Investigation of electrical conductivity and electromagnetic shielding effectiveness of polyaniline composite

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Abstract

With the increasing of electromagnetic pollution and the widely use of commercial and military products, there is an increasing interest in electromagnetic interference (EMI) shielding. This paper mainly aims at electrical conductivity and EMI shielding effectiveness (SE) of the conducting composites made from silicone rubber (SR) with different loading levels of HCl-doped polyaniline (PAN-HCl) in the low frequency range from 3 to 1500 MHz. The result indicates that SE of the composites increase and the volume resistivity decrease with increasing mass ratio loading of PAN-HCl in the SR. The measured SE of the composites are from 16 to 19.3 dB at 100 mass ratio loading of the PAN-HCl and the volume resistivity decrease nine orders of magnitude compared with that of the emeraldine base form of PAN (PAN-EB) composites.

Keywords: PAN-HCl; Silicone rubber; Electrical conductivity; Shielding effectiveness

1. Introduction

There is an increasing interest in electromagnetic interference (EMI) shielding as the use of commercial, military, and scientific electrical products and electronic devices increases rapidly. For EMI shielding materials, typical metals such as copper or aluminum have been used, which have high conductivity (\(\rho\)) and dielectric constant (\(\varepsilon\)). High conductivity and dielectric constant of materials contribute to high EMI shielding efficiency (SE) [1,2]. While typical metals have good mechanical and shielding properties, they have disadvantages such as heavy weight, easy corrosion, and poor processibility for shielding material. Conducting composites (esp. polymers) has inspired much interest because of their light weight, hard corrosion, good processibility and easy control of conductivity. Among conducting polymers, PAN has been studied most extensively since it has various structures, unique doping mechanism, excellent physical and chemical properties, and good stability, and its raw material can be obtained easily as well [3,4]. PAN is a kind of powder with metallic luster, and the conjugation of its molecule chain is so strong that in a long time it had been considered as a polymer with low solubility, accordingly its application in technology was limited [5]. During the recent few years, the problem of its solubility has been solved effectively through doped with protonic acids [4–6]. In this paper, we obtained PAN-HCl powder from PAN-EB through doping, prepared PAN/SR composites, and researched the effect of PAN on electrical conductivity and shielding effectiveness (SE) of the composites in order to search new application field of the PAN.

2. Experimental

2.1. Synthesis of PAN-HCl

Polyaniline is usually prepared by chemical redox polymerization of aniline using ammonium perdisulphate, \((\text{NH}_4)_2\text{S}_2\text{O}_8\), as an oxidant. Distilled aniline (0.02 M) is first dissolved in 500 ml of pre-cooled HCl (1.0 M) solution and maintained at 15 °C. A calculated amount of ammonium perdisulphate (0.534 mol) is dissolved in
378 ml of HCl (1.0 M) and pre-cooled to 15 °C, then is dropwise added to the above solution with constant electromagnetic stirring about 2 h and keep stewing at 15 °C about 20 h. The dark green precipitate resulting from this reaction is washed repeatedly in the filtering funnel with ammonia water (1.0 M) and distilled water until the filtrate became transparent. This precipitate is then dried in an oven at 60 °C to get the PAN-EB in the congeries form and then triturate it to get the PAN-EB powder. The dark green precipitate washed with ammonia water (1.0 M) and distilled water mentioned above is further added to HCl (1.0 M) with constant electromagnetic stirring about 1 h, and then keep stewing at 15 °C about 8 h. The product is washed repeatedly in the filtering funnel with distilled water until the filtrate became transparent. PAN-HCl powder is got by the same drying way mentioned above.

2.2. PAN/SR composites

The composites of conducting polymer PAN with hydroxyl terminated polydimethylsiloxane liquid silicon rubber (GMS331D) were made by blending technology in the room-temperature in a brabender mixing bowl for 5 min at 100 rpm. Cross-linking agent of the liquid silicon rubber is ethyl orthosilicate, and dibutyltin dilaurate is used for its catalyst. The detail of the composite preparation is given in Table 1. Supposed the mass of SR is 100, then different loading levels of PAN from 30 to 100 were blended with the SR and the composites were compression molded into plates of 20 × 100 × 2 mm³ and Ф115 × 2 mm which were then used for studying the electrical conductivity and EMI shielding behavior, respectively.

2.3. Measurements of electrical conductivity

A current–voltage method was used for the volume resistivity measurements (as shown in Fig. 1). A digital multimeter GDM-8055 and a Fluke 8840A were used to measure the electrical current and to provide the voltage. The volume resistivity of samples was calculated by following formula [7]: \( \rho_v = R \times \delta \times d/L (\Omega \text{ cm}) \), where \( R \) is the volume resistance of the measured sample (\( \Omega \)), \( \delta \) is the thickness of the measured sample (cm); \( d \) is the width of the sample (cm); and \( L \) is the effective length of the sample(cm). The calculated values are shown in Table 2.

2.4. Measurements of shielding effectiveness

The SE of the sample for plane-wave condition/simulation was measured using the coaxial cable method. The set-up as shown in Fig. 2 consisted of a DN15115 SE tester, which was connected to a Hewlett-Packard (HP) 8753D vector network analyzer. An HP 8753D type N calibration kit was used to calibrate the system. Then standard attenuators with a total attenuation 100 decibels (dB) were tested to ensure that the dynamic measurement rang up to 100 dB is valid for all sample measurements. The frequency is scanned from 3 to 1.5 GHz and 201 date points are taken in reflection and also in transmission. The attenuation under transmission and that under reflection were measured. The former is equivalent to the SE.

3. Results and discussion

3.1. Morphologies of PAN-HCl particles

TEM image of PAN-HCl prepared by chemical redox polymerization in bulk aqueous solution is shown in Fig. 3. It can be seen the particles is relatively large and irregular accumulation, which is composed of small grain. The smaller grains are considered as primary particles and the accumulation is named for secondary particles. It is thought that the size and dispersing of the secondary particles in polymer and the fabric of the primary particles in the secondary particles contribute to formation of electrical conductivity chain in the composites.

3.2. Effect of PAN on the conductivity of composites

The volume resistivities of the composites containing different PAN loading are shown in Fig. 4. It is observed that the resistivity decreases from 5.467 × 10³ Ω cm to 9.07 × 10⁵ Ω cm with increasing mass ratio of PAN-HCl powder from 30 to 100. From Fig. 4, the volume resistivity of 4# composites containing PAN-HCl...
decreases about nine orders of magnitude compared with that of the composites containing PAN-EB because the PAN-HCl filled composites shown much higher conductivity than PAN-EB filled composites, which indicates that the conductivity of PAN-EB increases greatly after doped.

Typical SEM micrographs of the sample fracture face are shown in Fig. 5. Even though there seemed to be some aggregates of primary particles in the images, it is found that the PAN-HCl powder has good dispersibility in the SR matrix and there are better disgregation as the content increases. From Fig. 5, it is seen that when the PAN loading is lower than 50, there are many enrichment zone of conductive PAN, namely ‘isolated conductive island’, and there are few conductive particles in some other areas, but Fig. 4 shows the resistivity of $10^3 \Omega \cdot \text{cm}$ approximately, which contribute to conduction via hopping or tunneling [9]. Although the electrical conductivity of composites depends mainly on through-going chain mechanism among conductive filler, Polley and Boonstra [10] have found that there is also conductive phenomenon because of elongation behavior of the SR while conductive filler in the matrix do not link each other for conducting chains or mesh. It was found that there was also conduction phenomenon even if the gaps between conductive particles were correspondingly large by research of the relationship of resistivity and conducting particles gaps in the matrix, which was considered to be result of molecular thermodynamic movement and electron transfer movement. When the PAN loading is above 50, ‘isolated conductive islands’ become many smaller accumulation or the primary particles dispersedly and link with each other for more conductive chains or network in the matrix gradually. So the volume resistivity decrease 2~3 orders of magnitude compared with that of 30 mass ratio loading composite.

### 3.3. Electrical conduction mechanism of PAN-HCl

From the results of the volume resistivity mentioned above, the composites made of PAN-HCl and SR have
excellent conducting properties, which is because PAN gains conducting property from doping.

The emeraldine base form of PAN is electrically insulating and can be changed from insulator to conductor through doping, and the doping process can be described as following [11,12]:

\[ y \text{ is the extent of oxidization, depending upon synthesis of the monomer;} \]
\[ x \text{ is the extent of doping, depending upon the doping of the polymer;} \]
\[ A^- \text{ is the anion of protonic acid, depending upon the dopant.} \]

In the doping process, the H\(^+\) of protonic acid protonate N atom in the PAN molecular chain and there are electron hole generated in valence band of doped section of PAN chain, i.e. P-doping. With external electric field, the electron hole moves in the whole chain by the resonance of conjugated \(\pi\)-electron and the electrical conductivity property of the PAN-HCl is shown. The electrical conductivity level has close relationship with the value of \(y\) and \(x\). The larger \(x\) value is, and the more current carrier there will be, then the better the electrical conductivity levels is.

3.4. Effect of PAN-HCl on shielding effectiveness

Electromagnetic shielding means that the energy of electromagnetic radiation is attenuated by reflection or absorption of an electromagnetic shielding material, which is one of the effective methods to realize electromagnetic compatibility. PAN-HCl is a kind of EMI shielding material with good prospect of application because of its electrical...
conductivity. The SE of the composites with PAN-HCl are following.

3.4.1. Theory of electromagnetic shielding

Total shielding efficiencies (SE_T) of the composites have been measured in the far-field with the coaxial cable method (shown as Fig. 1). The EMI SE is defined in terms of the ratio of the power of incoming and outgoing waves as the following expression:

$$SE_T = 10 \log \left( \frac{P_i(E_i)}{P_o(E_o)} \right) = 20 \log \left( \frac{E_i}{E_o} \right)$$

Here \( P_i(E_i) \) and \( P_o(E_o) \) are the power (electric field) of incoming and outgoing waves, respectively. The unit of SE is given as decibel (dB). When the plan wave is incident on shielding material, the phenomena such as reflection, transmission, absorption, and multiple reflections are observed. The SE is described as

$$SE = SE_A + SE_R + SE_M$$

here \( SE_A, SE_R, \) and \( SE_M \) are the shielding efficiency due to absorption, reflection, and multiple reflections, respectively. Reflection loss \( SE_R \) is the result of interaction between conducting particles in the conducting material (free electron or vacancy) and electromagnetic field, and it has relationship with the value of \( \mu_r / \sigma; \) the larger conductivity of the material is, the smaller magnetic permeability is, then the larger reflection loss will be. Absorption loss \( SE_A \) is caused by the heat loss under the action between electric dipole or magnetic dipole in the shielding material and the electromagnetic field. When the conductivity reaches to a certain value, the material with high magnetic permeability has high absorption loss. Multiple reflection loss \( SE_M \) is the loss caused by the constantly touch to the wall surface of the shielding material, but this loss is very low and is the correction term of reflection loss exactly [13].

3.4.2. Effect of PAN-HCl on SE

Fig. 6 shows the variation of SE with PAN loading in the frequency range of 3 MHz~1500 MHz. It is obvious that with the increase in PAN-HCl loading SE increases.

The perusal of Fig. 6 indicates that 30 and 50 mass ratio loading of the conducting PAN shows a SE of 1.8 and 2.5 dB whereas a 70 loading of the PAN-HCl in RS gives a SE of 9.9 dB at the frequency of 1000 MHz. When the loading of the PAN-HCl reaches to 100, the SE are above 16 dB in the whole frequency range of 3 MHz~1500 MHz, and the high peak especially reaches to 19.3 dB at 1000 and 1500 MHz. From the Fig. 5, we can also find that the PAN-EB almost has no SE for its poor conductibility. Comparing Fig. 4 with Fig. 6, it was indicated the direct corresponding relationship between SE and volume resistivity of the composites as well. With the loading of PAN-HCl increasing and the volume resistivity decreasing sharply, the SE increases obviously. This suggests that the reflection dominates the shielding mechanism. As the resistivity decreasing, electromagnetic impedance of the composite becomes smaller and smaller. The level of impedance mismatch to the air becomes larger and larger. Therefore, the reflection loss of the electromagnetic wave is strengthened and the SE increased. In addition, the SE of the composites depends on resistance loss and interfacial polarization loss as well. From SEM micrographs of the sample fracture face shown in Fig. 5, it is observed that the composite has large amount of ‘isolated conducting islands’ of PAN-HCl, which leads to interfacial polarization of electromagnetic wave [14]. As the content of PAN-HCl increases, the size of isolated conducting islands decreases and the number of isolated conducting islands increases, which contribute to the stronger interfacial polarization of electromagnetic wave and larger electromagnetic loss.

4. Conclusion

(1) Composites with PAN-HCl have better electrical conductivity than those with PAN-EB and as the increasing mass ratio loading of PAN-HCl powder the volume resistivity decrease greatly. This is mainly because that the isolated conducting islands become dispersedly and link with each other gradually as the content of PAN-HCl increases, then there is complete conducting network in the composites.

(2) As the increase in PAN-HCl loading and the decreases in the volume resistivity, SE increases rapidly, which depends not only on the conductivity, but also on resistance loss and interfacial polarization loss as well.

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