SIZE DEPENDENT ELECTRICAL PERCOLATION THRESHOLD AND ELECTRICAL TRANSPORT IN ONION-LIKE CARBON BASED COMPOSITES

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Abstract
Results of dielectric investigations of onion-like/polydimethysiloxane composites in very wide frequency (20 Hz – 3 THz) and temperatures (26 – 300 K) ranges are presented. The percolation threshold in these composites is strictly dependent from OLC aggregate size and it is lower for composites with bigger OLC aggregates. The electrical conductivity in the composites occurs mainly due electron tunneling between OLC clusters and quasi-one-dimensional hopping inside the clusters. The hopping almost vanish at frequencies above 100 GHz were phonon contribution dominates.

1. Introduction

Electrically percolative polymer-based composites have been attracting much attention because of their potential applications such as electroactive materials, sensitive materials, and electromagnetic coatings. In these composites an electrical percolation occurs at some critical concentration (called as percolation threshold) of fillers [1]. It is an important task to reach lower as possible percolation threshold in order to preserve optimal mechanical properties of polymers and to use lower as possible concentration of expensive fillers. Probably, the lowest percolation threshold was observed in carbon nanotubes composites due their high aspect ratio [2]. Nevertheless, the percolation threshold in other composites, for example in carbon black composites, can be also very low [3]. On the other hand the percolation threshold in nominally the same polymer matrix and for the same carbon nanotubes can be very different [2]. This suggests that the percolation threshold is strongly influenced by composite preparation technology. Moreover, a drawback of carbon nanotubes is their higher cost in comparison with other carbon allotropes, such as carbon black or graphite. Another serious disadvantage is the possible toxicity of CNTs, which has been debated for long [4], and which is still controversial today.

The onion-like carbons (OLCs), consisting of stable defected multishell fullerenes, exhibit high conductivity similar to carbon nanotubes [5]. However, most investigations of the dielectric properties of OLC-based composites, both theoretical and experimental, were performed below the percolation threshold, where the complex dielectric permittivity of composites increases slowly with OLC concentration, according to the Maxwell-Garnett theory [6]. In this case, it was demonstrated that the electrical polarizability is weakly dependent on the geometry of OLC molecules and chiefly proportional to the volume of the whole cluster [7]. Nevertheless, these investigations did not take into account the electrical conductivity of OLC and Maxwell-Wagner polarization effects, which usually appear in conductive composites [8]. Therefore, these conclusions are valid mainly below the percolation threshold. It was also find that percolation threshold in OLC composites is 15 wt % for polyurethane composites with mean aggregate size 130 nm [9]. The aggregate structure of conductive particles has strong impact on the composite dielectric/electric properties and percolation threshold and for some carbon black composites the effect was explained by aggregate structure model [10]. Onion-like carbons, similarly as carbon black, have a complex aggregate structure [5], however it influence on composite dielectric properties up to now not was investigated.

In this work we have investigated how further reduce percolation threshold in onion-like carbon composites. The search of electrical percolation was performed in composites with polymer matrixes Polydimethylsiloxane (PDMS) with different sizes OLC aggregates. It will be demonstrated that the lowest percolation threshold was obtained in OLC/PDMS composite with big OLC aggregates (250 nm and 100 nm).

2. Experimental

The OLC sample used to fabricate OLC/PDSM composite films was prepared as follows: NDs were obtained by explosion of TNT/RDX in a CO_2 atmosphere and oxidized in concentrated sulfuric acid and chromic anhydride at 110 °C, washed with water, and dried. NDs were fractionated by centrifugation down to 40 and 250 nm volumetric average size of the aggregates (when measured in water suspensions). NDs with 250nm, 100 nm and 40 nm average aggregate size were heated in vacuum (10^{-2} Torr) at 850 °C for 3 h. Then the sample was heated in vacuum (10^{-4} Torr) at 1800 K for 3h. The average size of OLC aggregates also was approximately 250 nm, 100 nm and 40 nm, correspondingly. The polydimethyl siloxane, Sylgard, was purchased from Dow-Corning as a two part material. When forming PDMS-OLC composites, an intermediate solvent was employed that served as a dispersion medium for the nanoparticles prior to mixing with the polymer matrix. The nanoparticles were dispersed in the solvent and sonicated to break up large agglomerates, then the suspension was combined with uncured PDMS and the solvent subsequently removed by vacuum. Curing of the PDMS-nanoparticle mixture at 60^{o}C for 2hrs and 40^{o}C overnight resulted in films with good nanoparticle dispersion.

Complex dielectric permittivity was measured as a function of frequency and temperature using an HP4284A precision *LCR* meter in the frequency range 20 Hz–1 MHz. For low temperatures measurements was used a helium closed cycle cryostat. Each measurements starts from room temperature. In frequency range 1 MHz–3 GHz dielectric measurements were performed by a vector network analyzer Agilent 8714ET. In microwave frequency range from 8 to 53 GHz a home-made waveguide spectrometer was used. The method of thin road in waveguide was used [11]. Silver paste has been used for contacting. In terahertz frequency range (from 100 GHz to 3 THz) a terahertz time domain spectrometer (Ekspla Ltd) based on femtosecond laser was used for measurements. The real part of complex electrical conductivity σ' was calculated via $\sigma' = \varepsilon_0 \varepsilon''$, with ε_0 being the permittivity of vacuum.

3. Results and discussion

3. 1 Room temperature dielectric properties

The frequency dependence of the room-temperature real parts of complex dielectric permittivity ε^* and complex electrical conductivity σ^* of PDSM composites with different OLC (250 nm aggregate size) concentrations is shown in Fig. 1. The complex dielectric permittivity ε^* and conductivity σ, for composites with $p \leq 5$ wt%, here *p* is OLC weight fraction, are very low; its values are similar to pure PDMS values. However, dielectric permittivity starts to increase for composites with 8 wt% inclusions. At low frequencies (below 1 kHz) DC electrical conductivity plateau is clearly expressed in conductivity spectra of composites with 8 wt% inclusions. It denote that percolation threshold is 8 wt% in OLC/PDMS composites with 250 nm OLC inclusions. The dielectric permittivity and electric conductivity are very high for composites with 10 wt % of OLC inclusions at low frequencies, the dielectric permittivity is in order of 10^3, and the electric conductivity is about 0.001 S/m. Nevertheless, the electric conductivity value at low frequencies is as small as corresponding value of the pure OLC typical value being of order 10^2 S/m [5]. The complex dielectric permittivity value is very similar to the complex dielectric permittivity of functionalized carbon nanotubes nearly percolation threshold [12]. An additional increase of dielectric permittivity with the decrease of frequency below 129 Hz is obviously due to Maxwell – Wagner contribution to dielectric permittivity [8]. In middle frequency range 129 Hz–1 kHz the dielectric permittivity and electric conductivity are almost frequency independent. When frequency increases above 1 MHz, dielectric permittivity decreases and electrical conductivity increases according to the Jonscher universal power law [13]. The loss tangent is also very high at low frequencies, indicating a high absorption ability of electromagnetic waves by composite with 10 wt % of OLC.

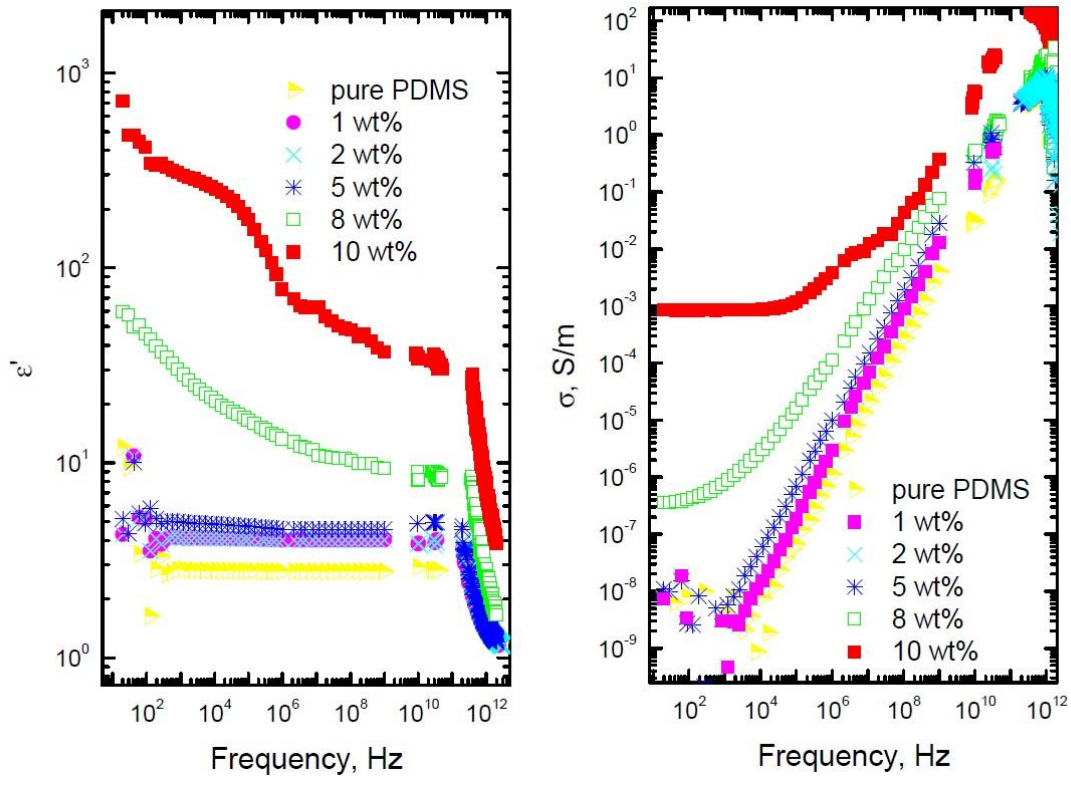

Figure 1. Frequency spectra of real parts of complex dielectric permittivity and electrical conductivity of OLC/PDSM (with 250 nm OLC inclusions) composites at room temperature.

In order to see more precisely influence of OLC concentration and aggregate size, the dielectric permittivity and electrical conductivity at frequency 129 Hz and room temperature for all investigated composites are plotted as concentration function (Fig. 2). Note, that in the frequency spectra of composites with 250 nm and 100 nm aggregate size OLC inclusions (concentrations 10 wt%, 8 wt%) and 40 nm aggregate size (concentration 10 wt%) at lower frequencies is observed a frequency independent DC plateau, so that the conductivity at 129 Hz and at room temperature for these composites coincide with DC conductivity. Therefore percolation threshold is 8 wt% for composites with 250 nm and 100 nm OLC aggregates inclusions and 10 wt% for 40 nm OLC aggregates inclusions. Below percolation threshold the dielectric permittivity ε' at 129 Hz was fitted according to classical law [14]:

$$\varepsilon' = \varepsilon_m \left(\frac{p_c - p}{p_c}\right)^{-q}, \quad (1)$$

here ε_m is the dielectric permittivity of polymer matrix, p_c is the critical mass fraction, q is the critical index. Obtained parameters are ε_m=2.55 for all type OLC, p_c=8 wt% for 250 nm and 100 nm OLC aggregates, p_c=10 wt% for 40 nm OLC aggregates, and q=1.35 for 250 nm OLC aggregates, q=1.25 for 100 nm OLC aggregates and q=1.04 for 40 nm OLC aggregates.

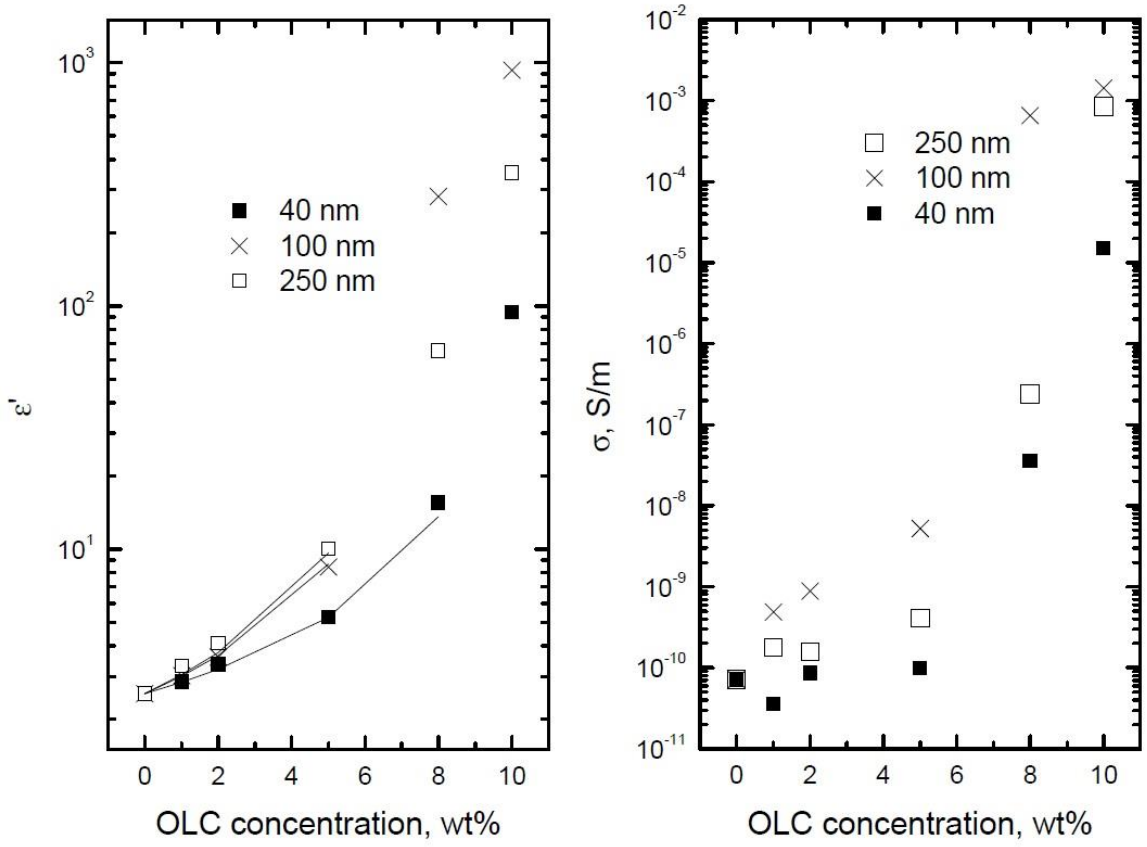

Figure 2. Real parts of the complex dielectric permittivity and the complex electrical conductivity of OLC/PDSM composites vs OLC concentration and aggregate size at frequency 129 Hz and room temperature.

Close to percolation threshold percolation theory predicts an exponent close to 2 in any three-dimensional medium [14]. So, obtained values of critical index are in good agreement with percolation theory. Nevertheless, the critical mass fraction is lower than should be expected from theory. Indeed, according to percolation theory for the two phase random composite whose fillers are spherical the percolation threshold should be about 0.16 (volume fraction) [14].

3.2 *Electrical conductivity at low temperatures*

At low temperatures the value of real part of complex dielectric permittivity and electrical conductivity increases on cooling and have a maximum close to temperature (250 K) of glass transition of pure PDSM matrix. The behavior can be explained by rapid shrinkage of PDSM matrix on cooling down to glass transition temperature. A similar behavior was observed also in other polymer composites [15].

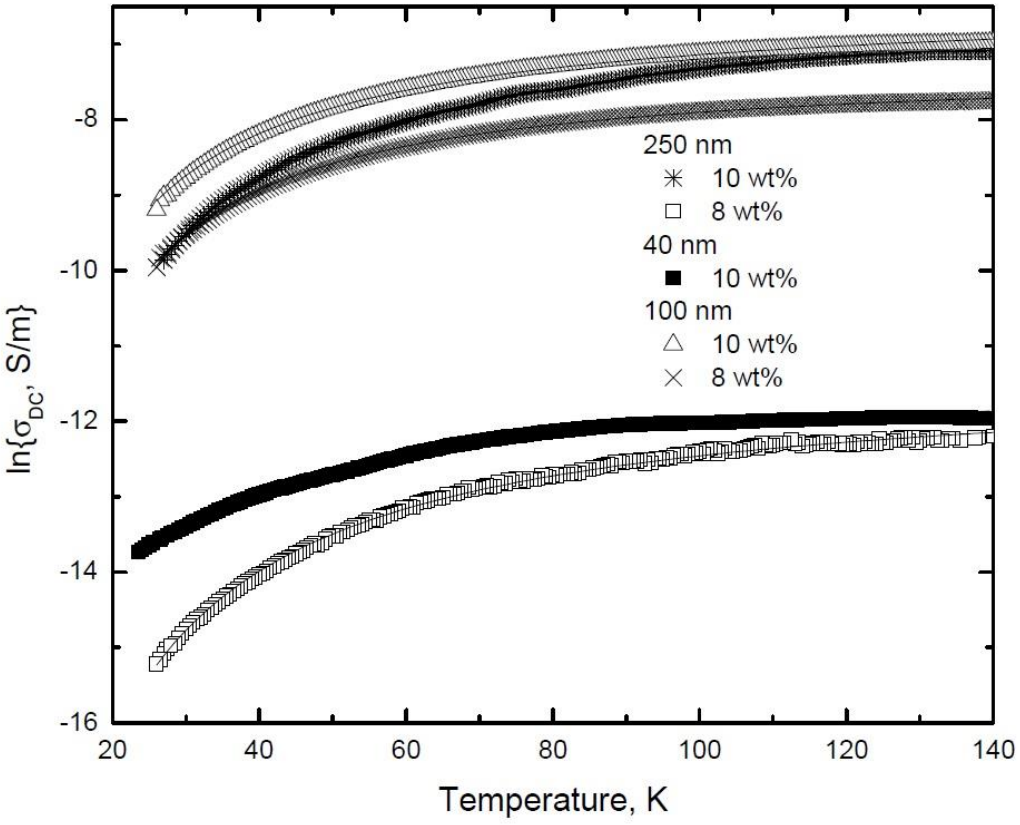

Figure 3. Temperature dependence of OLC/PDSM composites DC conductivity with tunneling law fit.

However, at low temperatures (below 170 K) both real parts of complex dielectric permittivity and complex electrical conductivity decrease on cooling. The frequency spectra of conductivity were fitted with the fundamental equation:

$$\sigma=\sigma_{DC}+A\omega^{s}. \quad (2)$$

Obtained parameters are presented in Figs. 3 and 4.

Table 1 Tunneling model fit parameters for DC conductivity at low temperatures

OLC type	Concentration, wt%	σ_{dc0}, S/m	T_1, K	T_0, K
250 nm	10	1.9 mS/m	110	4.2
	8	11.8 μS/m	115	3.7

100 nm	10	1.6 mS/m	75	2
	8	8.16 mS/m	83	5
40 nm	10	11.5 μS/m	70	5.2

For temperatures below 170 K, the dc conductivity data fit well to the fluctuation induced tunneling model, as one can be see in Fig. 3. [16]:

$$\sigma_{dc} = \sigma_0 \exp(-(T_1/(T+T_0))), \quad (2)$$

where T_1 represents the energy required for an electron to cross the insulator gap between conductive particles aggregate, and T_0 is the temperature above which thermally activated conduction over the barriers begins to occur.

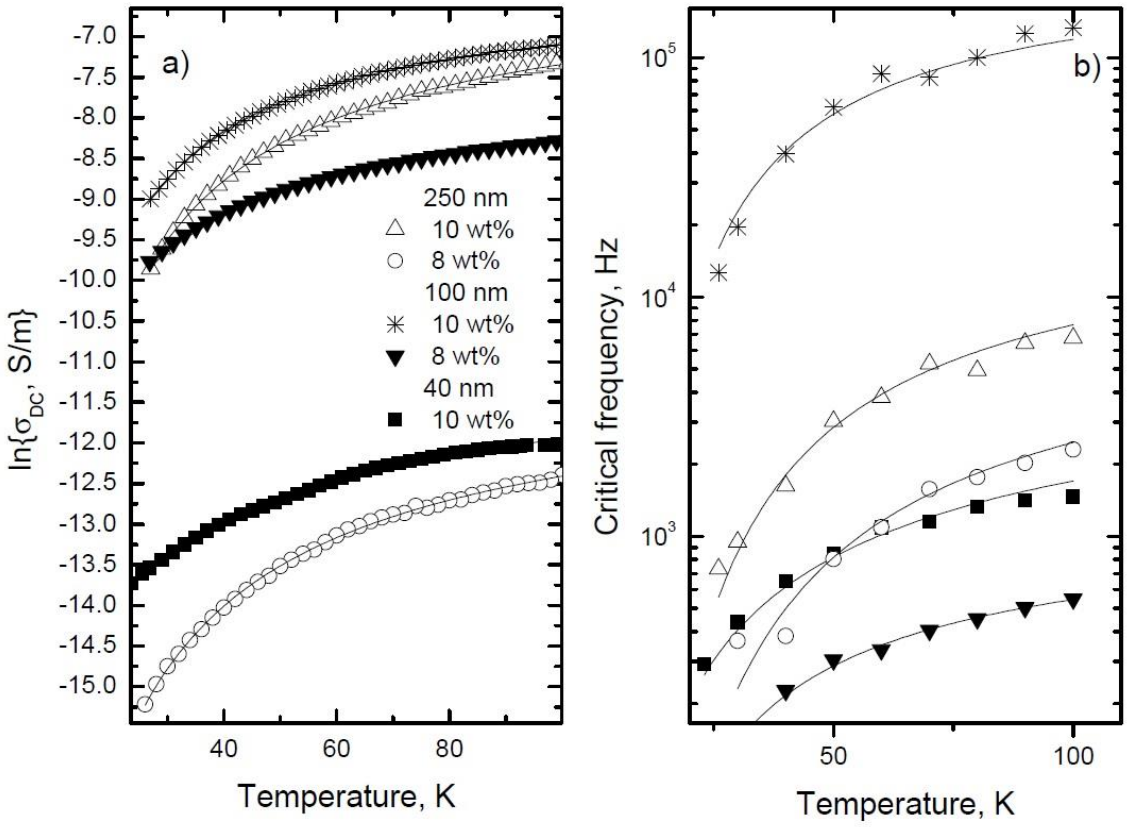

Figure 4. Temperature dependence of OLC/PDSM composites DC conductivity a) and critical frequency b) with Mott law fit.

However, below 100 K temperature not only DC conductivity but also the shape of conductivity spectra is temperature dependent (Fig.4). It denotes that critical frequency is also temperature dependent.

According to the tunneling model [16],

$$T_1=wA\beta_0/8\pi k, \quad (3)$$

$$T_0=2T_1/\pi\chi w, \quad (4)$$

where $\chi=(2mV_0)^{0.5}/h$ and $\beta_0=4V_0/ew$, m and e being the electron mass and charge, respectively, V_0 is the potential barrier height, w is the interparticle distance (gap width), and A is the area of capacitance formed by the junction. Obtained parameters are listed in Table 2. From Eqs. (6) and (7) follows that T_1/T_0 is proportional to gap width w, which is approximately proportional to $p^{-1/3}$ [17]. Thus the ratio T_1/T_0 should decreases with OLC concentration, as is observed in our composites.

Table 2 Mott law fit parameters for DC conductivity at low temperatures

OLC type	Concentration, wt%	σ_{dc0}	T_M, K	n	f_∞, kHz
250 nm	10	2.3 mS/m	130	1.19	26
	8	21.2 μS/m	196	1.35	12.7
100	10	1.8 μS/m	75	1.04	252
	8	6.7 mS/m	97	1.38	1.4
40 nm	10	51.1 μS/m	521	2.28	13

We assumed that the temperature dependence of dc conductivity at lower temperatures (below 100 K) can be fitted by the general Mott expression for variable range hopping [17]:

$$\sigma_{dc=}\ \sigma_0\exp(-(T_M/T)^{1/n}), \quad (8)$$

where T_M is a constant depending on the density of state and localization length of the system, n=1+d (d is dimensionality of the system). A similar behavior valid also for the critical frequency f_{cr}:

$$f_{cr=}f_{cr\infty}\exp(-(T_M/T)^{1/n}), \quad (9)$$

where $f_{cr\infty}$ is frequency at very high temperatures. Obtained parameters are summarized in Table 2. It follows that at low temperatures quasi-one-dimensional electron hopping occurs inside OLC clusters.

4. Conclusions

Dielectric properties of OCL/PDSM percolative composites were investigated in very wide frequency (20 Hz – 3 THz) and temperature (26 K – 500 K). The lowest percolation threshold was observed in composites with big OLC agglomerates (250 nm and 100 nm) – 8 wt%. The value of complex dielectric permittivity and electrical conductivity of composites above percolation threshold is very high, similarly to carbon nanotubes or carbon black composites. The dielectric/electric properties of composites are mainly governed by electron tunneling between OLC clusters and electron hopping in quasi-one-dimensional chains inside clusters.

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