Effect of Carbon Nanotube Pre-treatment on Dispersion and Electrical Properties of Melt Mixed Multi-Walled Carbon Nanotubes / Poly(methyl methacrylate) Composites

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Abstract: Multi-walled carbon nanotubes (MWNTs) pre-treated by concentrated mixed acid or oxidized at high temperature were melt mixed with poly(methyl methacrylate) (PMMA) using a twin screw extruder. The morphologies and electrical properties of the MWNT/PMMA composites were investigated. The thermally treated MWNTs (t-MWNTs) were well dispersed, whereas the acid treated MWNTs (a-MWNTs) were highly entangled, forming large-sized clusters. The resulting electrical properties of the composites were analyzed in terms of the carbon nanotube (CNT) dispersion. The experimental percolation threshold was estimated to be 3 wt% of t-MWNTs, but no percolation occurred at similar concentrations in the a-MWNT composites, due to the poor dispersion in the matrix.

Keywords: carbon nanotubes, CNT/polymer composites, electrical conductivity, acid treatment, thermal treatment, melt mixing.

Introduction

Since the discovery of CNT,[1] fundamental researches on CNT and their applications have made rapid growth.[2-5] Multi-walled nanotubes (MWNTs) have 10~50 nm diameter and several to tens of micron length, leading to exceptionally high aspect ratio. CNTs have been proposed for many potential applications such as high structural and high-performance functional materials due to their excellent physical properties.[6] CNTs can offer high stiffness, high strength, and good electrical conductivity to polymeric composites at relatively low concentrations.[7-12]

As-produced MWNTs exist as highly entangled clusters because of their extremely long length. As a result, it is very difficult to disperse highly entangled MWNTs uniformly in fluids or in polymer melts, resulting in only marginal improvement of mechanical and transport properties for the composite materials. Thus, one of the important challenges in developing CNT/polymer composites lies in their uniform and reproducible dispersion. In general, there are largely two types of impurities in as-produced CNTs; carbonaceous materials and catalytic metallic impurities, thus the purifica-

tion of the raw products through various oxidation processes including chemical or thermal oxidation is a prerequisite to various CNT applications, especially in the area of composites application. The acid treatment of nanotubes was a well-known technique for removing catalytic impurities, also serving to shorten the length of CNTs under simultaneous sonication. It is also well known that acid treatment generates the functional groups on opened ends or sidewalls of CNTs to facilitate easy dispersion of CNTs in solution and melt.[13,14] On the other hand, thermal treatment is usually used for annealing or improving the CNT surface as well as removing amorphous carbon.

In this article, we report the effect of CNT pre-treatment on dispersion and electrical properties in MWNTs/polymer composites, which were prepared by melt mixing using twin screw extruder. Two different approaches for the pre-treatment of MWNT,[13] concentrated acid treatment and thermal treatment were employed.

Experimental

Materials. As a matrix, poly(methyl methacrylate) (PMMA, Sigma Aldrich) with molecular weight of 350,000 in the form of spherical particles of 100~200 μm diameter was used. The MWNTs (obtained from Iljin Nanotech)
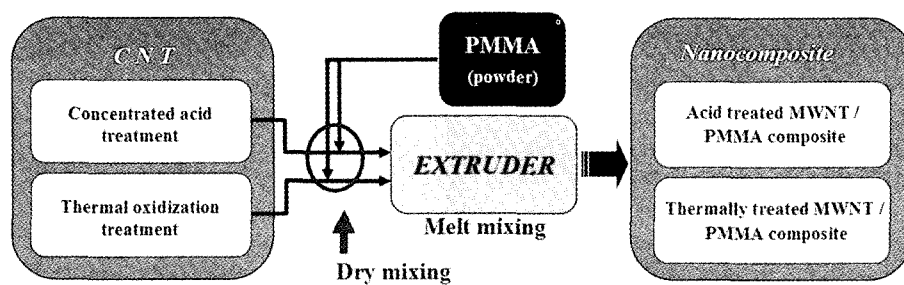
Figure 1. Schematic representation of experimental scheme used in this study.

grown by CVD method were used as a nanofiller. As-received MWNTs show severe agglomeration of interwinding entanglements of each CNT on SEM examination. Typical CNT diameters were in the range of 10 to 20 nm with tube lengths of 10 to 50 μm, resulting in aspect ratio of about 1,000.

Pre-treatment and Composite Preparation. Overall experimental procedure was schematically described in Figure 1. In the first step, MWNTs were pre-treated by two types of method, concentrated acid treatment and thermal treatment. Treated MWNTs and PMMA were then intensively mixed under high shear force.

(i) Concentrated acid treatment (a-MWNTs): MWNTs were treated with concentrated acid solution. As-received MWNTs were suspended in a 3:1 (v/v) mixture of H_2SO_4 (98%) and HNO_3 (68%), and the suspension was ultrasonicated in bath type sonicator for 12 h at room temperature, followed by refluxing at 140 °C for 3 h. The suspension was washed with distilled water to reach pH 7, and dried for one week in freeze dryer.

(ii) Thermal treatment (t-MWNTs): Pristine MWNTs were heated at 500 °C for 1 h in air condition.

(iii) Dry mixing: Pre-treated MWNTs and PMMA powder were mechanically mixed using high speed Henschel type mixer with branched two-blade propeller. The dry mixing was conducted at 3,500 rpm for 15 min.

(iv) Melt mixing: This process was performed on an extruder at 240 °C and 250 rpm of rotating screw speed. Twin screw co-rotating extruder (Bautech, Korea) with 11 mm screw diameter and L/D ratio of 40 was used. The composite was extruded out of circular die (1 mm diameter) and cooled in air.

Measurements. CNT dispersion in the polymer matrix was observed on optical microscope (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). OM was used for investigating macroscopic distribution of entangled MWNT clusters under transmission mode for the film of 100 μm thick containing 0.5 wt% of MWNT. SEM (FEI XL-30 FEG) operated at 8 kV was used to observe microscopic dispersion of MWNTs on the fracture surface of extruded strands. SEM images of pristine MWNTs were also obtained at 15 kV. The extruded strands

were ultramicrotomed into 70 nm thin slices at a room temperature (Reichert Ultracut S). The slices were observed by TEM (JEOL JEM-2010) at operating electron voltage of 120 kV.

FT-Raman spectroscopy was performed on RFS-100/s (Bruker) using 1064 nm incident laser wavelength. A power density of about 0.5 mW/cm^2 was used for avoid blackbody radiation arise from black color of CNTs themselves.

The volume resistivity was measured on composite samples with 0.5 mm thickness prepared by hot pressing of extruded strand at 240 °C. Electrical conductivity measurement was performed using the four-probe method to eliminate the effect of contact resistance. A Keithley 6512 digital multimeter equipped with a YEW 2553 DC voltage current standard (YEW Electronics, Japan) was used to measure the I-V characteristics of the samples at room temperature.

The dielectric measurements were performed on a frequency response analysis system using broadband dielectric analyzer (Novocontrol GmbH, Germany) with a frequency range from 10^{-2} to 10^7 Hz. The spectra of real (ε') and imaginary (ε'') part of the complex dielectric permittivity were obtained as a function of frequency.

Results and Discussion

Characterization of Pre-treated MWNTs. FE-SEM images of a-MWNTs and t-MWNTs are shown in Figure 2. It is shown that a-MWNTs are highly entangled and densely attached each other (Figure 2(a)), while t-MWNTs showed loosely clustered phase (Figure 2(b)). In addition, diameter of a-MWNTs was significantly decreased, whereas those of t-MWNTs were comparable to those of pristine MWNTs. This indicates that outer shell of a-MWNTs were partially destroyed and stripped off by concentrated acid treatment.

Raman spectra in Figure 3 show two major peaks in the high frequency range; the tangential mode or so-called G-band at 1601 cm^{-1} and D-band at 1289 cm^{-1} assigned to carbonaceous compounds or defects in CNTs.[15] Intensity ratio of D-band to G-band in a-MWNT is higher than that of t-MWNTs, implying that t-MWNTs are less defective than a-MWNTs. Through the acid treatment, pristine MWNTs are shortened in their length, and at the same time the opened
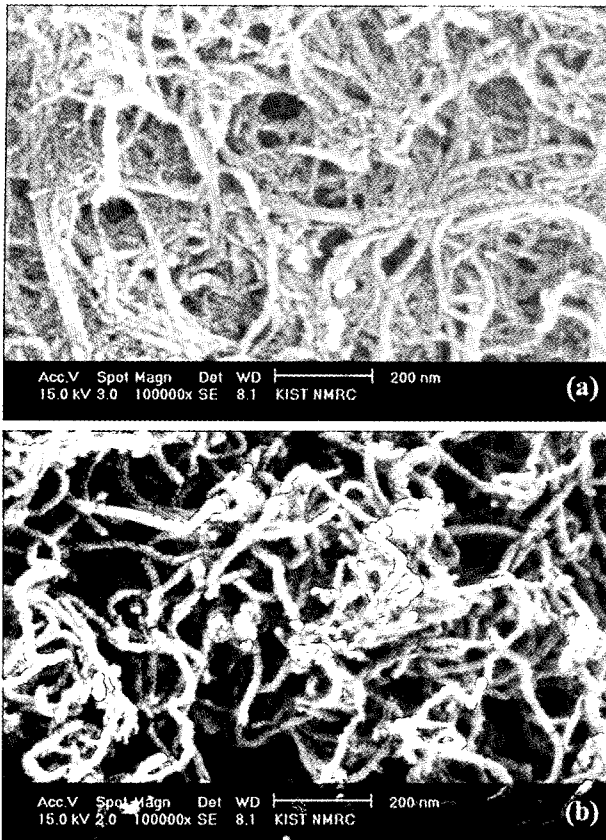
Figure 2. SEM images of pre-treated MWNTs (×100,000); (a) for a-MWNTs, strongly attached morphology with one another was shown after drying process and (b) for t-MWNTs, considerable reduction of entanglement in CNTs was achieved.
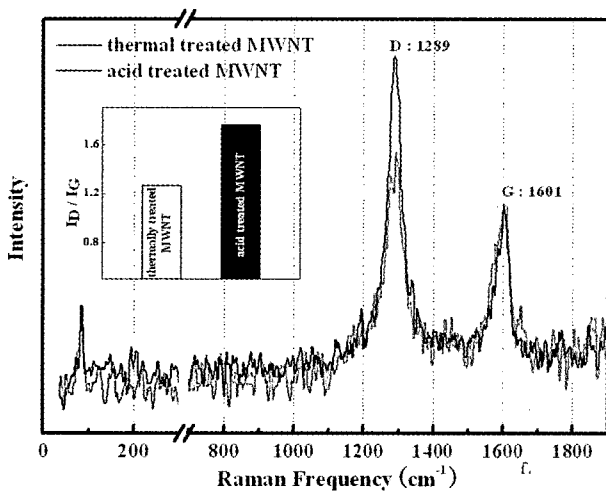
Figure 3. FT-Raman spectra of a-MWNTs (black line) and t-MWNTs (gray line) obtained at $\lambda_{exc} = 1064$ nm, inset is the ratio of peak intensity for D- and G-band.

ends and the sidewall defects are functionalized to form functional groups including carboxyl group, which would

contribute to the enhanced dispersion of CNTs in water or organic medium in solution process.[16-18] However, highly functionalized CNTs may attract one another through extensive hydrogen bondings between functional groups along with capillary bonding during drying process.[19] Therefore, highly entangled structure induced by acid treatment is expected to lead to the highly entangled aggregates in melt process.

Dispersion of MWNTs in Polymer Composites. Dispersion for the pre-treated MWNT in the composites was estimated using OM, SEM, and TEM as shown in Figure 4. OM images were obtained at 0.5 wt% MWNT concentration, SEM, and TEM images were obtained at 4.0 wt% MWNT, respectively. Highly entangled clusters and segregated phase of CNTs are shown in the fracture surface of composite containing a-MWNTs (Figure 4(a), (c) and (e)), whereas t-MWNTs were uniformly dispersed to form a three-dimensional network (Figure 4(b), (d), and (f)). In solution process, functionalization of CNTs is known to result in better CNT dispersion in polymer matrix such as PMMA.[18] However, highly entangled structure induced by association of excessive functional groups on a-MWNTs is hardly overcome by simple shear mixing in the melt process, leading to very poor dispersion of CNTs for a-MWNT/PMMA composites. On the other hand, a large amount of free volume surrounded by loose network of t-MWNT may allow an extensive polymer penetration that was facilitated by strong shear force, yielding better dispersion of CNTs for t-MWNT/PMMA composites. Through the comparison of their morphologies, it is found that thermal treatment of MWNT coupled with shear force is more effective than acid-treatment in achieving better CNT dispersion in melt process.

Electrical Properties of the Composites. It is well known that dispersion state of CNTs in the polymer matrix directly affects composite properties. We herein investigated the effect of CNT dispersion on permittivity and electrical conductivity.

Figure 5 shows the permittivity and the conductivity spectra with varying MWNT concentrations for different pre-treatment methods. Due to the high AC conductivity of the samples of CNT content higher than 3.0 wt% of t-MWNT, fluctuation of real permittivity for these compositions was unavoidable. However, it is clearly shown that the curves in Figure 5 can be characterized into two groups. In the first group electrical and dielectric properties are improved by increasing both concentration of MWNT and frequency. The second group exhibited no significant change of real ε' and imaginary permittivity ε'' with changing MWNT content and frequency. The composites with 1.0 wt% of t-MWNT and 1.0, 5.0 wt% of a-MWNT show nearly the same ε' and ε'' values irrespective of frequency. However, the composites containing more than 3.0 wt% of t-MWNT show decreases of ε' and ε'' with increase of frequency (Fig-
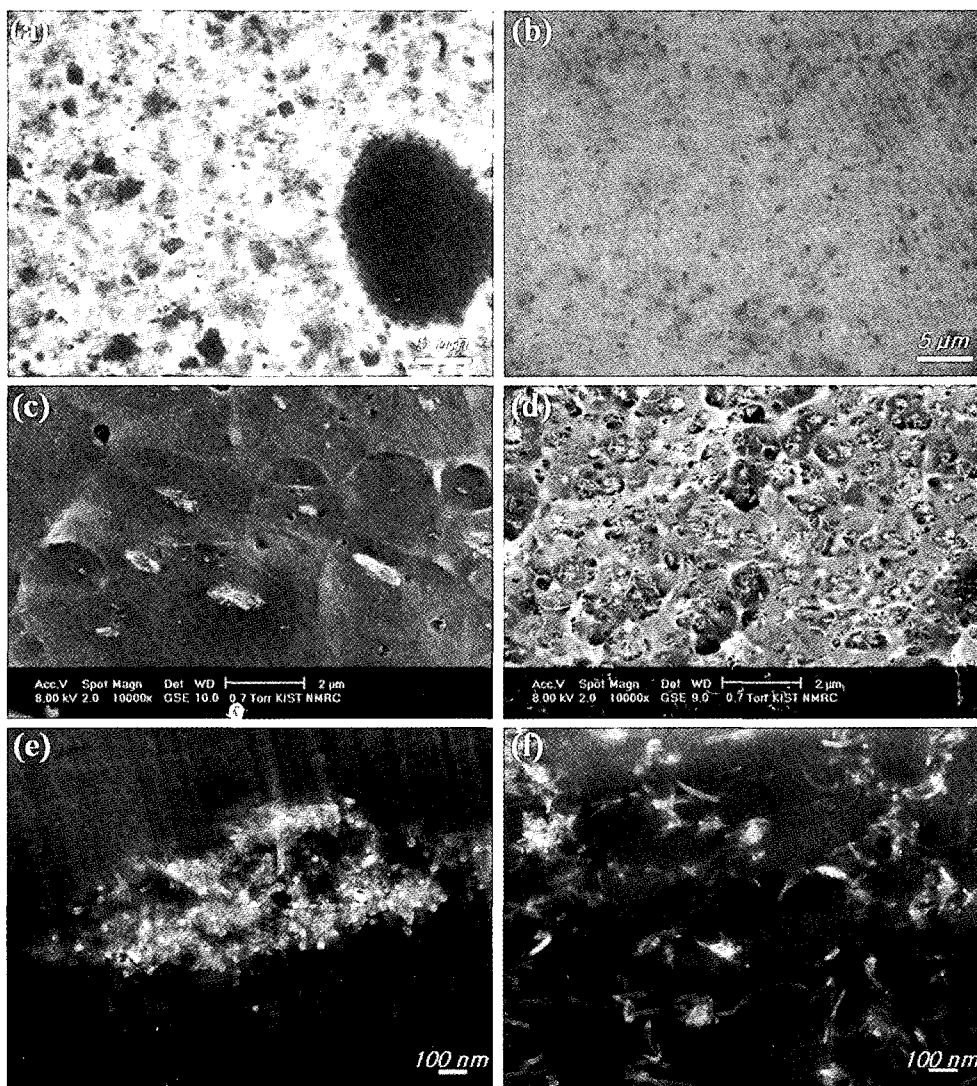
Figure 4. OM, SEM and TEM images of MWNT/PMMA composites; OM image (×1,000) of (a) a-MWNT composite and (b) t-MWNT composite, SEM images (×10,000) of (c) a-MWNT composite and (d) t-MWNT composite, TEM images (×50,000) of (e) a-MWNT composite and (f) t-MWNT composite.

ure 5(a) and (b)). In view of these facts, t-MWNTs composites are the first group and a-MWNT composites are the second group.

A significant difference between two groups is also observed in electrical conductivity, which is a measure of long range movements of charge carriers.[20] As shown in Figure 5(c) and Figure 6(a), the percolation threshold (p_c) clearly exists around 3.0 wt% of t-MWNT content. At this concentration, the conductivity increased sharply by ten orders of magnitude. In order to estimate the percolation threshold p_c and the critical exponent β, we draw the σ_{DC} data (Figure 6) for $p > p_c$ to equation;[20-22]
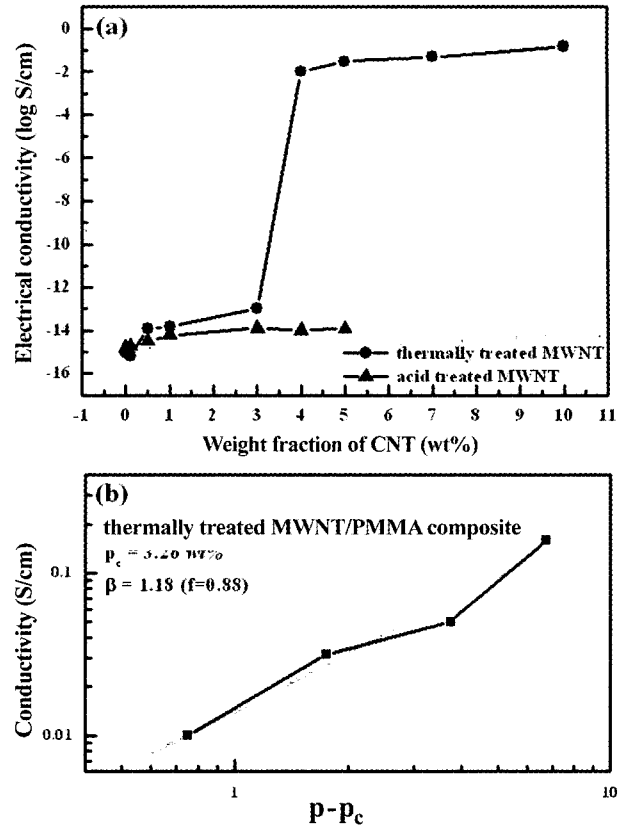
$$\sigma_{DC}(p) = C \cdot (p - p_c)^\beta$$

For each value of p_c, β has been determined from the slope of the linear relation of σ_{DC} and p-p_c on a log-log scale. Figure 6(b) shows the extrapolated static values of the DC conductivity versus the MWNT content and estimation of percolation threshold (p_c) for the t-MWNT/PMMA composite. From analysis of Figure 6(b), the values of p_c of 3.26 wt% and β of 1.18 (linear correlation coefficient, f = 0.88) were obtained, whereas those for a-MWNT composites were not obtainable. In Figure 6(a), we also observed that the conductivity shows typical percolation behavior and reaches 10^{-2} S/cm (DC) at 4.0 wt% t-MWNT loading, which is 13 orders of magnitude higher than that (10^{-15} S/cm) of pure PMMA.

Assuming an aspect ratio of 1,000, theoretical calculations for cylindrically shaped fillers[23] predicted that the onset of
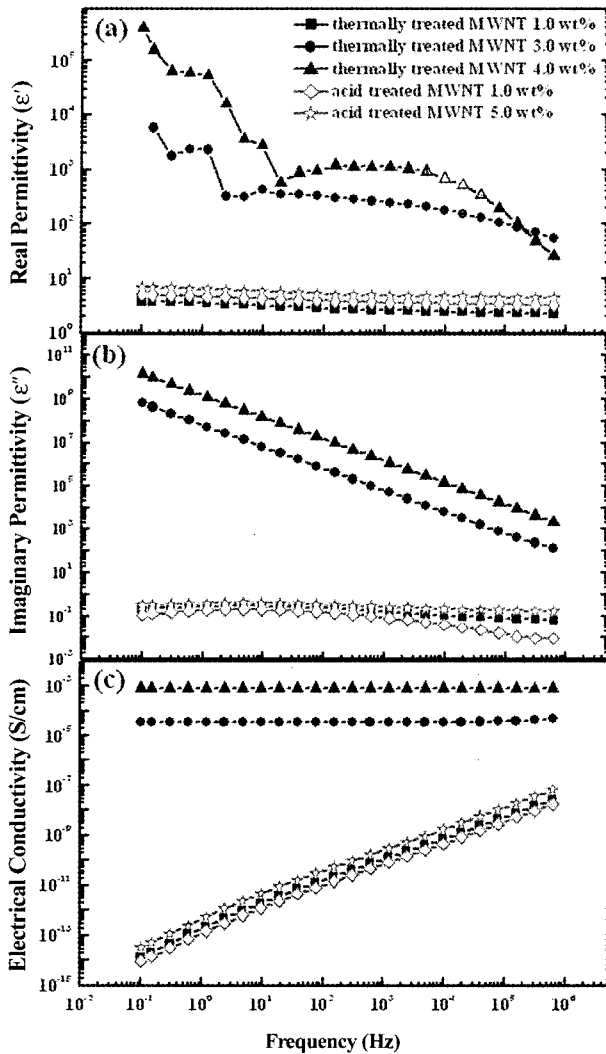
Figure 5. Permittivity and electrical conductivity as a function of frequency and CNT concentration; (a) real part ε', (b) imaginary part ε'' of the complex permittivity, and (c) AC conductivity. The black line is for t-MWNT and the gray line is for a-MWNT.

Figure 6. DC conductivity (a) and extrapolated values (b) versus weight fraction of MWNT in the composites. The straight line is a linear regression fit to the data points.

electrical conductivity of polymer/MWNT composites would begin at ~0.05 vol%. Experimentally, percolation concentrations as low as 0.04 wt% for epoxy/MWNT composites[24] and 0.05 wt% for PP/MWNT film[25] have been reported along with percolation behavior in the range of 1~5 vol% of MWNT for most of polymer/MWNT composites. In fact, most polymer/MWNT composites in the literature have been prepared by solvent-assisted processes such as solution mixing or *in-situ* polymerization. In terms of mixing efficiency, solvent-assisted process is superior to melt mixing, where viscosity of polymer melt is high enough to prevent sufficient mixing and there is lack of interfacial mediator between immiscible two phases. On the other hand, melt mixing has the advantages of simplicity without using solvent, and continuity to the conventional continuous pro-

duction system such as extrusion. Although not comparable to the lowest values reported in the literature,[26-29] the percolation concentration of ca. 3 wt% MWNT for the composites prepared by melt mixing process was obtained in this study. The melt processed composites in this study will find uses in applications such as electrostatic dissipation (ESD), electrostatic printing and electromagnetic wave interference (EMI) shielding by further improving or tuning its electrical properties.[30]

Conclusions

We have investigated the effect of pre-treatment methods such as concentrated acid and thermal treatment method for MWNT on dispersion of CNTs and electrical properties of MWNT/PMMA composites, which were prepared by melt mixing using twin screw extruder. For melt mixing, a-MWNTs were found to be ineffective in terms of dispersion probably due to excessive association of functional groups generated during the treatment causing aggregated clusters in the matrix, whereas t-MWNTs were found to be well dispersed in PMMA. The poor dispersion of a-MWNTs in the composites was manifested in electrical and dielectric pro-

perties of the composites, which were similar to those of the neat PMMA at given MWNT contents. On the other hand, t-MWNT/PMMA composites showed the typical percolation behavior and high electrical conductivity due to better dispersion of CNTs in the matrix facilitating easy formation of conductive networks.

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