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Increased flexural modulus and strength in SWNT/epoxy composites by a new fabrication method

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Abstract

A new method for preparing SWNT/epoxy nanocomposites has been developed which involves high shear mixing of the epoxy resin and SWNT and heat treating the mixture prior to introducing the hardener. The glass transition temperature of the epoxy resin is unaffected by the presence of nanotubes. An improvement of 17% in flexural modulus and 10% in flexural strength has been achieved at 0.05 wt% of nanotubes. These improvements in flexural modulus and strength are attributed to good dispersion of the nanotubes and grafting of epoxy resin to SWNT by an esterification reaction.

Keywords: Nanocomposites; Flexural modulus; Nanotubes

1. Introduction

Single wall carbon nanotubes (SWNT) possess high aspect ratio, high tensile strength, low mass density and high thermal and electrical conductivity [1,2]. The combination of these properties makes them ideal candidates for the fabrication of multifunctional polymer nanocomposites [3–5]. SWNT reinforced epoxy systems hold the promise of many potential applications that require lightweight, high strength materials e.g. space shuttle, aircraft etc. In spite of the ongoing efforts for the last several years to prepare SWNT/epoxy composites that achieve the theoretical potential of nanotube reinforcement, there has been little success due to several fundamental difficulties remain. The first difficulty arises from the poor dispersion of the nanotubes in the epoxy matrix. Due to the high aspect ratio of the nanotubes (up to 1000), there is strong intrinsic van der Waals attraction between the nanotubes that produces SWNT ropes and bundles [6]. Processing difficulties also arise from the significant increase in viscosity as the amount of nanotube loading increases in the epoxy matrix. Moreover, there is very limited load transfer from the matrix to the nanotubes due to the lack of interfacial bonding between the nanotubes and the polymer matrix [7].

A number of researchers have developed techniques to improve the dispersion of the nanotubes in epoxy including ultrasonication [8,9], addition of surfactants [10] and functionalization [11–13]. Addition of surfactants and functionalization of the nanotubes prove to be useful in improving the dispersion of nanotubes in the epoxy matrix. However, in both cases, the glass transition temperature of the epoxy matrix is found to be affected [10,11]. In other words, the degree of crosslinking has been affected. For example, Miyagawa et al. [11] found that the glass transition temperature of the epoxy matrix decreased approximately 30 °C with an addition of 0.2 wt% fluorinated single wall carbon nanotubes.

In terms of mechanical properties, SWNT/epoxy nanocomposites have been found to be either weaker or slightly higher strength than the pure epoxy [13–20]. In most of the reports, more than 1.0 wt% of nanotubes were added to get any improvement in the elastic modulus of the epoxy matrix. Recently Zhu et al. reported 30% improvement in Young's modulus of epoxy with 1.0 wt% loading of nanotubes when the nanotubes are functionalized with amino groups [12] or a combination of carboxyl and fluoride groups [13] prior to nanocomposite fabrication.

In this article we report a new method for the preparation of the SWNT/epoxy nanocomposites with improved dispersion of SWNT, without functionalization of the nanotubes. This method also provides a route to get improved mechanical

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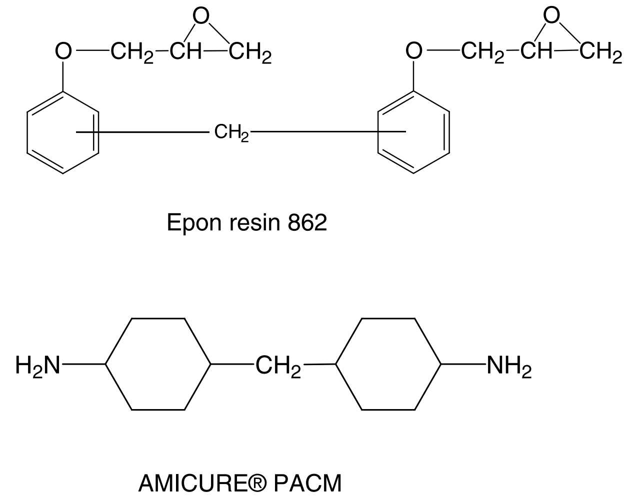


Fig. 1. Structures of Epon resin 862 and the curing agent AMICURE® PACM.

properties of the nanocomposites at a very low loading of SWNT.

2. Experimental

2.1. Materials

SWNT were synthesized by a high-pressure carbon monoxide method (HiPco) at Rice University [21]. The nanotubes were purified with HCl by the method described by Zhou et al. [22]. The metal residue in the purified nanotubes was less than 4 wt% as determined by thermogravimetric analysis (TA instruments SDT 2960 at 5 °C/min in air) and assuming that the residue was Fe_2O_3. Purified SWNT was stored in DMF to avoid agglomeration.

The epoxy resin used in this study was a DGEBF epoxy (diglycidyl ether of bisphenol F), EPON resin 862, obtained from Shell Chemicals. Processing can become difficult due to the increased viscosity during the preparation of SWNT/epoxy composites. Therefore, an epoxy resin with lower viscosity is ideal for the preparation of epoxy/nanotube composites. Bisphenol F epoxy resin is physically smaller than the most widely used bisphenol A epoxy resin, resulting in a lower viscosity (25–45 Poise at 25 °C). It has increased functionality, which allows higher crosslinking density. Another advantage is that it requires amine-based curing agents with higher functionality, which also has lower viscosities. AMICURE® PACM, a cycloaliphatic diamine (chemical name 4,4′-methylenebiscylohexanamine), obtained from Air Products and Chemicals Inc. was used as the hardener/curing agent in this study. The typical molecular structures of EPON resin 862 and AMICURE PACM are shown in Fig. 1.

2.2. Preparation of the nanocomposites

SWNT/epoxy composites were prepared with nanotube loadings of 0.01 and 0.05 wt%. Fig. 2 shows a schematic of the method for the preparation of the SWNT/epoxy nanocomposites. The purified nanotubes were dispersed in dimethylformamide (DMF) by bath sonication for 24 h. The epoxy resin was mixed with the nanotube suspension in DMF and sonicated for 1 h. The DMF was evaporated by heating the SWNT/resin suspension at 100 °C for 24 h. Another batch of the SWNT/resin mixture was further heated at 150 °C for 24 h under vacuum. The mixture was then subjected to high shear mixing (100 rpm) for 1 h at room temperature in a twin–screw batch mixer (MicroCompounder®, DACA Instruments). After high shear mixing of the SWNT/resin mixture, the curing agent (resin:curing agent =3:1) was added to the homogenous mixture and was compounded for another 30 min. The resulting mixture was then taken into a Teflon® pan, degassed for 4 h and was cured at 80 °C under vacuum for 2 h followed by another 2 h curing at 150 °C to complete the crosslinking reaction.

2.3. Sample characterization

Nanotube dispersion in the epoxy matrix was studied using transmission optical microscopy (Olympus, BH-2). A few drops of the SWNT/resin/hardener mixture was placed on a microscope slide after the mixture was subjected to high shear mixing, heated at 80 °C for 2 h, and then heated at 150 °C for 2 h. Thermal analysis was carried out using a DuPont 2920 differential scanning calorimeter (DSC) at a heating rate of

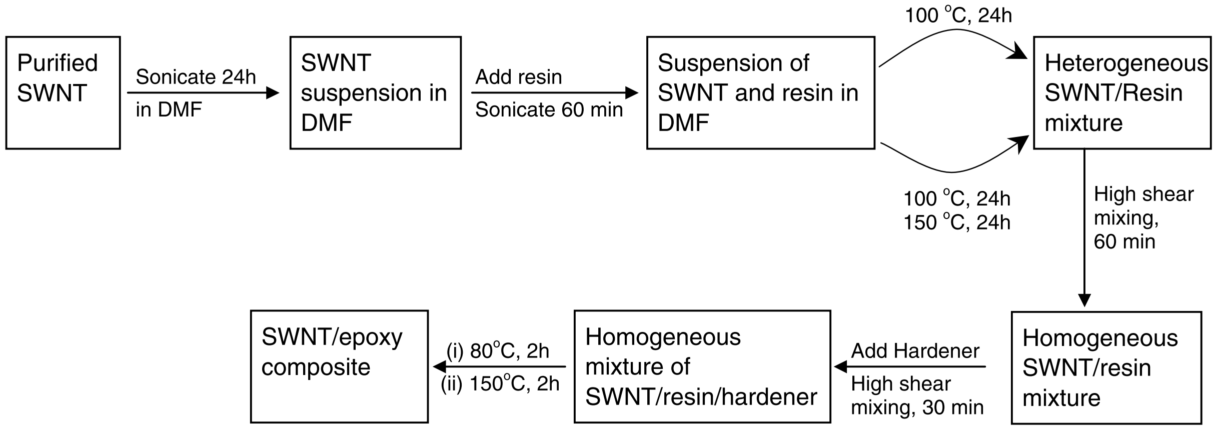


Fig. 2. Schematic of the preparation of SWNT/epoxy nanocomposites.

10 °C/min. The instrument was calibrated for temperature and energy with indium and tin reference samples. DSC traces were recorded with 7–10 mg of sample, in a nitrogen atmosphere. Scanning electron microscopy (SEM) (JEOL 6300FV) was used to investigate nanotube dispersion by imaging composites fractured at room temperature. To reduce charging the fracture surface was coated with a thin sputtered layer of Au/Pd (60:40) and imaged at 15 kV. FT-IR spectroscopic measurements were performed at ambient conditions using a Perkin–Elmer Series 2000 Fourier transform infrared (FT-IR) spectrometer. Samples for FT-IR were prepared with KBr to form transparent pellets. Three-point bending experiments were conducted on an Electromechanical Material Testing System (Instron Series 5564). The crosshead speed was 0.5 mm/min and typical dimensions of the sample beams were 20 mm×2.1 mm×2.1 mm.

3. Results and discussions

3.1. Morphology of the composites

After the ultrasonication of the SWNT/resin suspension in DMF followed by evaporation of the solvent at 100 °C for 24 h, agglomeration of nanotubes is visible in this mixture even with the naked eye, Fig. 3(a). This is consistent with previous studies, reporting that ultrasonication of the resin and nanotubes in the solvent produces poor dispersion of the nanotubes in the final composite [8,9]. Following our new procedure, the SWNT/resin mixtures were compounded in a MicroCompounder, compounded with the hardener and then cured to produce composites with uniform dispersion of nanotubes in the epoxy matrix. Fig. 3(b) shows the optical micrograph of the nanocomposite with 0.01 wt% of nanotube loading. Fig. 3(c) shows the scanning electron microscopy (SEM) image of the fracture surface of the same composite. The absence of any agglomerates in Fig. 3(b) and (c) indicates a uniform dispersion of SWNT in the epoxy matrix at the micron and submicron level, respectively. The composite with 0.05 wt% of nanotube loading shows similarly uniform dispersion of nanotubes. Therefore, high shear mixing of the nanotubes and epoxy resin for a period of time and subsequent high shear mixing of the hardener with the former mixture results in a composite with uniform dispersion of nanotubes. It should be mentioned that when the SWNT/resin mixture is heated for prolonged time (with or without compounding), an increase in viscosity has been observed which limits the amount of nanotube loading in the composites.

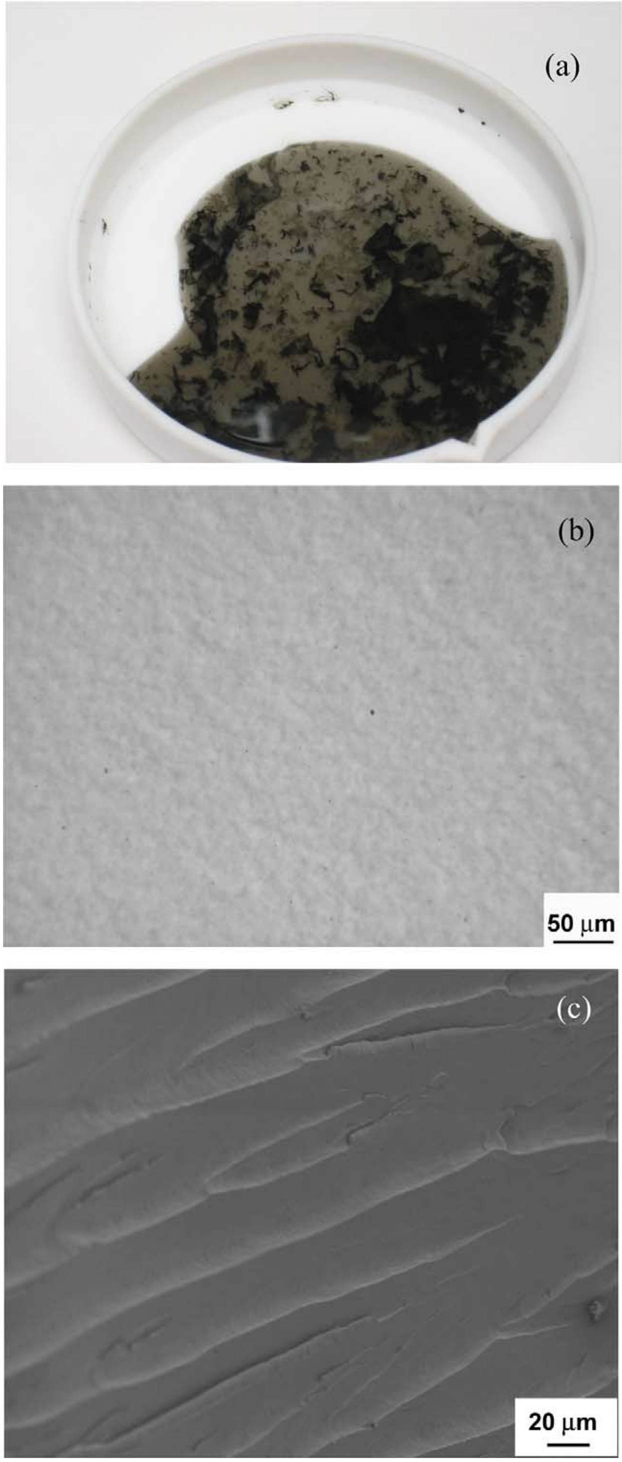


Fig. 3. (a) Photograph of the SWNT/resin mixture prior to high shearing step. (b) Optical micrograph of the SWNT/epoxy nanocomposite and (c) SEM image of the fracture surface of the composite. The nanotube loading is 0.01 wt%.

3.2. Thermal analysis

Lau et al. [23] reported that when DMF is used for the dispersion of nanotubes, the residual solvent has detrimental effect on the mechanical properties of the nanotube/epoxy composites. To evaluate the amount of residual solvent, the SWNT/resin mixture was subjected to thermogravimetric analysis after the solvent evaporation at 100 °C for 24 h. The TGA shows <2 wt% weight loss (due to the release of adsorbed water) between 80 and 220 °C indicating complete removal of the DMF. In addition, isothermal TGA (at 150 °C) was performed on epoxy resin for 24 h in air and found no significant decomposition of the epoxy resin. DSC analysis shows that the glass transition temperatures of the cured epoxies with and without SWNT are ~129 °C. This indicates that the removal of DMF prior to curing and the improved

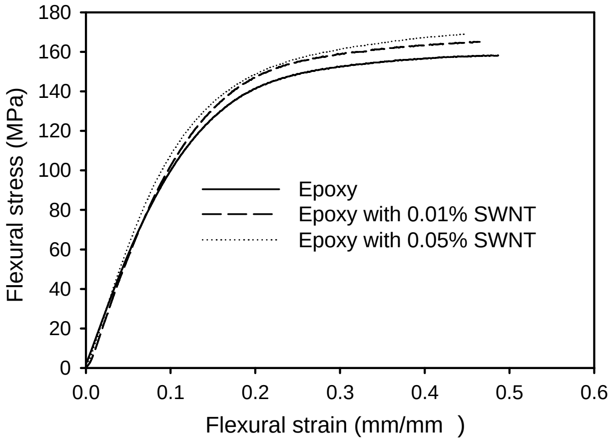


Fig. 4. Plot of flexural stress vs. flexural strain for epoxy and SWNT/epoxy nanocomposites. The SWNT/resin mixtures were heated at 100 °C for 24 h to prepare these composites.

SWNT dispersion of our SWNT/epoxy composites allow for comparable crosslinking in both epoxy and the nanocomposites.

3.3. Mechanical properties of the composites

Fig. 4 shows representative stress–strain curves from three point bending tests of the epoxy and its nanocomposites from which the flexural moduli were determined (from the slopes). Fig. 5 shows the flexural moduli of the epoxy and SWNT/epoxy composites where the flexural modulus increases with the nanotube loading. The flexural strength σ is calculated based on the following equation [24]:

$$\sigma = \frac{3P_L L}{2WT^2} \tag{1}$$

where P_L is the peak load of the load-extension curve, L is the support span and W and T are the width and thickness of the sample beam.

The flexural strength of the pure epoxy as well as of the composites is listed in Table 1. From Fig. 5 and Table 1, the composite with 0.05 wt% SWNT shows a 15% improvement in flexural modulus and a 8% improvement in flexural strength when the SWNT/ resin mixture is heated at 100 °C for 24 h. Further heating of the mixture (150 °C for 24 h) only slightly improves the flexural modulus and strength of the composite (17% increase in modulus and 10% increase in strength for 0.05 wt% of SWNT composite). Considering the very low concentration of the nanotube loading, these improvements in flexural modulus and strength are noteworthy as the largest improvements in flexural modulus and strength reported to date at this low loading of SWNT.

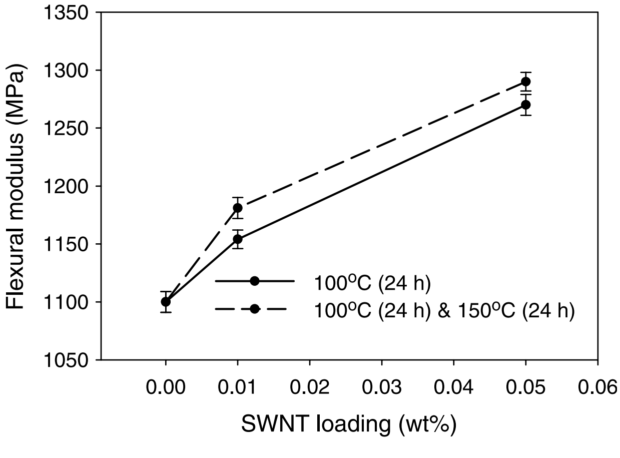


Fig. 5. Flexural modulus of the SWNT/epoxy composites as a function of nanotube loading.

Table 1
Flexural strength of epoxy and SWNT/epoxy nanocomposites prepared with either a one-step or two-step drying process. Standard deviations of these measurements are less than ±2 MPa

SWNT (wt%)	Flexural strength (MPa)	
	100 °C (24 h)	100 °C (24 h) & 150 °C (24 h)
0	158	158
0.01	164	167
0.05	170	173

Multiple factors can contribute to the improvements in flexural moduli and strengths in these SWNT/epoxy composites. One obvious factor is the improved dispersion of the nanotubes in the epoxy matrix (as evidenced from the optical microscopy images) achieved through the fabrication method developed in this study. Another factor might be an interfacial bonding between the SWNT and epoxy matrix that facilitates load transfer. To explore this possibility, FT-IR spectra of the samples were collected.

FT-IR can monitor small changes in functional groups due to a chemical reaction. Our fabrication method involves a long drying step that could produce some chemical changes. Four samples were studied by FT-IR: (i) purified SWNT, (ii) epoxy resin, (iii) SWNT recovered by washing away the epoxy resin prior the heat treatment (control sample), and (iv) SWNT recovered by washing away the free epoxy resin after the heat treatment, Fig. 6. The FT-IR spectra of pure SWNT and the control sample are found to be identical (compare Fig. 6(a) and (c)) indicating that the washing step effectively removes all the epoxy resin from the nanotubes. However, the heat-treated sample shows several epoxy specific bands in the FT-IR spectrum, Fig. 6(d). In addition to the bands characteristic to SWNT and epoxy resin, this FT-IR spectrum shows a band at 1730 cm^{-1} characteristic of an ester group. It is well known that acid treatments during the purification of SWNT produce defects in the nanotubes with the addition of few carboxylic acid groups (–COOH) at the defect sites [25–28]. In Fig. 6(a) and (c), we do not see the peak for the C=O stretching of the acid groups, in part because the SWNT are not heavily functionalized during our purification procedure. Furthermore, literature indicates that even when SWNT are heavily functionalized with acid groups by extended refluxing with acid, the C=O band of the acid is very weak and somewhat broad when attached to SWNT [26], whereas, the ester C=O band is comparatively strong and sharp and more intense [13]. The band at 1730 cm^{-1} in the heat-treated sample indicates the formation of ester groups by the reaction of carboxylic acid

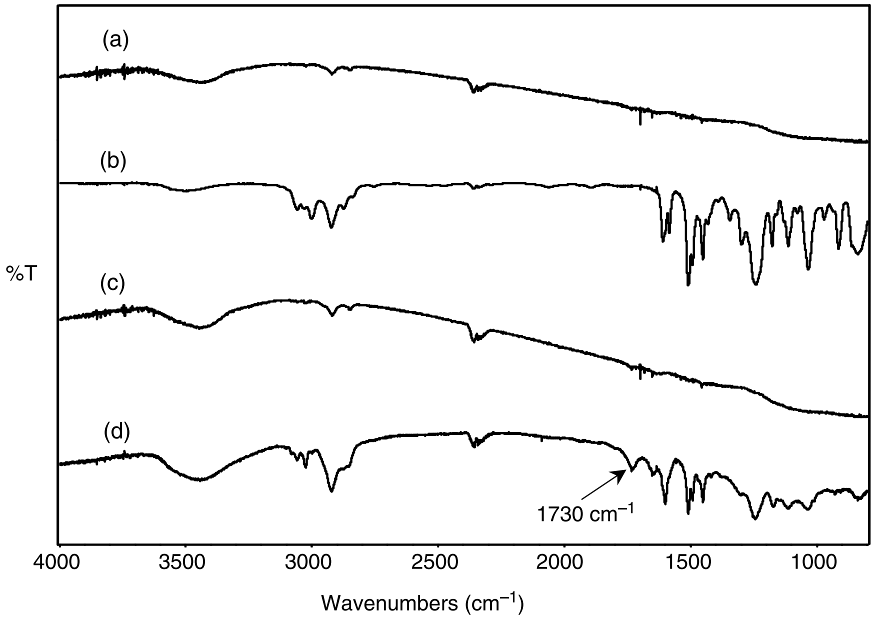
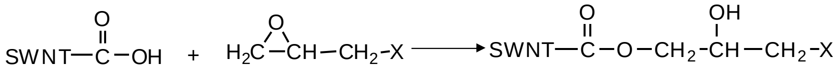


Fig. 6. FT-IR spectrum of (a) purified SWNT, (b) epoxy resin, (c) SWNT recovered by washing away the epoxy resin prior the heat treatment (control sample), and (d) SWNT recovered by washing away the free epoxy resin after the heat treatment.



Scheme 1.

functional groups on the nanotubes with the epoxy rings, Scheme 1. In other words, prolonged heating in the drying step grafts the epoxy resin on the SWNT. The reaction proceeds via the acid catalyzed ring opening of the epoxy [29], Scheme 1.

Zhu et al. [13] obtained similar ester C=O stretching in the FT-IR spectrum of the SWNT/epoxy composite when they deliberately functionalized SWNT with carboxylic acid groups and prepared SWNT/epoxy composites. Our preparation method does not require SWNT functionalization, but rather a simple heating step. The formation of covalent bonds between the SWNT and epoxy resin facilitates load transfer between the SWNT and epoxy matrix and contributes to the improvement in the mechanical properties of the composites.

4. Conclusions

A new method has been developed to prepare SWNT/epoxy composites. Improved dispersion of SWNT in epoxy matrix has been achieved by high shear mixing of the nanotubes with the epoxy resin. Preheating the SWNT/resin mixture prior to introducing the hardener produces covalent bonds between the nanotubes and the epoxy resin. After curing, the covalent bonds between SWNT and epoxy facilitate load transfer between the nanotubes and the epoxy matrix. Significant improvements in flexural modulus (17%) and flexural strength (10%) have been achieved at 0.05 wt% nanotubes. These improvements in flexural modulus and strength are attributed to both the improved dispersion of the nanotubes and grafting of epoxy resin to SWNT by an esterification reaction. However, preheating the SWNT/epoxy resin mixture to remove solvent increases the viscosity and prohibits processing at higher SWNT loading. Therefore, future study will be aimed at developing methods to reduce the viscosity of the mixture (e.g. using modifier) so that more nanotubes can be incorporated into the epoxy matrix.

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