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Fabrication and Dielectric Properties of Soft-core Helical Particles Using *Spirulina Platensis* as Templates[1]

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Abstract: Aiming at the lightweight filler particles with good dielectric properties in the composites, helical *Spirulina platensis* were chosen as templates to produce microscopic helical soft-core filler particles by an electroless deposition technique. The morphology and appearance of the coated *Spirulina platensis* was analysed with optical microscopy and scanning electron microscopy respectively, the result showed that the particles were successfully coated with a uniform metal coating and their initial helical shape were perfectly replicated. The dielectric properties of these helical soft-core filler particles embedded in epoxy resin were studied in detail, which showed that with the coating thickness increase, the real and imaginary part of permittivity of the composites both increase in a frequency of 2–18 GHz. These soft-core metallised helical microorganisms are lightweight and have good dielectric properties. The metal content in the composites is only 6.6 vol% when the percolation threshold occurs. Such low metal content can reach percolation point is attributed to the filler particles' soft-core structure and long helical shape advantage.

Keywords: Microorganism; bio-replicated forming; soft-core helical particle; electroless deposition; dielectric property

1. INTRODUCTION

The study on dielectric properties of particle-filled polymeric systems has been advancing at a rapid pace. Much of the interest in these materials stems from the fact that their physical properties can be

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systematically tuned by variation of the size and shape of the constituents. The reward of studying them is high since they combine cost effectiveness and flexibility of use with impressive performance in key parameters: electrical cable sheathing, electrically conductive adhesive, electromagnetic wave absorbing and shielding are just a few examples of their many uses (Christian, 2002; Myroshnychenko & Brosseau, 2008; ZHUO et al., 2008).

Targeting the engineering application, producing lightweight filler particles with attractive performance has become a trend since this is an effective way to make the composites lighter. Despite fabricating the fillers with lightweight composition material (such as carbon black (Achour et al., 2008), carbon nanotube (Park et al., 2009), etc.) directly, hollowing out the usual metal particles is an effective way to reduce their density. Different approaches have been carried out: Dawson et al. coated spherical glass bubbles with magnetizable materials to produce hollow filler particles (Dawson et al., 1979), Yan et al. deposit metal hydroxide/oxide nanostructures onto carbon nanotubes by electrochemical approach (YAN et al., 2008), the Naval Research Laboratory of USA used lipid tubules as templates to produce metal tubules by an electroless deposition method (Browning et al., 1998; Chiou et al., 2003). We proposed bio-replicated forming technology, using microorganisms as templates to produce soft-core particles with different shapes and studied the dielectric properties of rod-like metalized bacillus (LI et al., 2003; CAI et al., 2003; CAI et al., 2004). Compared with particle fabrication method using biomaterial such as liposome and protein as templates (Browning et al., 1998; YANG et al., 2004), the bio-replicated forming technology using microorganisms as templates has obvious advantages such as diversity of particle shape and size (Over 200,000 different kinds of microorganisms were found, lots of them have typical shape), convenience for raw material obtaining (The microorganisms are widely distributed on earth), low cost (Most of the microorganism can be easily bulk cultured) , and stability in fabrication process (The pH value of the plating solution can vary from 1 to 13, which is very strictly constrained for most biomaterial template). Yet the performance of the metalized rod-like bacilli in composites didn't show distinct improvement compared with other research, especially with the metalized liposome tubules, since the latter has bigger aspect ratio, which can generate bigger polarization effect and result in the improvement of dielectric properties (Browning et al., 1998; Chiou et al., 2003; Brosseau et al., 2000).

In this paper, we use helical microorganisms as templates to fabricate helical particles and further study their dielectric properties. Compared with the rod-like bacilli, the helical microorganisms have bigger diameter and higher aspect ratio, which may result in lower density of the filler particles and higher composite permittivity since they have more preferable shape (Brosseau et al., 2000). The morphology of the metallized helical microorganisms was studied with optical microscope and scanning electron microscope respectively. The dielectric properties of metallized helical microorganisms with different coating depth and different loadings were studied in detail. The shape mechanism is also proposed to explain the excellent dielectric performances.

2. MATERIALS AND METHODS

2.1 Materials and sample preparation

The microorganisms selected as templates were *Spirulina platensis*, which are multi-cell species and appear standard helical shapes in general. The overall dimensions are as follows: diameter of the cells, 5-8μm; total length, 300-500μm; diameter of spin, 26-36μm; pitch distance, 43-57μm. They can be cultured in open-air pool system or closed bioreactor system then harvest for further treatment.

The metallization process of the CoNiP-plated *Spirulina platensi* was similar with that of CoNiP-plated *Bacilli cereus*, as described in previous studies (LI et al., 2003). In brief, the collected *Spirulina platensis* were fixed with glutaraldehyde and osmic acid first, subsequently treated with a colloidal Pd-Sn catalyst, followed by accelerating the catalyst with solution containing 30 g/l $NaH_2PO_2 \cdot 2H_2O$ for a few minutes at room temperature. The activated *Spirulina platensis* were then washed and stored in water. Finally, the *Spirulina platensis*' surfaces were plated with CoNiP coat through an electroless plating process with self-prepared solution, which composition was shown in Table 1. During the plating process, mechanical stirring was applied to avoid aggregation and achieve uniform coat. The thickness of the coat was controlled from batch to batch by the ratio of the solution volume added in bath to the microorganism content.

Table 1: Composition of electroless plating baths for depositing CoNiP coating (mol/L)

Bath	Ni^{2+} or Co^{2+}	Reducing agent	Complex agent	Buffer agent	pH
CoNiP	0.04 $NiSO_4 \cdot 6H_2O$ 0.06 $CoSO_4 \cdot 7H_2O$	0.20 $NaH_2PO_2 \cdot H_2O$	$0.40C_4H_6O_5$ $0.30C_3H_4O$ $0.50C_4H_4Na_2O_4 \cdot 6H_2O$	0.10 $(NH_4)_2SO_4$	pH=9

Annotations: temperature was kept at 80°C for electroless deposition.

The metallized microorganisms were rinsed with distilled water, then dehydrated in an alcohol series, then dehydrated twice in acetone and suspended therein to be used for composite formation. The concentration of metallized microorganisms in organic solvent suspension was determined by drying and weighing an aliquot of the mixture. The metallized microorganisms were cast in epoxy by adding the microorganism/acetone slurry to the epoxy resin, Epon 812; this mixture was stirred by hand for several minutes to make them more homogeneous, removing the acetone by rotary evaporation under vacuum for about 2 h. Then the curing agent (DDSA), solidifying agent (Methylnadic anhydride), and accelerator agent (2-4-6 Tris Phenol) were added in proportion and mixed for another 10 min. The concentrations of metallized microorganisms in the composites were varied from 10 to 40 vol%. The composites were then poured into particular tubules and placed in a vacuum oven for degassing again for 1 h, after which the samples were placed in a thermotank and allowed to cure at 60 ^{o}C for 24–36 h. The samples were removed from the molds after full cure, machined to sizes suitable for dielectric measurement.

2.2 Optical microscopy

An optical microscope (Nikon measuring Microscope MM-40, Japan) was used to examine the overview and completeness of *Spirulina platensi* before and after plating. The mixture of *Spirulina platensi* and alcohol was dropped onto a glass slide, and then put a cover slide on the droplet. The specimen was placed in the view field of the microscopy and observed with the reflect flight, the micrographs were taken by using a digital camera attached to the microscope.

2.3 Electron microscope

A scanning electron microscope (CAMBRIDGE STEREOSCAN 250 Mk2) was used to examine the morphology of metallized *Spirulina platensi* in detail. Samples were dehydrated in an alcohol series and dried in air, and mounted on an aluminum stub using an adhesive carbon tab.

2.4 Dielectric measurements

A vector network analyzer (HP8510, Hewlett-Packard, Palo Alto, CA) was used to measure the dielectric properties of the samples over a frequency range of 2–18 GHz. Each toroidal sample, $7^{+0.03}_{-0.02}$ mm in outer diameter and $3^{+0.05}_{0}$ mm in inner diameter, approximately 4 mm thick, was placed in a coaxial measurement fixture. The S-parameters of all the samples were subsequently measured.

3. RESULTS AND DISCUSSION

Figure 1a and b show the optical micrograph of *Spirulina platensis* before and after being coated with CoNiP. The helical particles after plating show metal luster in view when the reflected light was applied, which means the *Spirulina platensis* was successfully metallized by the elecroless depisition process. Compare Fig. 1a and Fig. 1b, it is very clear that the *Spirulina platensis* keep their initial helical shape and there are fewer breaks, and they show good dispersion in the solution. Figure 2 shows a typical SEM image

of the coated *Spirulina platensis* with the cross section. It could be noticed that the coating was compact and uniform, and the helical particle is hollow in view since its inner template is *Spirulina platensis* which is different from its outer metallic coating, so the metallized *Spirulina platensi* is a kind of soft-core metallic filler particle. The coating thickness can be varied from 0.1μm to 0.5μm according to the added solution ratio per unit weigh *Spirulina platensis*. Though even thicker coating can also be achieved, yet considering the metal content increase will improve the particle density, so the coating thickness was not encouraged to further improve. If the coating thickness is less than 0.4 μm, the density of the particles is below 2 g/cm^3 according to the test result, so they are lightweight filler particles.

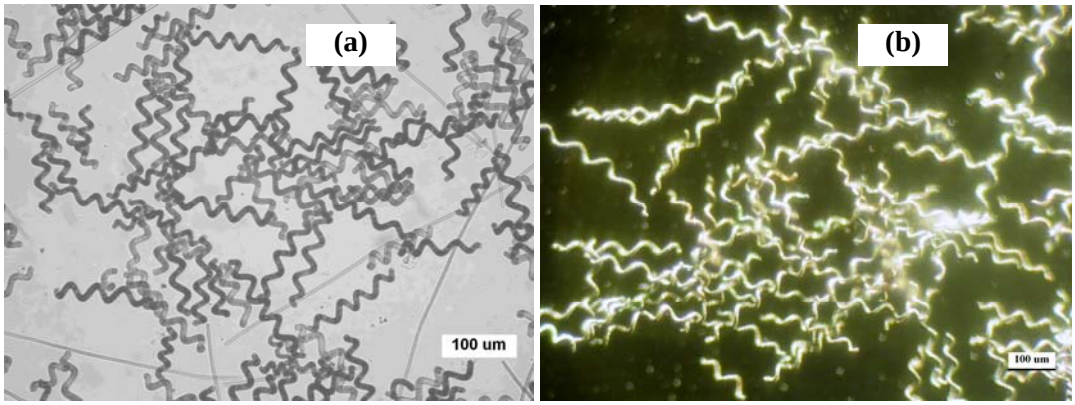

Fig. 1: Optical micrograph of *Spirulina platensis* before and after electroless deposition with CoNiP coating（Scale 100μm）

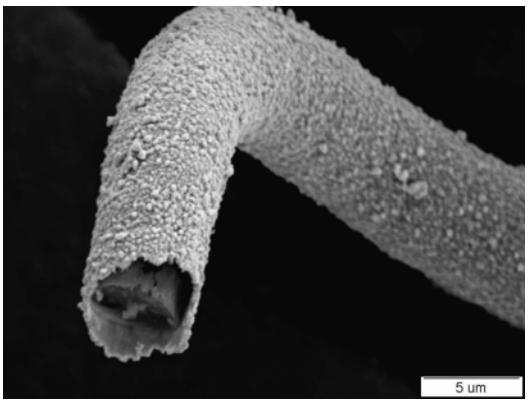

Fig. 2: SEM micrograph of *Spirulina platensis* with CoNiP coating（Scale 5μm）

To invest the influence of coating thickness and adding volume of the metallized *Spirulina platensis* on the dielectric properties of the composites, samples containing filler particles with coating thickness of 0.2 μm and 0.4μm were tested for different volume ratio to composite (10 vol%, 20 vol%, 30 vol% and 40 vol%). Fig 3 shows the real (ε′) and imaginary (ε″) parts of permittivity of the composites containing 10 vol% metallized *Spirulina platensis*. The result shows that the real part and imaginary part of the permittivity keep constant respectively at 10 vol% for both samples over the whole frequency range examined in this study. The coating thickness has obvious impact on the permittivity, the real (ε′) and imaginary (ε″) parts of permittivity of the composites containing filler particles with 0.4μm coating thickness [Fig3. (b)] are both higher than that of composite containing filler particles with 0.2μm coating thickness [Fig3. (a)]. And the same result was found for the composites with other volume ratios of the soft-core fillers. For simplicity, only the permittivity of the composites with different adding volume ratio of the soft-core particles with 0.4μm coating thickness was presented, as shown in Fig. 4.

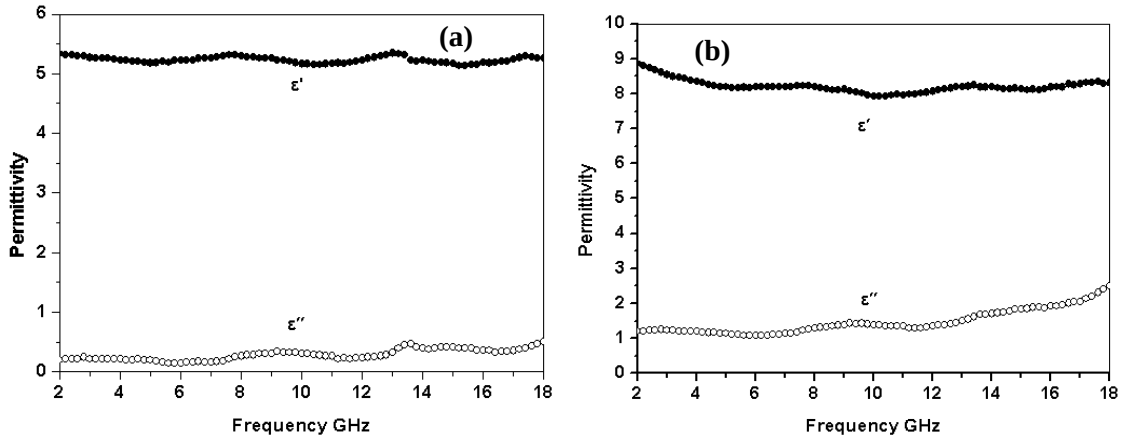

Fig. 3: Real and imaginary parts of the permittivity vs frequency in the range 2–18 GHz for the typical samples containing 10 vol% metallized *Spirulina platensis*. (a) filler particles with coating thickness 0.2μm and (b) filler particles with coating thickness 0.4μm.

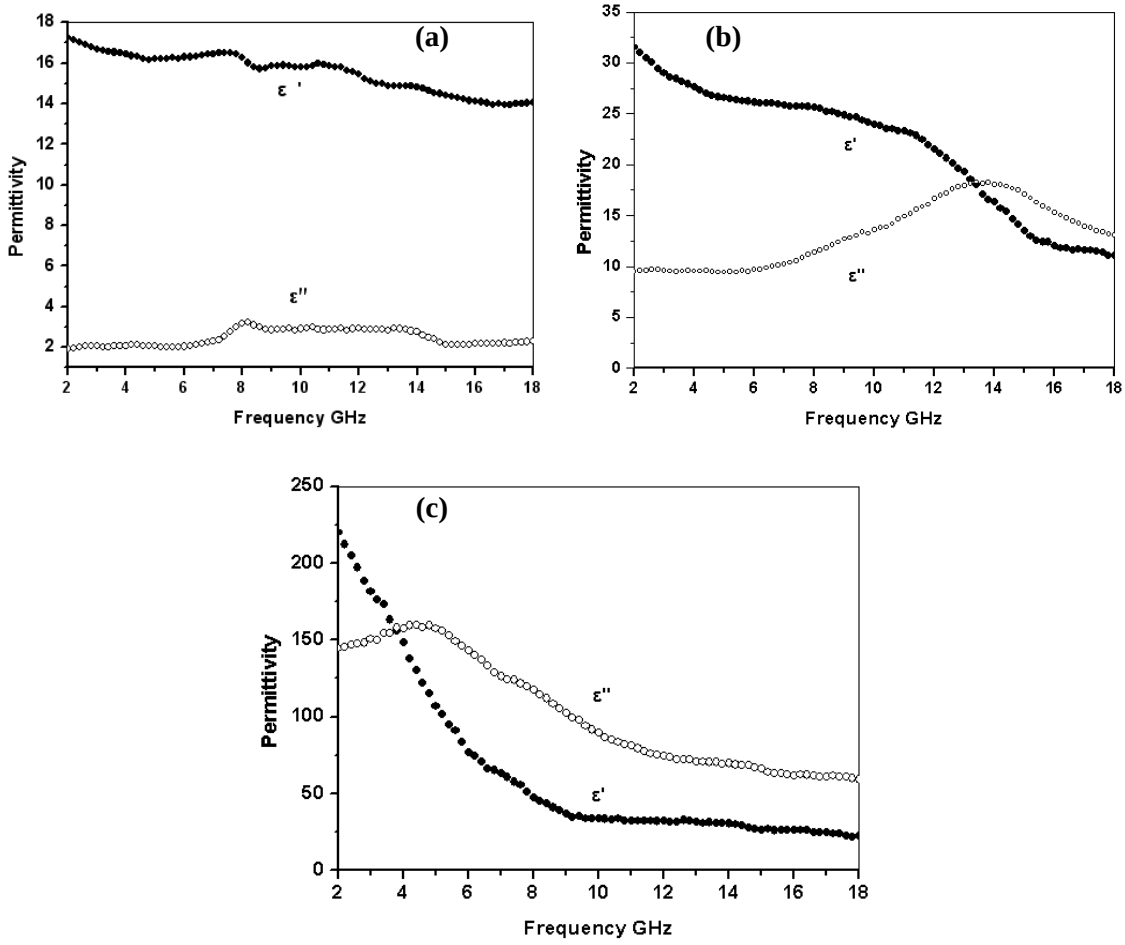

Fig. 4: Real and imaginary parts of the permittivity vs frequency in the range 2–18 GHz for typical samples containing different volume faction metallized *Spirulina platensis with coating thickness 0.4μm.* (a) 20 vol%, (b) 30 vol% and (c)40 vol%.

It could be noticed that with the volume ratio of the filler particles adding, the real (ε′) and imaginary (ε″) parts of permittivity of the composites both improve rapidly, and the value vary according to the frequency. The real part is lower in the higher frequency for all these three samples, the peak value of imaginary part increase sharply and moves to the lower frequency direction when the volume fraction increases from 20% to 40%. For the 20 vol% sample, the imaginary part is only around 2 to 3, for the 30 vol% sample, the imaginary part is above 10, when the frequency is over 13.3 GHz, its value is higher than the real part of the permittivity, which means the percolation point threshold occurs (Myroshnychenko & Brosseau, 2008). And for the 40 vol% sample, the imaginary part is higher than the real part of the permittivity over most tested frequency range. Noticing the diameter of the Spirulina platensis is only around 6 μm, and the coating thickness is 0.4 μm, the volume fractions of the metal coating to the volume of the metallized microorganisms is about 22%, the percolation threshold occurs at the metal coating volume fraction of 6.6% (30 vol% × 22%), which is much lower than that of any solid particles. Since the dielectric properties of the microorganisms are similar to the resin base (CAI et al., 2004), this optimal result is due to the metallized helical microorganisms are soft-core and they have favorable shapes. The soft-core structure make the contributing metal materials on the particle surface and reduces the filler particle density, the high aspect-ratio structure bring significant polarization effect; furthermore, its helical shape may have chiral effect, which also is helpful to improve its dielectric properties (Motojima et al., 2003).

4. CONCLUSIONS

With the bio-replicated forming technology based on microorganisms, the *Spirulina platensis* were used as templates to produce microscopic helical soft-core filler particles by an electroless deposition of CoNiP coating. The density of the particles is below 2g/cm^3 when the coating thickness is less than 0.4μm. The dielectric properties of helical soft-core filler particles embedded in epoxy resin were studied in detail; the results show that bigger metal coating thickness has bigger permittivity value for the same filler volume content. The dielectric properties of composites containing this kind of helical soft-core particle are excellent, with the filler volume adding increase, the real and imaginary part of permittivity of composites both increase significantly. When the volume adding is 30%, the percolation threshold occurs at the higher frequency range. If considering the metal content in the composites, it's only 6.6 vol% when the percolation threshold occurs. Such low metal content can reach percolation point is attributed to the filler particles' soft-core structure and helical shape advantage.

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