender Plasticorder laboratory mixer (Germany), rotors operating with speed of 20 rpm (components incorporation phase, 10 min) and with 40 rpm (components homogenization phase, 20 min). Samples were vulcanized in electrically heated laboratory press, in steel molds, at 130 °C, during 10 min.

Techniques

Prepared mixes were vulcanized in form of cylindrical shape (height 14 mm, radius 16 mm). The samples were heated in two different conditions. In the first one, composites were heated from room temperature up to 950 °C (heating rate ∼8 °C min^{-1}); in the second method, samples were treated by placing in previously heated furnace up to 600, 800 or 1000 °C and left for 20 min. After that,

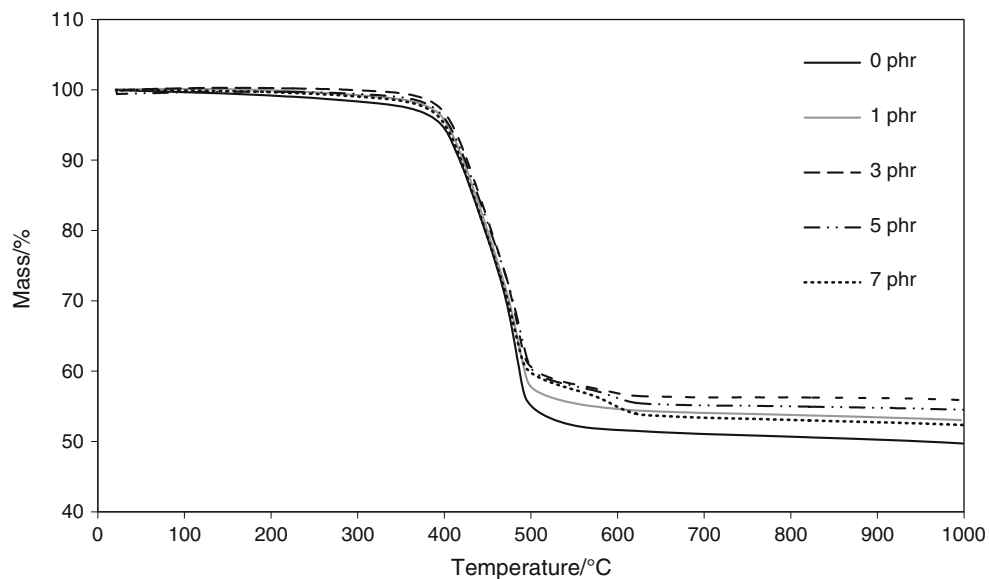**Fig. 3** TG analysis of the samples studied
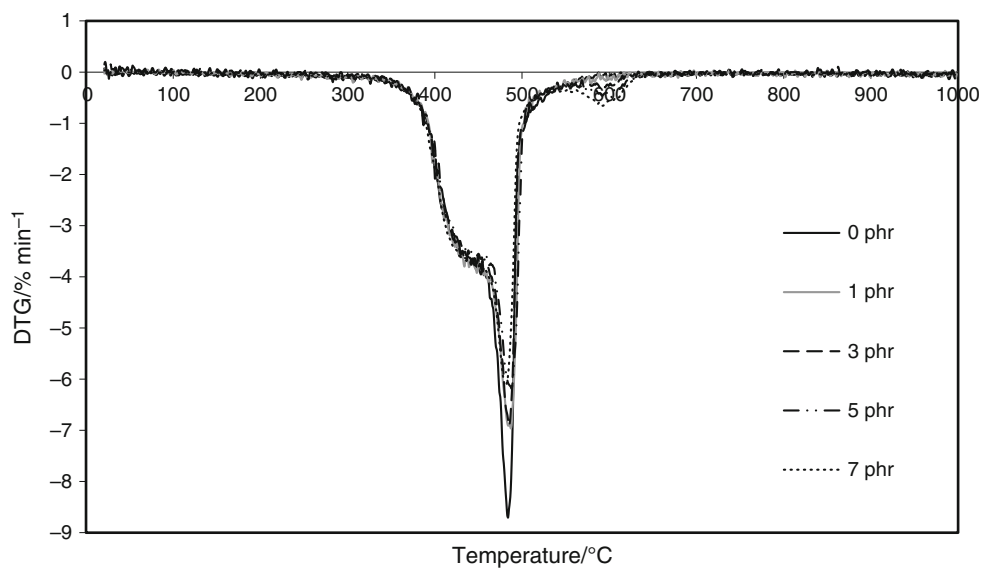

**Fig. 4** DTG analysis of the samples studied

Table 3 Parameters of thermooxidative decomposition of the samples

Carbon fibers content/phr	Maximal degradation rate/% min^{-1}	First exothermal maximum/mW mg^{-1}	Second exothermal maximum/mW mg^{-1}	Amount of ceramic char/%
0	−8.70	1.13	None	49.7
1	−6.96	1.86	0.61	53.0
3	−6.91	1.90	0.92	55.9
5	−6.18	1.83	1.03	54.5
7	−6.13	1.97	1.24	52.4

Fig. 5 DSC analysis of the samples studied
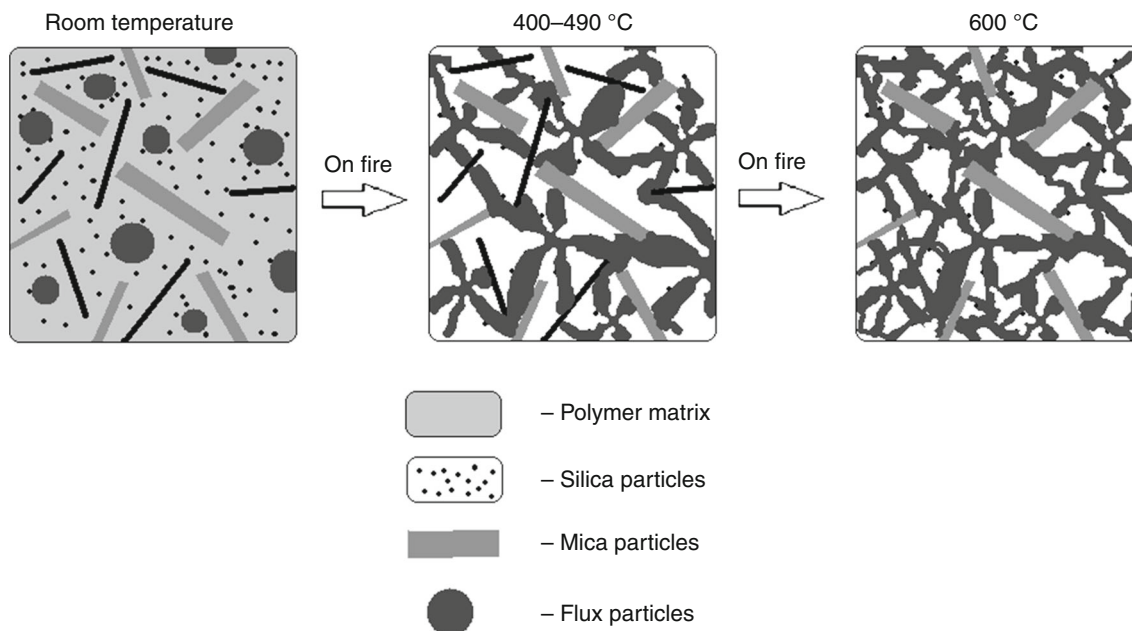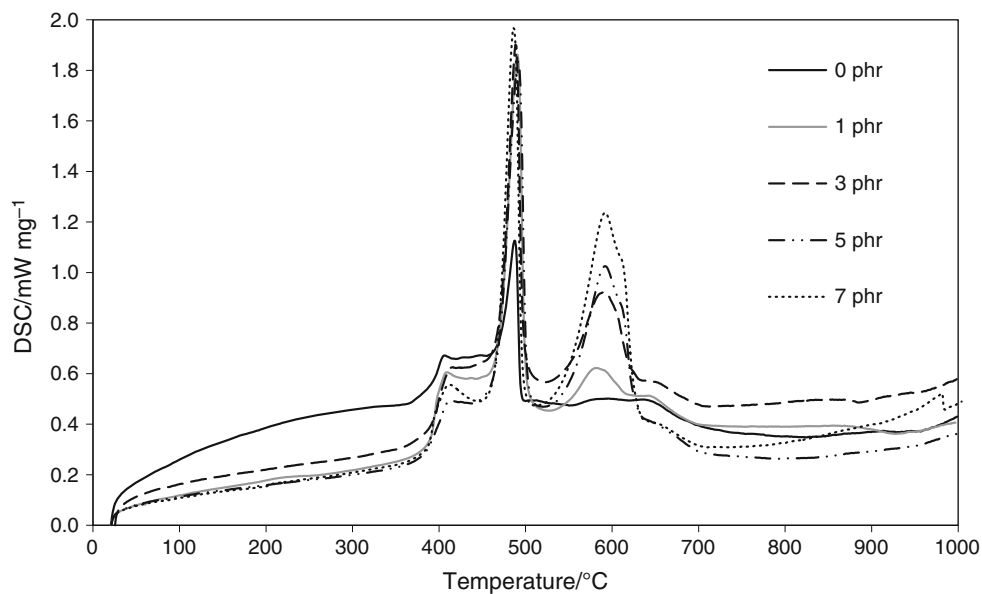
Fig. 6 Scheme illustrating ceramization process of silicone composites filled with carbon fibers

samples were subjected to compression test by means of Zwick Roell Z2.5 apparatus (Germany). Average values of maximal force required to crush the samples were calculated from three samples measurement.

Micromorphology of ceramized samples was examined by means of FEI Nova Nano SEM 200 scanning electron microscope (UK).

Thermal stability of the composites was determined by means of Netzsch STA 449F3 Jupiter (Germany) TG-DSC device. All samples were heated from room temperature to 1000 °C with the heating rate of 10 °C min^{-1} under air atmosphere (mass of the samples: 0 phr—18.0 mg; 1 phr—21.3 mg; 3 phr—16.7 mg; 5 phr—19.8 mg; 7 phr—20.4 mg).

Results and discussion

Ceramization of the composites

The photographs presented in the figure one illustrate the composites after different kinds of ceramization. Samples

heated fast, by placing in furnace previously heated up to 600, 800 or 1000 °C, exhibit irregular cracks, shape-changes and appearance of black powder, which is most probably carbon black-char created as a result of rapid crosslinking and carbonization of silicone rubber exposed to very high temperature. The amount of carbon char visibly increases with the rise in furnace temperature. Samples heated slowly up to 950 °C show higher dimensional stability and integrity (lack of cracks) than other samples. What is more, less severe conditions of heat treatment resulted in lack of organic carbon char (Fig. 1).

Properties of ceramic phase after heat treatment

Compression strength of the composites depends on the heat treatment type and temperature, as well as content of carbon fibers. The results of compression strength test are shown in Table 2.

Not all composites were able to create a strong ceramic structure at 600 °C because of too low temperature of treatment. In higher temperatures, robust ceramic structures were created. Compression strength of the studied samples increases significantly with an increase in carbon fibers. The highest increase in compression strength was obtained after rapid treatment in 800 °C, where sample filled with 7 phr of carbon fibers exhibited over 6 times higher strength than unfilled reference sample. This considerable increase in compression strength value is a result of reinforcing properties of unburned carbon fibers present in ceramic structure even after 1000 °C, 20-min heat treatment (Fig. 2b). The significant percolation threshold of mechanical properties increase can be observed for 800 °C, 20-min treatment after addition of 1 phr of fibers, for 1000 °C, 20-min treatment after addition of 3 phr of fibers and for 950 °C slow treatment after incorporation 5 phr of fibers. Addition of 7 phr of carbon fibers does not enhance compression strength of the composite in comparison with the sample filled with 5 phr of the fibers. Samples, which were subjected to a slow heat treatment, show enhanced compression strength, even without the presence of carbon fibers in the composites structure (Fig. 2a).

Thermal properties of composites

The above result can be explained by DSC analysis, which shows additional, exothermal effect for samples containing carbon fibers, around 600 °C, being result of carbon fibers firing (Fig. 5). Additional amount of heat, provided over temperature of fluxing agent softening point, was probably consummated on decrease in fluxing agent viscosity, which resulted in more efficient bonding of mica flakes and silica particles created by silicone matrix firing (Fig. 6).

TG/DTG analysis shows that addition of carbon fibers enhances thermal stability of ceramizable composites with an optimal amount of 3 phr (Figs. 3, 4). Amount of ceramic, protective char created after thermooxidative degradation of this sample equals 55.9 % (Table 3). The beginning of the siloxane matrix degradation starts at roughly 400 °C. At ca. 490 °C, the samples undergo maximal degradation rate, which decreases with an increase in carbon fibers content. However, addition of carbon fibers also increases the amount of heat generated during thermooxidative degradation of the samples (Fig. 5). Addition of even 1 phr of the fibers resulted in a significant increase in first exothermal peak value, though this value is independent of amount of carbon fibers in the composites. The increase in first exothermal peak is probably an effect of carbon fibers surface oxidation. Second exothermal peak, present at ca. 600 °C, is an effect of carbon fibers firing, and its value increases with an increase in the fibers content. Heat released from carbon fibers burning additionally enhances mechanical properties of the ceramic residue structures (Fig. 6).

Conclusions

The results of this study show that addition of even relatively low amount of carbon fibers can successfully enhance mechanical properties of ceramic char structure, what is very important from the point of view of ceramizable cable covers utilization. Ceramic phases, which were formed from silicone rubber composites, exhibit even several times higher compression strength after addition of carbon fibers. Combustible fibers emit additional heat during slow thermal treatment, which allows the fluxing agent to create stronger bonds between the mica and silica particles. After rapid heat treatment, most of the fibers remained unburned and they reinforced the ceramic structures significantly. Moreover, thermal stability of the composites filled with the fibers was enhanced, with an optimum for the sample containing 3 phr of carbon fibers. On the other hand, addition of flammable carbon fibers increases summary amount of heat generated during thermooxidative degradation what can accelerate spreading of fire. However, in situation when maintaining of integrity of an electric network plays a major role, the addition of carbon fibers can increase safety of the network significantly.

Additional information

Ceramizable silicone composites presented in this publication are subject of Polish Patent Application No. P.411011.

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