Study on Structure and Properties of Commercial Conductive Polymer Materials

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Abstract: The conductive polymer is a kind of polymer material with conductive properties, and has the advantages of easy electrical processing and controllability of electrical conductivity while having metal conductivity. Compared with traditional conductive materials, it also exhibits special photoelectric and thermoelectric properties, and has broad and attractive commercial application prospects in the fields of energy, optoelectronic devices, sensors and molecular wires. In this paper, the composite polymer conductive material filled with acetylene black is taken as an example to analyze its structure and properties, including mechanical test, electrical conductivity and dielectric properties. It has been found to be excellent in performance and has great commercial application value.

1. Introduction

In the last 20 years, conductive polymer materials have been used in the field of electronic devices, energy, information sensors, molecular devices, electromagnetic shielding, metal anti-corrosion and stealth technology due to their adjustability during processing. Thus, this has caused a lot of scholars' enthusiasm for their research [1-3]. The conductive polymer material is a polymer composite material which can exhibit electrical conductivity under the condition of an applied electric field. Conductive polymer materials can be used as a substitute for metal conductive materials in some fields due to their light weight, easy processing, and controllable electrical properties. More and more conductive polymer materials are being commercialized, especially in lithium batteries, electromagnetic shielding and stealth materials.

At present, commercial conductive polymer materials are mainly divided into two types, the first type is a structured conductive polymer, and the other is a composite conductive polymer [4-5]. The former refers to a polymer material itself or a material having electrical conductivity after a small amount of doping, and its electrical conductivity is comparable to that of a semiconductor or a part of a metal. According to the different conductivity principle, it can be divided into an ionic conductive polymer and an electronic conductive polymer. The composite conductive polymer mainly refers to a composite material obtained by adding a conductive filler to a polymer material by means of filling, surface compounding or layering, three-dimensional composite, wherein the polymer material as a matrix is an insulator. Since the conductivity of this type of material is different, there are several classifications of polymer semiconductors, polymer metals and polymer superconductors. The difference in electrical conductivity can also be divided into electronically conductive polymer materials and ion conductive polymer materials [6].

The research on conductive polymer materials has been widely concerned by the outside world. The application of conductive polymer materials in life should continuously summarize its characteristics and advantages, so as to make better improvements in subsequent research. In this paper, the structure and conductive principle of conductive polymer materials are analyzed firstly, then the properties of carbon-based composite conductive polymer materials are analyzed, and the preparation process of commercial conductive polymer materials is expounded.
2. The Structure of Conductive Polymer and Conduction Principle

2.1 Special structure of conductive polymer

2.1.1 Structured conductive polymer

The structural conductive polymer, also known as the intrinsic conductive polymer, has a molecular structure containing a conjugated long-chain structure, and the delocalized π electrons on the double bond can migrate to form a current on the molecular chain, making the polymer structure inherently conductive. In such a conjugated polymer, the longer the molecular chain, the larger the number of π electrons, and the lower the electron activation energy, that is, the electrons are more easily delocalized, and the conductivity of the polymer is better. A common conductive polymer having a conjugated structure and its conductivity are shown in Table 1.

<table>
<thead>
<tr>
<th>Conductive polymer</th>
<th>Structure</th>
<th>Conductivity(s/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyacetylene</td>
<td><img src="image" alt="Polyacetylene" /></td>
<td>(1.7 \times 10^4)</td>
</tr>
<tr>
<td>Polypyrrole</td>
<td><img src="image" alt="Polypyrrole" /></td>
<td>(7.5 \times 10^4)</td>
</tr>
<tr>
<td>Polythiophene</td>
<td><img src="image" alt="Polythiophene" /></td>
<td>(1.0 \times 10^4)</td>
</tr>
<tr>
<td>Polyphenylene 1.0×102</td>
<td><img src="image" alt="Polyphenylene" /></td>
<td>(1.0 \times 10^2)</td>
</tr>
</tbody>
</table>

2.1.2 Composite conductive polymer

The composite conductive polymer is a material in which various conductive materials are filled in a polymer matrix in different processing techniques. Among them, the filler material provides the electrical conductivity of the material, while the polymer matrix bonds the conductive filler together and provides the processing properties of the material. The conductive filler plays a role in providing carriers in the composite conductive polymer material. The amount, nature and dispersion form of the conductive filler directly determine the conductivity of the material. Commonly used conductive fillers are carbon black, carbon nanotubes, graphene, metal and metal oxides.

2.1.3 Theoretical background of conductive composites

Conductive polymers are mainly divided into two major categories, one is intrinsically conductive polymers (ICPs), and the structure of such materials can facilitate the transmission of electrons and therefore can conduct electricity. The other type is conductive composites (CPCs) whose conductivity is the electrical conductivity due to the conductivity of the conductive filler added to the polymer material. Conductive composites are more processing-friendly and more environmentally friendly than conductive polymers. The conductivity of the conductive particles increases the conductivity slowly decreases. This phenomenon is called conductive percolation:

\[
\sigma = \sigma_p (\nu - \nu_c)^x (1)
\]

where \(\sigma_p\) is the conductivity of CPCs, \(\nu\) is the volume fraction, and \(\nu_c\) is percolation threshold of CPCs [9]. \(x\) is an index related to the dimension of the conductive network within the CPCs. It has been reported that the large variation of the \(x\)-index can range from 1 to 12, due to the narrower tunnel distance distribution in the system, the lower \(x\) value, and the higher \(x\) value caused by the external tunnel distance distribution [8]. This difference between theoretical predictions and experimental data is still an unresolved problem.

2.2. Conductive mechanism

The conductive mechanism of composite conductive polymers mainly includes conductive
pathways, tunneling and field emission [8]. The conductive path mechanism means that the conductive fillers in the composite material overlap each other to form a conductive path to make the material exhibit electrical conductivity; when the tunneling effect is to guide the distance between the electrical fillers sufficiently close, the electrons can jump beyond the base barrier to the adjacent conductive filler. The tunneling current is formed. The field emission means that under the action of a strong internal electric field, when the distance of the conductive filler is large, the electrons can also jump to the adjacent conductive filler to form a field emission current. The three conductive mechanisms in the conductive composites coexist and compete with each other as shown in Figure 1.

![Fig.1. Conductive mechanism model diagram of composite conductive polymer materials](image)

3. Study on Properties of Composite Conductive Polymer Materials

3.1. Mechanical performance test

A polymer conductive material made of the most widely used filler material is selected, and the spline obtained by the reaction blending is processed according to the specifications. These conditions included an angle of 45° and a lateral notch depth of 2.25 mm, and were subjected to a shock test after being kept at a constant temperature of 23 °C for 24 hours. Ten samples were tested for each component, and the average value was taken to obtain the impact strength data.

3.2. Conductivity test

The volume resistivity of the composite was measured at room temperature using a high resistance meter. Five samples were taken for each component, and five points were taken for each sample. The volume resistivity obtained was converted into conductivity by the following formula:

$$\sigma' = \frac{1}{\rho'} \quad (2)$$

Where $\sigma$ is the electrical conductivity and $\rho$ is the volume resistivity.

The conductivity of the conductive polyurethane elastomer of the superconducting carbon black filler has superior electrical conductivity compared to other carbon-based fillers, and the percolation value is also decreased more than other fillers. When the pressure range is from 0 to 20 N, the linearity is preferably that the amount of acetylene black is 5% to 6% of the conductive polyurethane elastomer resistance. When the filler is a carbon nanotube, the linearity of the resistance is highest when the amount of the filler is 6%, and the pressure sensitive range is 0 to 40N. When the conductive polyurethane elastomer whose filler is nanographite has a pressure exceeding 50 N, its resistance value does not substantially change.

3.3. Electrical test

A sample that needs to be measured for its dielectric properties is placed in a test machine to
measure the dielectric constant and dielectric loss at different frequencies of the sample. The conductivity of high-density polyethylene increases as the amount of carbon black increases, but its impact strength decreases at the same time. The critical concentration of carbon black in the matrix is high density polyethylene around 9%. At the critical concentration, the concentration will have a significant effect on the conductivity of high density polyethylene.

4. Test results

4.1. Mechanical properties

Table 2 shows the mechanical properties of this commercial polymer conductive material as a function of filler material and acetylene black content. It can be seen from the Table that the acetylene black-filled polymer conductive material has higher yield strength and tensile modulus. Therefore, its yield strength and tensile modulus increase as the content of acetylene black increases.

<table>
<thead>
<tr>
<th>Acetylene black fraction</th>
<th>0/100</th>
<th>40/60</th>
<th>60/40</th>
<th>100/0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yield strength /MPa</td>
<td>56.2±0.6</td>
<td>54.7±0.3</td>
<td>53.2±0.5</td>
<td>51.9±0.2</td>
</tr>
<tr>
<td>Tensile modulus /MPa</td>
<td>1870±25</td>
<td>1760±36</td>
<td>1650±20</td>
<td>1590±35</td>
</tr>
</tbody>
</table>

4.2. Conductivity and dielectric properties analysis

For the conductivity, when the addition amount of acetylene black is 0.4%, the direct current conductivity is $3.93 \times 10^{-18}$ s/cm, which is equivalent to the direct current conductivity of pure acetylene black.

For its dielectric properties, when the amount of acetylene black added is very low, the relationship between the dielectric constant and the frequency is not significant, that is, the nature of the conventional insulator. When the addition amount reaches 0.6% or more, the dielectric constant will have a substantial increase.

5. Conclusion

Since the advent of conductive polymer materials, a variety of novel conductive polymers have emerged, and more and more researchers have also carried out a wealth of research work in this field. In the future, conductive polymer materials will be more widely used in future applications and applications, especially for their commercial value, which can be used as more sensitive sensors, more efficient information transfer materials and more static materials. In addition, there is a lot of room for development in terms of mechanical properties and electrical conductivity.

References


