Contents lists available at ScienceDirect

# **Composites Part A**

journal homepage: www.elsevier.com/locate/compositesa



# Preparation of ultrashort composite nanotubes by twin-screw extruder

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#### ARTICLE INFO

Keywords:

A. Polymer-matrix composites (PMCs) A. Nano-structures

B. Fracture

E. Extrusion

#### ABSTRACT

The preparation of nanocomposites with controllable structure is important. There are few reports on preparation of ultrashort composite nanotubes with core–shell structure from long nanotubes, and how to maintain structural integrity and to avoid shell falling off or damaging are still challenging. Here we prepare ultrashort core–shell composite nanotubes with the outer layer of SiO<sub>2</sub> or TiO<sub>2</sub> and the inner layer of sulfonated PDVB by mixing their long composite nanotubes with polymer resin and shearing at a high strength with a twin-screw extruder. By contrast, using ultrasonic crushing or mechanical stirring to interrupt the composite nanotubes can destroy the SiO<sub>2</sub> or TiO<sub>2</sub> outer layer seriously. The method of preparing ultrashort composite nanomaterials by twin-screw extruders is very promising in the field of nanocomposite processing.

#### 1. Introduction

The processing of nanomaterials, especially nanocomposite materials, is an important research direction in the field of materials processing. Nanotubes or nanofibers with longer length can be broken into the shorter by the strain of polymer materials when mixed in the polymer. Carbon nanotubes have been widely added in polymer matrix materials to improve the mechanical properties of materials. When deformation or fracture of matrix polymer materials occurs under the external force, the rupture of the carbon nanotubes mixed is also observed [1–6]. By wrapping nanofibers with polymer resin and by colddrawing the composite fibers along the axis, the ultrashort fibers with uniform size can be obtained after removing the resin [7]. However, there are few reports on preparation of ultrashort composite nanotubes with core-shell structure through analogous methods. Especially for the composite nanotube which shell is easily damaged, how to avoid the shell falling off or damaging is a still challenging in the process of interrupting.

In our previous work, we broke the long three-layer core–shell structure composite nanotubes into about 2  $\mu m$  in length under vigorous

ultrasonic cell crusher processing without seriously destroying the core-shell structure. The long composite nanotubes had sulfonated PDVB (sPDVB) in the inner layer, iron oxyhydroxide (FeOOH) in the middle layer and SiO<sub>2</sub> in the outer layer. We synthesized PDVB nanotubes through cationic polymerization [8,9], and then sulfonated its surface with concentrated sulfuric acid. FeOOH layer is grown onto the surface of the sPDVB nanotube under the adsorption of the sulfonic acid groups of sPDVB [10]. Then SiO<sub>2</sub> layer was grown onto the surface of FeOOH@sPDVB nanotubes through sol-gel reaction. The three-layered composite nanotube had a tick FeOOH and SiO<sub>2</sub> coating layers, and there is no obvious shedding under the effect of ultrasonic crusher [11]. However, when we prepare sPDVB@SiO2 or sPDVB@TiO2 double-layer composite nanotubes with similar method and try to produce its ultrashort composite nanotubes using ultrasonic cell crusher, we find that the outer layer of SiO2 or TiO2 layer fall off very seriously. Therefore, finding a suitable interruption method to prepare such ultrashort composite nanotubes are very meaningful.

We prove that the long  $sPDVB@SiO_2$  or  $sPDVB@TiO_2$  composite nanotubes can be interrupted into ultrashort nanotubes in a short time without destroying the core-shell structure seriously (Fig. 1) by using

https://doi.org/10.1016/j.compositesa.2022.106999

Received 17 January 2022; Received in revised form 21 April 2022; Accepted 12 May 2022 Available online 18 May 2022 1359-835X/© 2022 Published by Elsevier Ltd.



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Fig. 1. Diagram of preparing ultrashort sPDVB@SiO2 or sPDVB@TiO2 composite nanotubes using twin-screw extruder.

the twin-screw extruder. The double-layer composite nanotubes have sPDVB inner layer and SiO<sub>2</sub> or TiO<sub>2</sub> outer layer. In detail, we use the twin-screw extruder to mix the composite nanotubes with polycarbonate resin (PC) at a high temperature in tens of minutes [12–14]. Under the high shear stress of PC, the length of the composite nanotubes is interrupted into less than 2 µm from dozens of micrometers. Some proportion of nanotubes retain the core–shell structure and the SiO<sub>2</sub> or TiO<sub>2</sub> outer layer of the nanotubes is not destroyed after interruption, and the two heads of the ultrashort composite nanotubes are bare sPDVB.

#### 2. Experimental

#### 2.1. Materials

Tetrabutyl titanate (TBT, 98%), Coumarin 6, Rhodamine B and Sudan III are purchased from Sigma-Aldrich. Ammonia solution (NH<sub>3</sub>·H<sub>2</sub>O, 25%), Tetraethyl orthosilicate (TEOS, 98%), ethanol, concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98%), Tetrahydrofuran (THF) and ndecane are purchased from Sinopharm Chemical Reagent Beijing. Lexan Polycarbonate (PC, SABIC 103R) is purchased from HuaSuStar New Material Ltd., China. Polystyrene (PS, BASF 495F) and Polymethyl methacrylate (PMMA, LG if830) are purchased from Hongte Material Ltd., China. All chemicals are analytical grade. All other reagents were used as received without further purification.

#### 2.2. Preparation of the sulfonated PDVB nanotubes (sPDVB)

The PDVB nanotubes are synthesized as previously reported [8]. 1 g PDVB nanotubes is added into 20 g concentrated sulfuric acid and stirred at 25  $^{\circ}$ C for several hours. Eventually, the mixture is dropped into excess ice water and filtered to collect sulfonated PDVB nanotubes (sPDVB) [11].

# 2.3. Preparation of the sPDVB@SiO2 nanotubes

0.05 g sPDVB powder is dispersed in 40.5 mL ethanol. 200 µL TEOS is added and stirred for 8 h at room temperature. Then 6.75 mL H2O is added and stirred for 8 h at room temperature. The precipitate is separated by centrifugation and washing with ethanol [11].

#### 2.4. Preparation of the sPDVB@TiO<sub>2</sub> nanotubes

0.05 g sPDVB powder is dispersed in 40.5 mL ethanol. 200 µL TBT is added and stirred for 8 h at room temperature. Then 6.75 mL H2O is added and stirred for 8 h at room temperature. The precipitate is separated by centrifugation and washing with ethanol [15–21].

# 2.5. Preparation of ultrashort composite nanotubes with the twin-screw extruder

0.05 g sPDVB@SiO<sub>2</sub> nanotubes or sPDVB@TiO<sub>2</sub> nanotubes mixed with 3 g PC are added in the twin-screw extruder. The initial temperature is set as 280 °C to ensure good fluidity of the PC, after mixing for 5 min at 80 rpm the composite nanotubes can be fully dispersed in the PC [9]. The processing temperature is gradually lowered to 215 °C in 5 min and the hybrid is mixed at 215 °C for 10 min with the running speed of 30 rpm, at which temperature PC has strong enough mechanical properties to break the composite nanotube. The products are separated by washing with THF and centrifugation to remove PC, and more details about separation process are shown in Supporting Information.

# 2.6. Rheological measurements

Rheological measurements were carried out on a TA ARES G2 rheometer with 25 mm plate-plate geometry [22].

## 2.7. Characterization.

Morphology of the samples is characterized using the transmission electron microscopy (TEM, JEOL 100CX operating at 100 kV) and scanning electron microscopy (SEM, HITACHI S-4800 apparatus equipped with an energy dispersive X-ray (EDX) analyzer operating at 15 kV). The samples for SEM observation are ambient dried and vacuum sputtered with Pt. The samples for TEM observation are prepared by spreading diluted dispersions in ethanol onto carbon-coated copper grids and dried at room temperature.

FTIR spectroscopy measurement is performed after scanning 32 times using a Bruker EQUINOX 55 spectrometer with KBr pressed pellets.

Morphology of the emulsions stabilized with the ultrashort sPDVB composite nanotubes is characterized using OLYMPUS IX71 microscope. Fluorescence microscopy images are recorded using a confocal laser



Fig. 2. (a) TEM images of sPDVB nanotubes; (b) TEM images of sPDVB@SiO<sub>2</sub> nanotubes; (c) TEM images of sPDVB@TiO<sub>2</sub> nanotubes; (d) TEM images of SiO<sub>2</sub> nanotubes after calcination in air at 700  $^{\circ}$ C; (e) TEM images of TiO<sub>2</sub> nanotubes after calcination in air at 700  $^{\circ}$ C;



**Fig. 3.** TEM images of sPDVB@SiO2 nanotubes prepared with different sulfonated time of the sPDVB nanotubes (a) 5 min; (b) 1 h; (c) 10 h; (d) 24 h. Other reaction conditions: the TEOS/sPDVB weight ratio is 4:1; TEM images of sPDVB@TiO2 nanotubes prepared with different sulfonated time of the sPDVB nanotubes (e) 5 min; (f) 1 h; (g) 10 h; (h) 24 h. Other reaction conditions: the TBT/sPDVB weight ratio is 4:1; (i) FT-IR spectra of sPDVB nanotubes with different sulfonated time: (a) 5 min; (b) 1 h; (c) 10 h; (d) 24 h.

scanning microscope (CLSM, Leica TCS-sp2). n-decane is labelled with Coumarin 6 (blue), water is labelled with rhodamine B (red). There are three fluorescence channels are used 405 nm (blue), 488 nm (green) and

559 (red). All fluorescence channels are measured simultaneously.



**Fig. 4.** TEM images of sPDVB@SiO<sub>2</sub> nanotubes prepared at different TEOS/sPDVB weight ratio: (a) 1:2; (b) 1:1; (c) 2:1; (d) 4:1. Other reaction conditions: the sulfonated time of the sPDVB nanotubes is 24 h; and TEM images of sPDVB@TiO<sub>2</sub> nanotubes prepared at different TBT/sPDVB weight ratio: (e) 1:2; (f) 1:1; (g) 2:1; (h) 4:1. Other reaction conditions: the sulfonated time of the sPDVB nanotubes is 24 h.



Fig. 5. TEM images of broken ultrashort sPDVB@SiO<sub>2</sub> nanotubes under (a) mechanical stirring; (b) vigorous ultrasonication; (c) twin-screw extruder. TEM images of broken ultrashort sPDVB@TiO<sub>2</sub> nanotubes under (d) mechanical stirring; (e) vigorous ultrasonication; (f) twin-screw extruder.

#### 3. Results and discussion

#### 3.1. Preparation of the sPDVB composite nanotubes

We prepare sPDVB composite nanotubes wrapped by  $SiO_2$  or  $TiO_2$  layer without using FeOOH. The  $SiO_2$  or  $TiO_2$  outer layer can reach more than 20 nm (Fig. 2b and Fig. 2c). After the composite nanotubes calcining in air at 700 °C for 2 h, pure  $SiO_2$  or  $TiO_2$  nanotubes with such thickness can be obtained (Fig. 2d and Fig. 2e).

We test the effects of different sulfonated time of the sPDVB nanotubes on the SiO<sub>2</sub> or TiO<sub>2</sub> layer. [10,16] The amount and thickness of SiO<sub>2</sub> in the composite nanotubes prepared with low sulfonated time is smaller than that of high sulfonated time (Fig. 3a to Fig. 3d). Through analyzing with infrared spectroscopy, we find that the characteristic peaks at 1170 cm<sup>-1</sup> and 1040 cm<sup>-1</sup> corresponding to -SO3- group becomes stronger gradually with increasing of sulfonated time of sPDVB nanotubes (Fig. 3i and Fig. S1) [23]. So, the higher sulfonation degree of sPDVB nanotubes have more sulfonic acid and is beneficial to the adsorption of TEOS and the formation of SiO<sub>2</sub> layer. In comparison, for the coated TiO<sub>2</sub> layer, all the sPDVB sulfonated from 5 min to 24 h can have good coating (Fig. 3e to Fig. 3h). We test the effect of different amounts of TEOS or TBT on the coating [16]. A lower amount of TEOS or TBT can be obtained a thinner outer layer of SiO<sub>2</sub> or TiO<sub>2</sub>. As increasing the amount of TEOS or TBT, the thickness and amount of the SiO<sub>2</sub> or TiO<sub>2</sub> outer layer is added gradually (Fig. 4). However, using excessive TEOS or TBT can lead to some imperfection in the core–shell structure (Fig. S2).

# 3.2. Preparation of ultrashort composite nanotubes by twin-screw extruder

To interrupt the long sPDVB composite nanotubes into below 2  $\mu$ m, but without causing the SiO<sub>2</sub> or TiO<sub>2</sub> outer layer falling off seriously, we try different instruments including the twin-screw extruder, mechanical stirrer, ultrasonic cell crusher, soymilk mixer, tissue grinder and oscillator. Only blending the composite nanotube with some thermoplastic polymer and high strength shearing in the twin-screw extruder (Fig. 1) can achieve the above object in a short time that some proportion of the ultrashort composite nanotubes can keep the relative intact core–shell structure (Fig. 5c and Fig. 5f), and the integrity of ultrashort sPDVB@TiO<sub>2</sub> nanotubes is better than sPDVB@SiO<sub>2</sub> nanotubes. Furthermore, composite sPDVB nanotubes with sulfonated time of 24 h



Fig. 6. TEM images of ultrashort sPDVB@TiO<sub>2</sub> core-shell nanotubes prepared with PC under twin-screw extruder at different processing temperature: (a) original nanotubes; (b) 280 °C; (c) 250 °C; (d) 215 °C; (e) length distribution of core-shell nanotubes broken at different temperatures.



Fig. 7. (a) TEM images of ultrashort sPDVB@TiO<sub>2</sub> nanotubes interrupted with PMMA using twin-screw extruder; (b) TEM images of ultrashort sPDVB@TiO<sub>2</sub> nanotubes interrupted with PS using twin-screw extruder; (c) The relationship between the temperature and torque of PC, PMMA, and PS tested using the Revolving Rheometer.

can keep relative integrity of core–shell structure when interruption, whereas the coating of sPDVB with low sulfonated degree are easier to fall off than that with sulfonation for 24 h. By contrast, when dispersing the long sPDVB composite nanotubes in ethanol with the concentration of 0.002 g/ml, then interrupting by soymilk mixer, tissue grinder, or oscillator for 3 h respectively, majority of the composite nanotubes are kept at dozens of micrometers. When using mechanical stirring to interrupt the composite nanotube into less than 2  $\mu$ m in ethanol, it takes more than 24 h but most of the outer layer of SiO<sub>2</sub> or TiO<sub>2</sub> is destroyed or peeled off (Fig. 5a, Fig. 5d and Fig. S3). When using ultrasonic cell crusher to interrupt the nanotubes, but before the composite nanotubes are broken into a few microns, almost the SiO<sub>2</sub> or TiO<sub>2</sub> coating has detached (Fig. 5b and Fig. 5e).

As the temperature gradually increasing, thermoplastic polymer will undergo five states including glass region, glass transition, rubber elastic region, viscosity flow transition, and viscose flow region. The polymer can be processed in twin-screw extrusion processing above the viscous flow temperature ( $T_f$ ) and below the thermal decomposition temperature. Different polymers have different  $T_f$  and different suitable processing temperature ( $T_p$ ). At the  $T_f$ , the polymer is in the viscosity flow transition state, which is between the rubber elastic state and viscose flow state, and the polymer has both certain elasticity and fluidity. As the temperature increasing, the material changes into viscous flow state, and the mechanical strength gradually decreases. PC has a higher mechanical strength and higher processing temperature ( $T_p$ ). When the temperature of twin-screw mixing is reduced from 280 °C to 215 °C, the torque and shearing force gradually increases and the length of the composite nanotubes gradually decreases, but the SiO<sub>2</sub> or TiO<sub>2</sub> outer layer of the interrupted composite nanotubes has not fallen off (Fig. 6). As the temperature dropping to 215 °C, the PC is close to the viscosity flow transition state and its mechanical properties increase to a certain extent, reaching the maximum torque limitation of the twin-screw extruder (100 mN•m), so the lower temperature twin-screw mixing and breaking tests have not performed.

We also mix and interrupt sPDVB composite nanotubes with different polymers (such as PS or PMMA). PS or PMMA has lower  $T_p$  and poor mechanical strength than PC. At 140 °C and 180 °C, it reaches the maximum torque limit (100 mN•m) of the twin-screw extruder using PS and PMMA respectively, and PS and PMMA are also close to the viscosity flow transition state. The PS or PMMA can also break the sPDVB composite nanotubes into 2  $\mu$ m at certain temperature (Fig. 7 a and Fig. 7b). We use the Revolving Rheometer to test the relationship between the temperature and torque of PC, PMMA, and PS [22,23]. At 210 °C, 180 °C, and 140 °C, the three materials reach similar torque values, and as temperature increases, the torque reduces rapidly (Fig. 7c). Thus, the ultrashort composite nanotubes with a length of below 2  $\mu$ m can be prepared by mixing the long composite nanotubes with different polymer resin and shearing at a high enough strength using a twin-screw extruder.

The ultrashort composite nanotubes have certain oil–water emulsification effect (Fig. 8a) and the ultrashort composites nanotubes lie on the oil-in-water interface (Fig. 8b). Particularly, the ultrashort sPDVB@TiO<sub>2</sub> nanotubes with sulfonated time of 24 h can form a stable oil-in-water high internal phase emulsion (HIPE) [24,25]. A small amount of the nanotubes can emulsify 350 times its own mass of oil and



**Fig. 8.** (a) microscopy image of the emulsion stabilized with the ultrashort sPDVB@SiO<sub>2</sub> composite nanotubes; (b) SEM image of the paraffin droplets stabilized with the ultrashort sPDVB@SiO<sub>2</sub> composite nanotubes; (c) a n-decane /water mixture (left) and a n-decane-in-water emulsion stabilized with the ultrashort sPDVB@TiO<sub>2</sub> nanotubes (right), Sudan III is added to n-decane as a chromogenic agent. The ultrashort sPDVB@TiO<sub>2</sub> nanotubes can emulsify 350 times its own mass of oil and forming an oil-in-water high internal phase emulsion (HIPE); (d) CLSM image of the HIPE: n-decane (blue), water (red) and ultrashort sPDVB@TiO<sub>2</sub> nanotubes (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the oil can account for 77.8 vol% of the total solution quality (Fig. 8c). Observed by laser confocal microscopy (Fig. 8d), the emulsion is in the form of oil-in-water emulsion.

#### 4. Conclusion

By mixing the sPDVB@TiO<sub>2</sub> or sPDVB@SiO<sub>2</sub> composite nanotubes with thermoplastic polymer resin and shearing at high strength using a twin-screw extruder, the ultrashort composite nanotubes below 2  $\mu$ m in length can be prepared and some proportion of them keep the core–shell structure. Preparing ultrashort composite nanomaterials with the twinscrew extruder provides a new method for the processing of nanocomposites.

#### CRediT authorship contribution statement

Hongyu Meng: Conceptualization, Methodology, Investigation, Formal analysis, Writing – original draft, Resources, Funding acquisition. Caidan Zhang: Methodology, Writing – review & editing. Yansong Gai: Writing – review & editing. Qiao Yu: Formal analysis. Zhou Li: Methodology, Funding acquisition, Writing – review & editing.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgements

This work was supported by the National Natural Science Foundation of China (T2125003, 61875015); Beijing Natural Science Foundation (JQ20038).

# Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.compositesa.2022.106999.

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