Flexible and anisotropically conductive sandwich film by assembly of liquid silicone rubber and cobalt coated glass fiber composites via magnetic field inducement

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Research Article

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Abstract

In this work, we have prepared electromagnetic cobalt coated glass fiber (Co@GF) composite via electroless plating method firstly. And then a conductive sandwich flexible film consisted of Co@GF composite and liquid silicone rubber (RTV-2) is successfully formed, through tape casting method at room temperature. Based on the perfect coating and excellent electrical conductivity of Co@GF composite, the resultant RTV-2/Co@GF/RTV-2 sandwich flexible film shows high electrical conductivity of 0.264 Ω·cm and can stretch to 100% (of 4.40 Ω·cm) without obvious fracture. When the magnetic field was applied to the curing process, the electromagnetic Co@GF composite aligned automatically in the RTV-2 matrix on account of its ferromagnetic nature. The as-prepared film shows anisotropy in electrical performance. The volume resistivity parallel to the magnetic field direction is about two times lower than that of perpendicular direction. The maximum difference in volume resistivity ($\rho_{//}$ of 0.768 Ω·cm and $\rho_{\perp}$ of 1.549 Ω·cm) is obtained at magnetic field intensity of 800 mT. In addition, a certain magnetic field intensity at 100mT is helpful to improve the electrical conductivity of the as-obtained sandwich film. The anisotropic RTV-2/Co@GF/RTV-2 sandwich flexible film would be considered as promising flexible electronic sensor where discrepant sensing sensitivity is required in orthogonal directions.

1. Introduction

The rapid development of portable, wearable and implantable flexible electronics has attracted tremendous attention. Those optimized and superior characteristics will facilitate the development of electronic devices with different functionalities, such as flexible displays [1], smart mobile devices, implantable biosensors [2], etc. As a series of performance such as excellent electrical conductivity, robust construction, super flexibility and sensitivity [3-6] have been improved. One new challenge is to create anisotropic flexible materials [7, 8] which possessed discrepant sensing sensitivity in different directions. To date, some strategies have been proposed for the alignment of fillers in matrix, basically applying external fields including shear flow [9], magnetic [10] and electric field [11]. The magnetic field inducement method shows irreplaceable superiorities, intelligent control and different orientations at arbitrary directions. In such approach, the conductive component is required to have response to the external magnetic field, particularly magnetic metals such as Co and Ni. For instance, Xu et al. suggested the magnetic field inducement processing to align nickel coated glass fiber in polypropylene matrix along the magnetic direction and observed obvious anisotropy in electrical and electromagnetic interference (EMI) shielding performance [12]. Knaapila et al. also used magnetic field to align nickel particles into stringlike assemblies in urethane oligomer mixtures and create a Ni particle/polymer composite with anisotropic electrical conductivity [13]. It is well known that Ni and Co metals are easily oxidized at high temperature and bare environment. To solve this problem, we need choose a novel forming method at low temperature, and also the finally conductive fillers must not be exposed to the air. According to common flexible matrix materials, liquid silicone rubber [14, 15], thermoplastic polyurethane (TPU) [16], dimethylsiloxane (PDMS) [17, 18], and epoxy [19, 20] so on, liquid silicone rubber must be the best choice, owing to its enough flexibility and mechanical property, most of all, it can be molded with a desired size.
at room temperature. In addition, some reports about sandwich-like structure [21-23] conductive film indicated its unique advantages, such as structure stability, persistent electrical conductivity and lower fillers consumption.

Glass fiber possesses excellent chemical and thermal stability, low-cost, large aspect ratio and high mechanical strength. Electroless plating is a kind of surface treatment technology, usually to make non-electromagnetic filler electromagnetization [24, 25]. Therefore, it is promising to realize the magnetic inducing alignment of such fillers in flexible matrix.

In this work, we reported a novel strategy, namely, magnetic-assistant tape casting method to prepare conductive flexible film comprising cobalt coated glass fiber (Co@GF) as conductive filler and liquid silicone rubber (RTV-2) as flexible matrix. The resulting RTV-2/Co@GF/RTV-2 sandwich film showed high flexible and excellent conductivity, which stretched to 100% without severe damage of mechanical property and conductivity. After magnetic inducing, the as-prepared film exhibited significant response to the magnetic field during the curing process and thus oriented automatically in RTV-2 matrix. A significant difference in volume resistivity between parallel and perpendicular to the direction of magnetic field has been observed. And appropriate orientation contributed to form a more perfect conductive network, so the excellent volume resistivity ($r_\parallel$ of 0.153 Ω·cm and $r_\perp$ of 0.211 Ω·cm) has been achieved at magnetic field intensity of 100 mT.

2. Experimental Procedure

2.1 Synthesis of Co@GF composite

Co@GF composite, with volume resistivity of $4.2 \times 10^{-3}$ Ω·cm, saturation magnetization (Ms) of 21.4 emu/g and coercivity (Hc) of 382.7 Oe, was prepared via electroless plating technology, which similar to our previous work [26]. Glass fiber (density: 2.5 g/cm³, diameter: 15 μm, and length: 40-200 μm) was used as the core material. All other materials, solvent and reagent were obtained from commercial sources and used without further purification. The process parameters and conditions of electroless cobalt plating are presented in Table 1.

Table 1 Process parameters and conditions of electroless cobalt plating
2.2 Preparation of conductive RTV-2/Co@GF/RTV-2 sandwich flexible film

RTV-2/Co@GF/RTV-2 sandwich flexible film was prepared via tape casting method at room temperature, the schematic illustration is provided in Fig. 1. First, 2 g of RTV-2, 5 g of xylene \((C_8H_{10})\), and 0.06 g of tetraethyl orthosilicate (TEOS) were mixed homogeneously under vigorous stirring. \(C_8H_{10}\) was worked as diluent solvent, and TEOS was served as curing agent in the liquid silicone rubber system. Subsequently, the diluent silicone rubber solution was poured into the die plate (PMMA, \(r=10\text{cm}\)), and then cured at room temperature for 45 min. The obtained film was marked as the pure RTV-2 film. The RTV-2/Co@GF/RTV-2 sandwich flexible film was composed of pure RTV-2 film and Co@GF/RTV-2 composite film. The Co@GF/RTV-2 composite film was prepared by the same method using Co@GF as a filler. Typically, 3 g of RTV-2, 7.5 g of \(C_8H_{10}\), and 0.09 g of TEOS were mixed homogeneously under vigorous stirring. After that, different content of Co@GF filler (0.5~3.0 g) was added into the mixed solution with mechanical agitation for 5 min. Finally, the resulting mixed solution was poured cautiously onto the pure RTV-2 film, which the surface must be hard enough to make sure that the mixed solution flowed by gravity. After curing at an ambient temperature for 24 h, the RTV-2/Co@GF/RTV-2 sandwich flexible film was fabricated.

### Table 2 Process parameters of anisotropic conductive flexible film

| Parameter       | Content and conditions |
|-----------------|------------------------|
| CoCl\(_2\)·6H\(_2\)O | 30 g/L                 |
| Na\(_3\)C\(_6\)H\(_5\)O\(_7\) | 40 g/L                 |
| NH\(_3\)H\(_2\)O | 12 mL/L                |
| NaH\(_2\)PO\(_2\)·H\(_2\)O | 30 g/L                 |
| Temperature     | 80 °C                  |
| Time            | 50 min                 |

2.3 Preparation of anisotropic conductive flexible film

The anisotropic conductive flexible film was prepared via magnetic-assistant tape casting method at room temperature, the schematic illustration is presented in Fig. 6a. Herein, two kinds of anisotropic conductive flexible film were prepared, sandwich film (RTV-2/Co@GF/RTV-2) and simple film (Co@GF/RTV-2), respectively. The foregoing conductive RTV-2/Co@GF/RTV-2 flexible sandwich film was induced magnetic field ranging from 0 to 800 mT during the curing process, which so called anisotropic sandwich film. In order to observe the orientation of filler more clearly, a simple film was prepared. The preparation method was similar to Co@GF/RTV-2 composite film, just also being induced magnetic field (0~800 mT) during the curing process. The process parameters of anisotropic conductive flexible film are presented in Table 2.

Table 2 Process parameters of anisotropic conductive flexible film
| Type      | RTV-2/g | Co@GF/g | C₈H₁₀/g | TEOS/g      | T/°C | t/min+h | B/mT               |
|-----------|---------|---------|---------|-------------|------|---------|--------------------|
| Sandwich  | 1+1     | 0+0.5   | 2.5+2.5 | 0.03+0.03   | 25+25| 45+24   | 0, 50,100,300,500,800 |
| Simple    | 1       | 0.5     | 2.5     | 0.03        | 25   | 24      | 0, 50,100,300,500,800 |

**Notes:** The data before and after “+” are the process parameters of pure RTV-2 film and Co@GF/RTV-2 composite film, respectively.

2.4 Characterizations and measurement

XRD pattern was recorded on a Bruker D8 focus diffractometer using CuKα radiation (λ = 0.15406 nm) with the 2θ angle ranging from 30 to 85°. SEM images were taken by a Hitachi SU-1500 scanning electron microscope, and volume resistivity values were obtained by a SB120 four-point-probe instrument, and the tensile strain-volume resistivity curved line was tested by virtue of the self-regulating manual stretching equipment based on SB120 four-point-probe instrument.

3. Results And Discussion

SEM has been used to characterize the morphology of the as obtained Co@GF composite in the typical synthesis. It could be seen from Fig.2a that the uniform and compact cobalt layer formed on the surface of the glass fibers, the length-diameter ratio was about 2~14. A close-up view of the single composite fiber revealed that the cobalt coating was consisted of nanoparticle which tightly adhered to glass fiber (Fig.2b). Powder XRD has been used to determine the crystal structure and chemical composition of the resultant product. Fig. 2c displayed the XRD pattern of the as-prepared product. Five diffraction peaks index to (100), (002), (101), (102) and (110) planes of the hexagonal close-packed cobalt crystals (JCPDS Card no. 05-0727). No peaks due to the impurities of cobalt oxides or hydroxides could be observed, which indicates that high quality of cobalt layer on glass fiber has been achieved. The magnetic properties of Co@GF composite obtained from the typical synthesis were investigated at room temperature, as exhibited in Fig. 2d. it can be confirmed that the Co@GF composite showed typical ferromagnetic behavior with saturation magnetization (Ms) of 21.4 emu/g and coercivity (Hc) of 382.7 Oe separately. The volume resistivity value of the as-obtained Co@GF composites was as low as 4.2×10⁻³ Ω·cm. It proved that uniform and compact Co layer on the surface of glass fiber was successfully prepared, both possessing outstanding electrical conductivity and magnetic property.

The conductive RTV-2/Co@GF/RTV-2 sandwich flexible film has been prepared at different content Co@GF composites of 0.5 g, 1.0 g, 1.5 g, 2.0 g, 2.5g and 3.0 g. Fig.3 showed the SEM morphology of sample with 2.5 g of Co@GF composites. From Fig. 3a, it can be found that a sandwich structure film was successfully prepared, which Co@GF composites were embedded between two layers of silicone rubber. The middle layer also contained small amounts of silicone rubber which used to bond conductive
fillers. In an enlarged view (Fig. 3b), Cobalt layer coating on the surface of glass fibers kept intact and barely peeled off, which could carry high density of current and result in high electrical conductivity. Thus the cobalt layer formed a continuous conductive network successfully, attributing to its well distribution at the interface between glass fiber and liquid silicone rubber. The exciting innovative point of such sandwich film is that some advantages such as stability of electrical conductivity, highly flexible property, low content of fillers, high tolerance to stretch and excellent mechanical stability could be found, presented in Fig.1 a, b and c.

As shown in Fig.4a, volume resistivity of conductive RTV-2/Co@GF/RTV-2 sandwich flexible film notably decreased with the increasing Co/GF composites content, owing to the gradually formed conductive network. The volume resistivity of sandwich film was 4.409 Ω·cm at 0.5 g of Co@GF content because of the relatively low content of Co@GF composites, for which could not achieve efficient touch and form conductive network in flexible matrix. When the content of Co@GF composites increased gradually, the volume resistivity of sandwich film could achieve 0.757 Ω·cm at 1.0 g of Co@GF content which indicated the formation of conductive network. After that the volume resistivity of the sandwich film decreased slowly as the increasing Co@GF composite content from 1.5 g to 3.0 g. The sandwich film with 2.5 g Co@GF content possessed the lowest volume resistivity of 0.264 Ω·cm, which exhibited superior conductivity. To further investigate the relationship between volume resistivity of the sandwich film and tensile strain ranging from 0 to 100%, the stretchable performance test has been showed in Fig.4b. At different Co@GF content, the volume resistivity decreased firstly and then increased with increasing tensile strain. This phenomenon could be explained by that certain tensile stress (less than 20%) contributed to contact of Co@GF composite with each other, and further improved the electrical conductivity of the obtained flexible film. Besides, the amount of Co@GF composites directly affected the tensile conductivity of the sandwich film. The less fillers, the more sensitive of the tensile conductivity. And the more fillers, the more stable of the tensile conductivity. Considering the above analysis, the optimum dosage of Co@GF composite must be 2.5 g, both possessing excellent conductivity and flexibility (0.264 Ω·cm at tensile strain of 0% and 4.40 Ω·cm at tensile strain of 100%).

As described in Tab.2 and Fig.5a, anisotropic conductive RTV-2/Co@GF/RTV-2 sandwich film and Co@GF/RTV-2 simple film have been prepared by magnetic induced method, the SEM images have presented in Fig.5c and Fig.5d. In order to explore the influence of magnetic field on the electrical performance of film, $r_∥$ and $r_⊥$ were measured, as displayed in Fig. 5b. It was obvious that the volume resistivity of sandwich film was 1~2 orders of magnitude lower than simple film. In addition, a significant difference in volume resistivity between $r_∥$ and $r_⊥$ have been observed, which was strongly depended on magnetic intensity. In order to explain the mechanism of conductive anisotropy, SEM images of Co@GF composites in simple film under different magnetic intensity have been showed in Fig.6. It could be seen that Co@GF composites were gradually orientated along with the magnetic field direction. However, a high magnetic field strength was easy to form discontinuous conductive network, thus the volume resistivity increased and it gradually transfered to non-conducting material (Fig. 6f).
So a sandwich film has been suggested to solve this problem, the detail data of volume resistivity showed in Fig. 5b. The excellent volume resistivity ($r_\parallel$ of 0.153 $\Omega \cdot$cm and $r_\perp$ of 0.211 $\Omega \cdot$cm) was achieved at magnetic field intensity of 100 mT. This phenomenon could be interpreted as following point, since Co@GF composites showed appropriate orientation parallel to magnetic field direction, a more perfect conductive network have been formed in the parallel direction, so $r_\parallel$ displayed an downtrend after inducement. Co@GF composites were easy to form interconnected network because of the high aspect ratio, thus cobalt coated on the surface of glass fibers could form an efficient conductive network in aligned direction. However, $r_\parallel$ and $r_\perp$ increased when the magnetic field intensity further increased, the maximum difference in volume resistivity ($r_\parallel$ of 0.768 $\Omega \cdot$cm and $r_\perp$ of 1.549 $\Omega \cdot$cm) was obtained at magnetic field intensity of 800 mT, the corresponding SEM images showed in Fig. 7. Obviously, the Co@GF composites, paralleled to the direction of magnetic field, oriented in alignment. It was understandable that much higher alignment would reduce the interconnection of adjacent Co@GF to some extent, which resulted in the increasing volume resistivity consequently. This result was consistent with Xu et al.’ report [12]. Comparing with simple film, sandwich film exhibited much higher electrical conductivity based on the stability of conductive network.

4. Conclusions

In summary, a novel structure of conductive sandwich flexible film consisted of Co@GF composite and liquid silicone rubber (RTV-2) have been successfully prepared via tape casting method at room temperature, which possessed excellent electrical conductivity of 0.264 $\Omega \cdot$cm and could stretch to 100% without serious mechanical property and conductivity damage. At different content of Co@GF composite, a same experimental rule have been found, which the volume resistivity value decreased firstly and then increased with increasing tensile strain ranging from 0 to 100%. This phenomenon could be explained by that certain tensile stress (less than 20%) contributed to contact of Co@GF composites, and further improved the electrical conductivity of the obtained flexible film. When different magnetic field intensity (0~800mT) was applied to the curing process, the electromagnetic Co@GF composites aligned automatically in the RTV-2 matrix. The as-prepared film showed anisotropy in electrical performance. A significant difference in volume resistivity between $r_\parallel$ and $r_\perp$ have been observed, the excellent volume resistivity ($r_\parallel$ of 0.153 $\Omega \cdot$cm and $r_\perp$ of 0.211 $\Omega \cdot$cm) was achieved at magnetic field intensity of 100 mT. This result revealed that appropriate orientation contributed to form a more perfect conductive network, so both $r_\parallel$ and $r_\perp$ displayed a downtrend after inducement. By contrast with the simple film, the anisotropic RTV-2/Co@GF/RTV-2 sandwich flexible film highlighted some advantages such as superior electrical conductivity, less filler content, more stable structure and excellent weatherability. So it would be considered as promising flexible electronic sensor where discrepant sensing sensitivity is required in orthogonal directions.

Declarations

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