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A Full Printed Flexible Pressure Sensor with Improved Temperature Performance based on Optimized Curing Mechanism

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Abstract. *Printable flexible pressure sensors have many important applications in wearable systems. One major challenge of such a sensor is to maintain sensing properties in high temperature. By optimizing the curing mechanism of the flexible pressure sensor functional materials, this paper proposes a new method of achieving high temperature properties for a full printed sensor. The establishment of curing theory is mainly studied. The printing process of this kind of sensor is systematically stated and tested to check whether it can continue to function at high temperatures. Ultimately a fully-printed flexible pressure sensor with good temperature performance is achieved. The paper focuses around the technical route of "material selection—theoretical analysis—function material preparation—design and preparation of device—device performance evaluation". Suitable materials are used in flexible pressure sensors and the curing mechanism is established. This proposed technique can be extended to the development of other printable flexible sensors, which can lead to a huge impact on future applications of the flexible electronics.*
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1. INTRODUCTION

With the continuous integration of informatization and industrialization, Printing Electronics Technology, as one of the representatives of modern intelligent industry, is rising rapidly. A variety of flexible sensors are considered as typical products of printed electronics in the market, such as pressure sensors and bending sensors. They are widely used in many different fields, such as electronic skin, intelligent robots, health monitoring, intelligent sensing, wearable devices, modern automation and intelligentize [1–3]. For example, an ultra-thin printed flexible piezoresistive pressure sensor (Flexiforce) was developed by Tekscan and integrated into shoes to analyze the wearer's gait [4]. Compared with traditional electronic devices and sensors, printing electronic technology is realized by additive manufacturing, which is a graphic printing optimized by functional materials on flexible substrates, thus was wildly used in the production and manufacturing of various sensors and electronic products for its one-time forming [5]. Today's research of the fully printable flexible pressure sensor is very vibrant. Its research direction caters to improving its flexibility, sensitivity, integration and other performance optimizations [6, 7]. However, as an important parameter of the sensors, there are few related research reports about temperature performance, which has great significance. Many flexible pressure sensors have excellent performance but are limited by the ambient temperature conditions. Therefore, this paper starts from the curing mechanism of the functional material of the printable flexible pressure sensor, selects the appropriate curing agent to improve the properties of the composite materials, so as to achieve the purpose of improving the high temperature resistance and creep resistance of such full printed sensors.

There are many kinds of flexible pressure sensors. According to the sensing mechanism, the flexible pressure sensors in the literature mainly include piezoresistive flexible pressure sensors, capacitive flexible pressure sensors and piezoelectric flexible pressure sensors [8–10]. But both Tekscan sensor from America [11] and Aidong sensor from China [12] have two layers of plastic film structure. The principle of this kind of piezoresistive sensor is not piezoresistive effect. In this paper, we attribute it as Interface Effect, which means to sense pressure by changing the contact area of the upper and lower functional layers as applying pressure. Therefore, the actual test is the contact resistance of the upper and lower functional layers, as shown in Figure 1 below. The flexible pressure sensor structure of Tekscan company [13] is composed of two pieces of polyester film, When the external pressure is applied, the resistance of the semiconductor will change in proportion to the external pressure. The resistance value goes to the maximum when there is no pressure; The higher the pressure, the smaller the resistance. It is understood that this kind of sensor is mainly manufactured by TSCAN in the United States, I-Motion in China and Nengstar. However, the serviceable range of the Nengstar and other thin-film pressure sensors is severely restricted in terms of region, domain and so on, for its working temperature cannot exceed 60°C. Thus, it is very important to improve the temperature resistance of the flexible pressure sensors.

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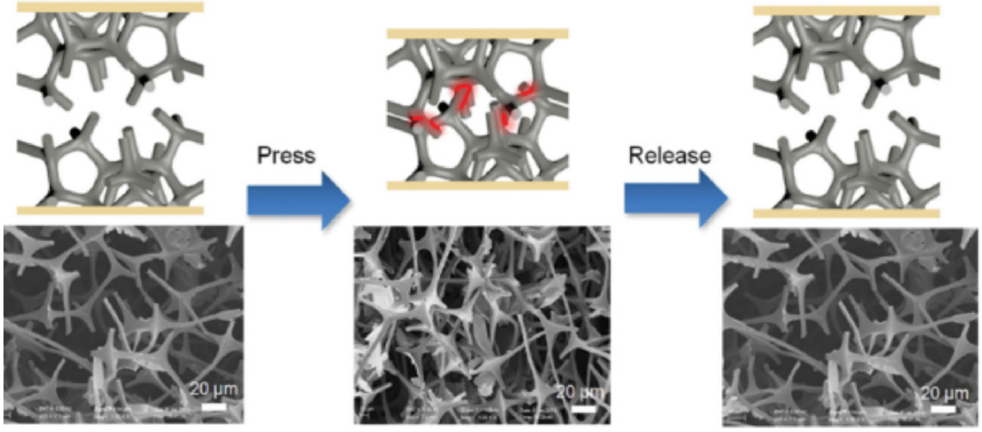


Figure 1. Schematic diagram of interface effect.

The method of improving the temperature resistance of flexible pressure sensors filling composites with carbon series materials has not been reported. Due to the nature of the material itself, the functional materials on the two films are easy to stick together when the ambient temperature exceeds 60°C while pressure is being applied. Based on this situation, this article starts from the perspective of composite material, improves the performance of the material by changing the resin structure, and on this basis, to improve the performance of devices.

2. MATERIAL PREPARATION

The temperature resistance of the flexible pressure sensor mainly depends on the resin matrix composite, and this physical property of the composite in turn depends on the performance of the selected resin matrix [14]. Therefore, the improvement of temperature resistance of the resin matrix directly affects the use of the sensor. The cross-linking reaction of polymer materials is promoted by curing of resin matrix composites, that is, the resin with linear macromolecular structure forms a network molecular structure through cross-linking [15].

2.1 *Selection of Materials and Curing Agent*

Firstly, starting from the characteristics and properties of relevant materials, and then selecting the appropriate functional material matrix and filler by the investigation of composite materials with different uses at home and abroad, and taking into account the curing principle, the appropriate curing agent is selected.

A large amount of research data shows that some conductive composites have pressure sensitive properties [16, 17]. This kind of pressure sensitive composite can be used as the functional material matrix of flexible pressure sensor. Due to its good comprehensive properties, polyphenoloxy resin has been widely used in the fields of adhesives, coatings and modifiers abroad [18]. Polyphenoloxy resin can have good adhesion with high polarity materials. Therefore, polyphenoloxy resin is selected as the matrix material in this study. For the selection of conductive fillers in conductive polymers, VXC-72R high resistance carbon black was used to prepare conductive composite samples. The selection of curing agent is directly related to the molecular structure of polyphenoloxy resin and different curing conditions [19]. From the consideration of temperature resistance, anhydride curing agent is the most suitable for polyphenoloxy resin. There are a number of alternative dianhydrides, such as homophthallic acid dianhydride, benzophthallic acid dianhydride, 2,3,3',4'-biphthalic acid dianhydride, ethylenediamine tetraacetic acid dianhydride, bisphenol a-type diether dianhydride, among others. As can be seen from the dotted frame in Figure 2, in terms of structure, bisphenol a-type diether dianhydride (BPDEDA) is the same as the matrix material, which is the backbone of ethers. Secondly, there are benzene rings and hypopropyl groups in the main chains of both molecules, and the material body has a high compatible-complexation.

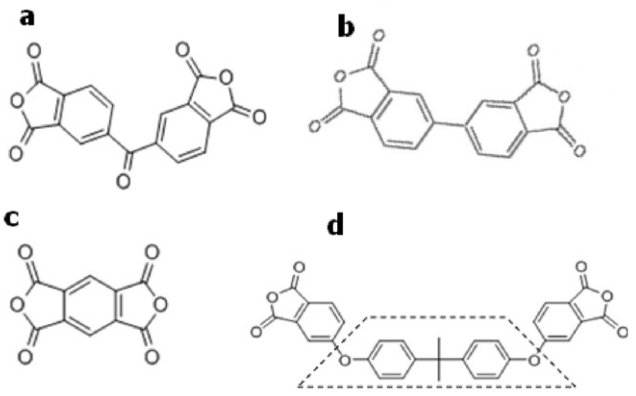
It is feasible to improve the temperature resistance of the resin by adding a curing agent to form a three-dimensional network structure through cross-linking reaction of resin molecules. And the chemical formula of the reaction is shown in Figure 3. Because of the high rigidity of the resin with high degree of cross-linking and curing, and the resin with too high rigidity is not suitable for sensor substrate material, so the degree of cross-linking should be controlled during the experiment.

2.2 *Preparation of Carbon Black(CB)/Polyphenoxy Composites by Solution Copolymerization*

In this topic, nano carbon black/polyphenoloxy resin composites were prepared by solution copolymerization.

(1) 360 g glycol butyl ether acetate solvent, 140 g polyphenolic oxygen resin, 16.5 g VXC-72R conductive carbon black, 27 g EFKA-4310 dispersant, 20 g LM-D sensor additive, 2.7 g EFKA-3580 leveling agent, appropriate amount of bisphenol a-type diether dianhydride for reserve.

(2) Preparation of resin carrier: Add ethylene glycol butyl ether acetate into 1000 ml three-mouth flask and heat it



Structural formulas of several dianhydrides:
(a)Homophthallic acid dianhydride; (b)Benzophthallic acid dianhydride;
(c)2,3,3',4' -biphthalic acid dianhydride; (d)Bisphenol a-type diether dianhydride.

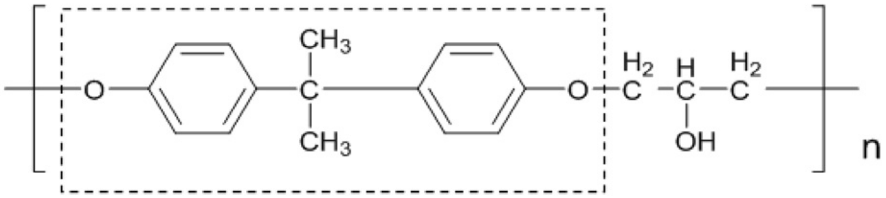


Figure 2. Linear macromolecular structure formula of polyphenolic oxygen resin.

in 100°C oil bath. Stirring rotor speed is about 500 r/min. Add polyphenolic oxygen resin into a three-hole flask several times in a small amount and stir it with solvent until it is completely dissolved.

(3) Preparation of conductive carbon slurry prepolymer: pour the prepared resin carrier into the 800 ml flask, stir the rotor at speed of about 200 r/min, add the pre-weighed dispersing agent EFKA-4310, LM-D sensor additive, VXC-72R conductive carbon black, EFKA-3580 leveling agent successively, and seal the film for preservation.

(4) The prepared carbon slurry prepolymer was divided into N parts, and the curing agent of bisphenol a-type diether dianhydride with anhydride equivalent ratio of 0, 0.08, 0.16 and 0.24 was added respectively. The curing agent was completely dissolved in the carbon slurry prepolymer after ultrasonic 30 min, and the mixture was ground by three rollers until the homogenous phase was formed.

3. TESTING OF COMPOSITE MATERIAL

3.1 *Fourier Infrared Spectroscopy Characterization*

To observe the changes in the reaction of resin during curing process, a Nicolet6700 Advanced Fourier Transform Infrared Spectrometer was used at room temperature (27°C). Since the main chain segment of the functional material matrix is the same as that of the curing agent, the only difference before and after crosslinking is the product group. And the FTIR spectra of bisphenol a-type dietheric anhydride/polyphenoxy resin curing system is shown in Figure 4.

In the figure, curve a is the IR diagram of the polyphenoxy resin polymer system without curing agent; curve b is the polyphenoxy resin polymer with anhydride equivalent ratio of 0.16 cured at 120°C for 30 min; and curve c is the polyphenoxy resin polymer with anhydride equivalent ratio of 0.16 cured at 120°C for 1 h. It can be seen that curve a has no peak at 1716–1800 cm^{-1}, while curve b has peaks at both 1739 cm^{-1} and 1778 cm^{-1}, which is judged to be the peak of unreacted anhydride at 1778 cm^{-1}, and the peak of carbonyl group in the ester bond of the product at 1739 cm^{-1}. And in curve c, the characteristic absorption peak of anhydride at 1778 cm^{-1} nearly disappeared; the characteristic peak of carbonyl group in ester bond at 1739 cm^{-1} was strengthened, indicating that the reaction was basically complete.

3.2 *Dynamic Mechanical Thermal Analysis (DMTA)*

The influence of different contents of bisphenol a-type dietheric anhydride curing agent on the dynamic thermo-mechanical properties of polyphenoxy resin curing system was studied by DMA in this paper. The test was carried out on the dynamic mechanical thermal analysis instrument with the single cantilever beam mode, the frequency was set as 1 Hz, and the heating rate was set as 5.0°C/min. Testing from room temperature until the sample is too soft

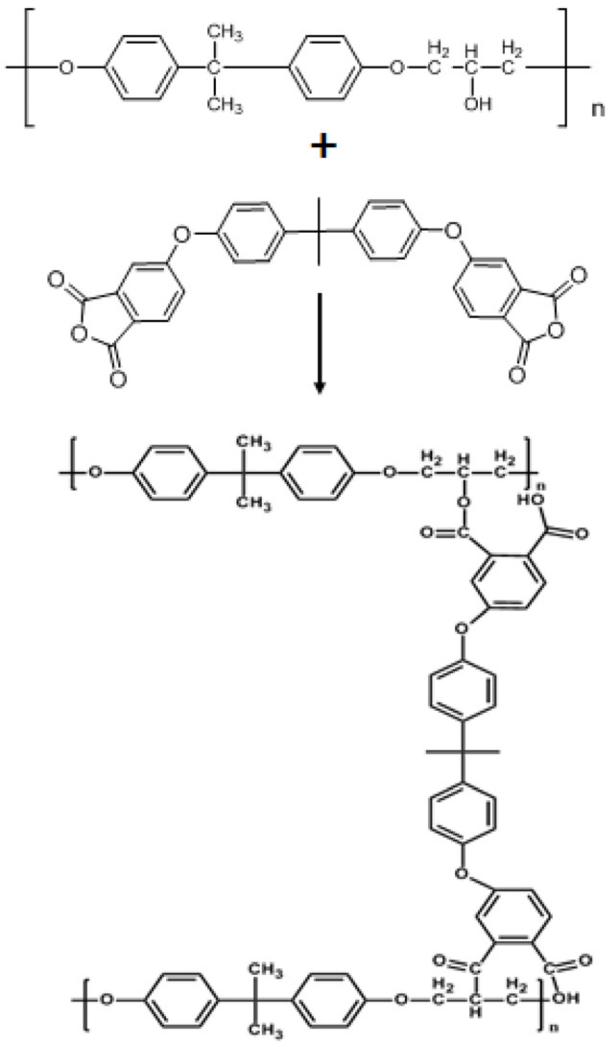


Figure 3. Curing reaction structure formula.

to test. The spectra of loss modulus tan δ and temperature dynamic mechanical properties of bisphenol a-type dietheric anhydride—polyphenoxy resin curing system is shown in Figure 5 below.

It can be seen from the figure that in a certain range, the curing agent has a certain influence on the glass transition temperature of polyphenoxy resin. The glass transition temperature (T_g) of pure polyphenol oxygen is about 85.7°C, the glass transition temperature (T_g) of functional polymer with equivalent anhydride ratio of 0.16 is about 111.6°C. With the increase of equivalent ratio of anhydride, the glass transition temperature of functional materials increased, indicating that the crosslinking reaction increased the rotational resistance of molecular chain, reduced the conformation entropy of polyphenoloxy resin segment, and thus increased the glass transition temperature T_g. With the increase of anhydride content, the glass transition temperature of functional materials increased significantly, that is, T_g transferred from the low temperature zone to the high temperature zone. Within a certain range, the relationship between curing degree α of bisphenol a-type dietheric anhydride-polyphenoxy resin curing system and glass transition temperature T_g is shown in Figure 6, and the linear fitting is: $T_g = 84.7 + 0.43\alpha$.

4. FABRICATION OF FLEXIBLE PRESSURE SENSOR BASED ON COMPOSITE MATERIAL

To produce a flexible pressure sensor, printing the conductive carbon slurry prepared before on the PET with electrode by the method of screen printing, and then cutting and encapsulating. And elucidate the influence of bisphenol a-type diether dianhydride curing agent on the characteristics and temperature resistance of flexible pressure sensor, in order to obtain a film pressure sensor with high temperature resistance, creep resistance and excellent performance.

(1) Preparation of electrode for film pressure sensor

The silver paste was screen printed on PET substrate with a thickness of 50 μm (radius of 0.8 cm) using a 200 mesh screen plate, and then placed in an oven at 80°C for drying for 0.5 h.

(2) Preparation of the single film

Using the prepared silver electrode as the substrate, and the center of the circular electrode as the printing center, to screen print the functional material on the silver electrode (radius of 1 cm) with a 300 mesh screen, and then place in an oven at 120°C for drying and curing for 1 h.

(3) Cutting and encapsulating

After cooling, laminating the monolithic film face to face is done as shown in Figures 7 and 8 for packaging. In order to ensure that the package of the flexible pressure sensor is intact, a laser cutting machine was used to define the graphics to be printed by 3M screen printing adhesive water to ensure that the functional layers on the two layers of the film could be sealed without seam. The 3M screen printing adhesive used in the packaging process was screened with 100 mesh polyester screen plate and dried at room temperature (27°C) for 20 min. The graphic definition of 3M screen printing adhesive also needs to consider the size allowance [20], that is, to ensure that the structure of each layer can be tightly encapsulated, and at the same time, there should be a certain amount of encapsulation allowance. The size relationship of the above three-layer structure can be simply expressed as the relationship shown in Figure 9.

Therefore, the film piezoresistive sensor in this study is printed with silver electrode, functional material and 3M screen printing adhesive water on PET substrate by screen printing and then encapsulated. In the static state, the sensor resistance value is relatively large (>1 MΩ). The functional resistance part of the two films will contact gradually, causing the corresponding decrease of the resistance value between the two leads on the sensor, by applying pressure to the effective area of the sensor. The greater the force applied, the larger the contact area between the upper and lower film, which means the smaller the resistance becomes.

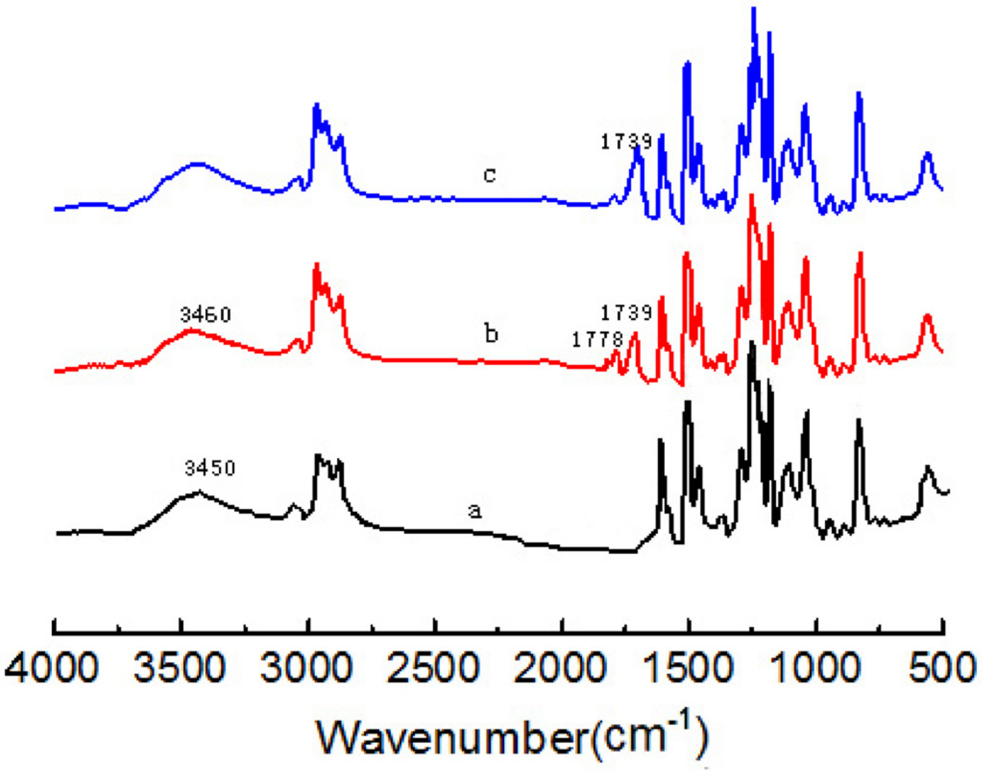
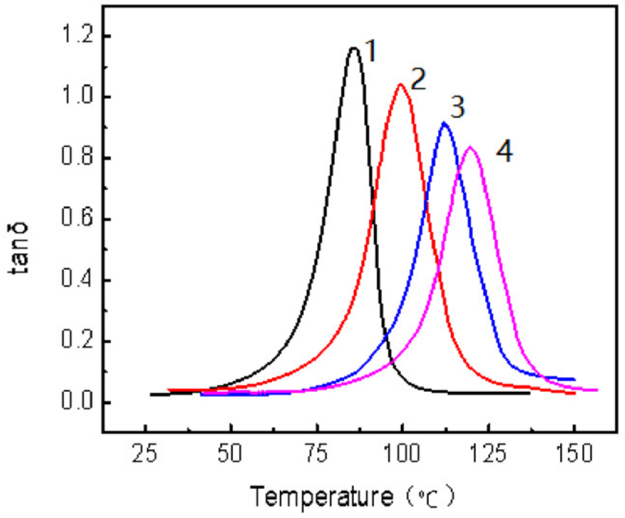


Figure 4. IR diagram of uncured system and cured products at different curing time.



Curves 1-4 represent the equivalent ratio of anhydride r=0, r=0.08, r=0.16, r=0.24 respectively

Figure 5. The relationship between temperature of different curing systems and loss factor.

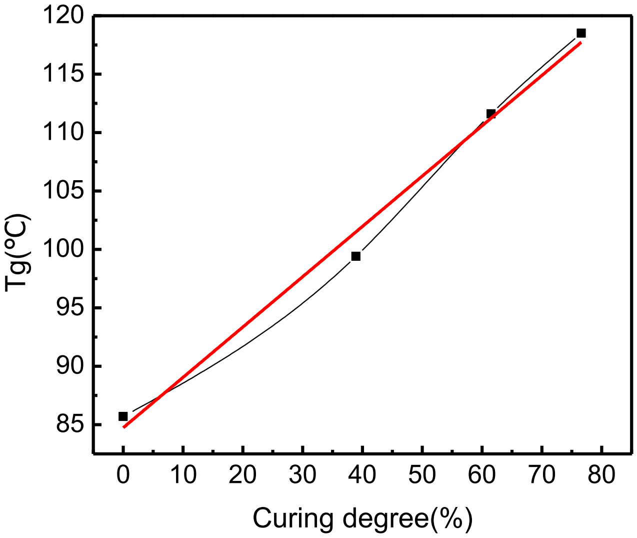


Figure 6. Linear fitting curve of glass transition temperature and curing degree.

5. TESTING OF FLEXIBLE PRESSURE SENSOR

5.1 *Creep Property of Flexible Pressure Sensor's Resistance Value*

A comparison test was set, conductive carbon slurry with anhydride equivalent ratio of $r = 0$ and $r = 0.16$ was used as the functional material to prepare the flexible pressure sensor, and then the creep performance was tested. Under a constant pressure of 5 N, the test time of each group was 10 min, and the two groups of samples were respectively subjected to pressure loading experiment.

Start timing from pressure loading 2 s, skipping the loading moment phase. Record the resistance value at this time as R_0, the resistance response of the sensor is tested. The resistance change rate $\Delta = 1 - R/R_0$, which R means the

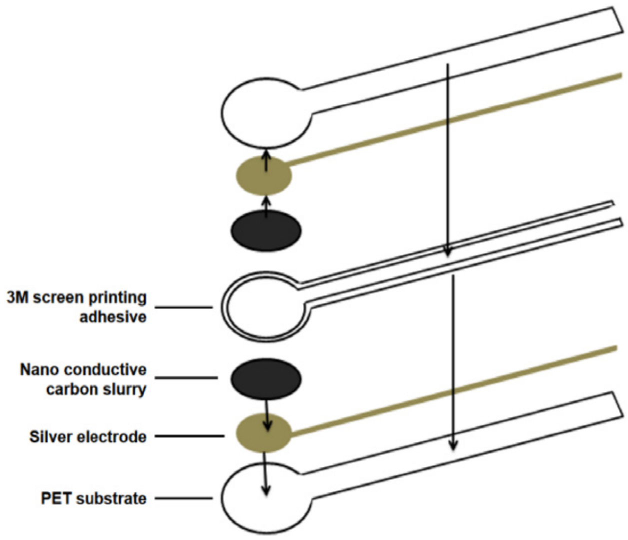


Figure 7. Internal structure diagram of the film pressure sensor.

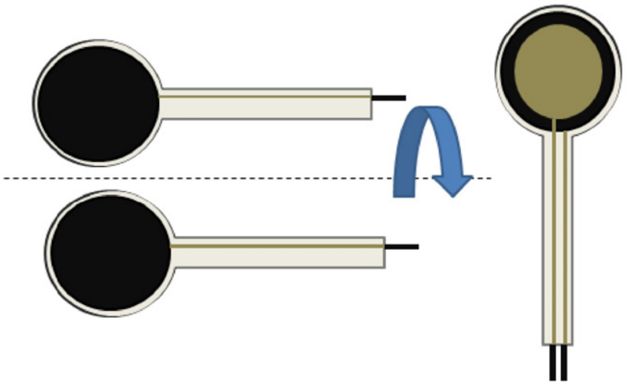


Figure 8. Schematic diagram of the sensor preparation.

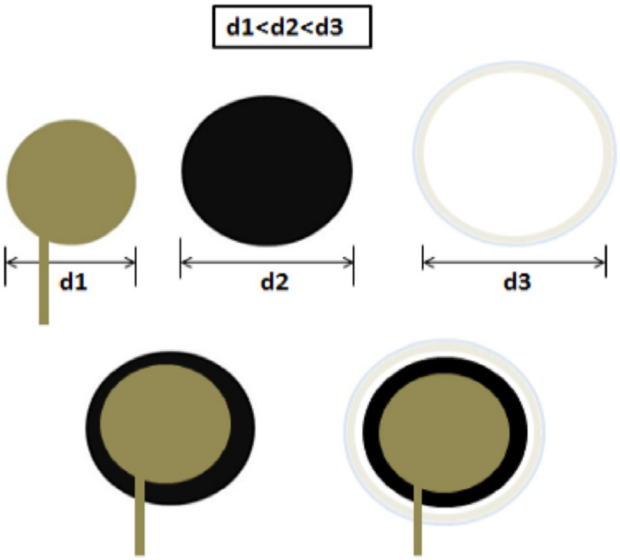


Figure 9. Simple dimension diagram of the structure layer.

current resistance value, and R_0 means the initial resistance value. The smaller the resistance change rate is, the better the resistance creep performance will be. The test results are shown in Figure 10 below.

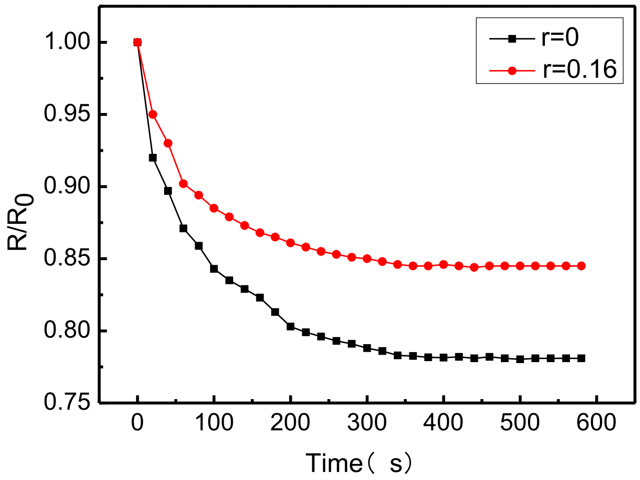


Figure 10. Relation curve between creep rate and time of sensor.

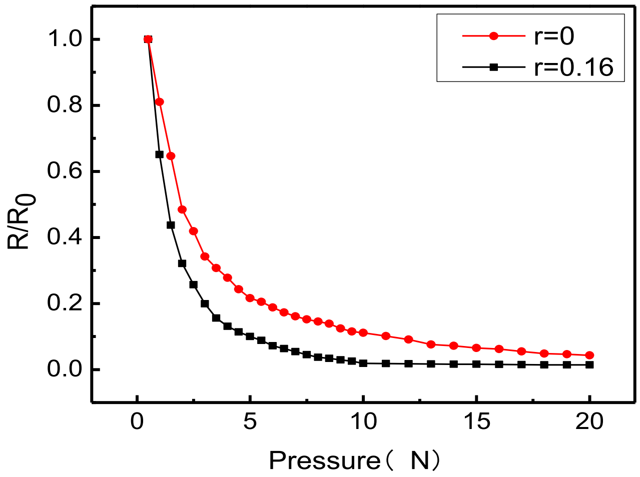


Figure 11. The piezoresistive characteristic curve of the sensor.

After creep for 10 min, $\Delta 1 = 23\%$; $\Delta 2 = 14\%$.

Using the resistance creep time and the resistance creep amplitude to measure the response speed and the maximum resistance variation of the flexible pressure sensor. As the curing agent is added, the microstructure of functional material surface becomes sharp. And the contact area of the film's upper and lower layers quickly reached a stable state under external pressure. The sharpening of the microstructure will increase the contact area between functional materials, and the higher the curing degree is, the original conductive network of functional materials will be less damaged after being stimulated by external pressure. Therefore, the smaller the resistance creep time, the smaller the resistance creep amplitude.

5.2 *Piezoresistive Characteristics of Flexible Pressure Sensor*

The piezoresistive test was carried out on the film pressure sensor with anhydride equivalent ratio $r = 0$ and $r = 0.16$ respectively, and the results are shown in Figure 11.

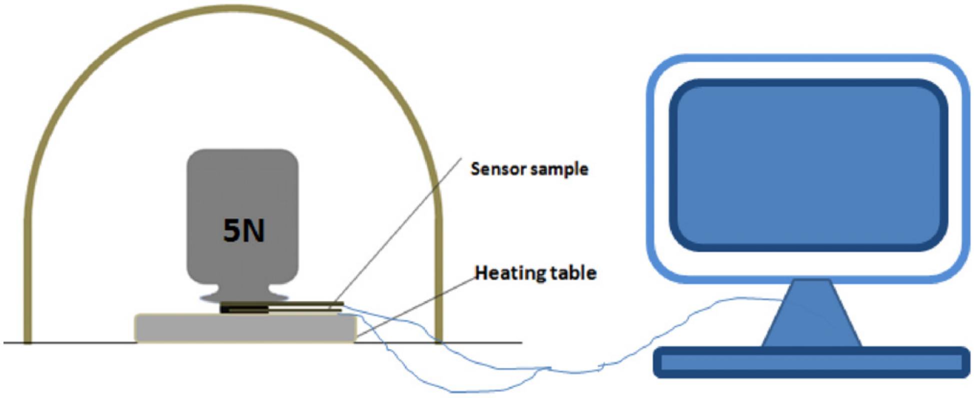


Figure 12. Schematic diagram of the temperature resistance test devices.

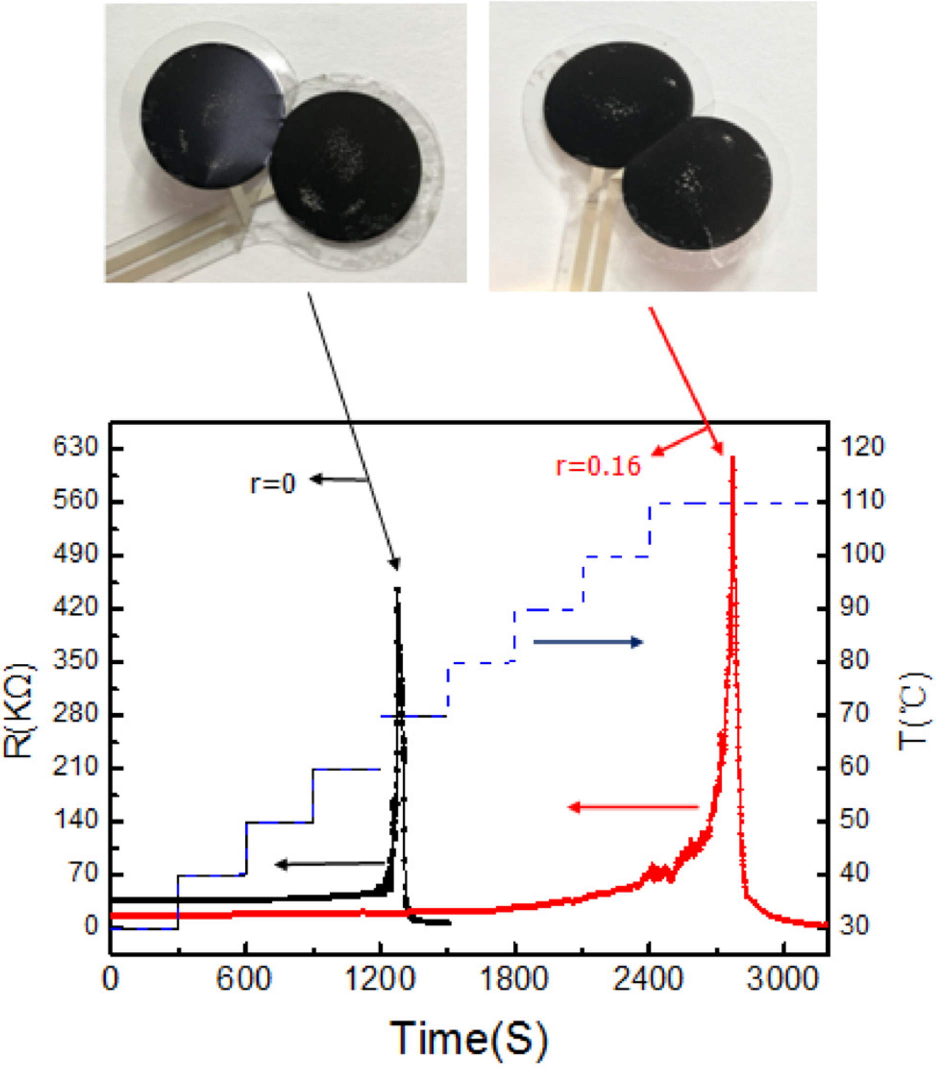


Figure 13. Temperature-resistance test.

According to the analysis above, bisphenol a-type dietheric anhydride has certain influence on the sensor characteristics of flexible pressure sensor. In a certain range, with the addition of bisphenol a-type diether anhydride in the functional material, the effective range of the sensor decreases, but the change rate of the resistance value within the effective range increases. That is, the better pressure sensitivity and curve smoothness are, the more stable the resistance variation regularity is.

5.3 *Temperature Resistance of Flexible Pressure Sensor*

Use the intelligent gas sensitive analyzer to record the resistance value of the sensor when the temperature of the heating table reaches 30°C, then keep the constant temperature and record the resistance value. Every 3 min, increase the temperature by 5°C, continue to maintain constant temperature, observe and record. The temperature resistance test devices are shown as Figure 12 below.

As can be seen from Figure 13, with the increase of temperature, the film pressure sensor has been presenting irregular temperature drift phenomenon. When the temperature of the film pressure sensor with anhydride equivalent ratio $r = 0$ is increased to 65°C, the resistance increases instantaneously and then decreases to 300 Ω. It is inferred that the functional material is softened and deformed, so that the two electrodes are bonded together, resulting in the instantaneous decrease of the resistance. Cooling the film pressure sensor in this state to room temperature and after uncovering it, it was found that the silver electrode was exposed and the two electrodes were short circuited. Moreover, the point of the resistance value of the film pressure sensor with anhydride equivalent ratio $r = 0.16$ suddenly increases and then decreases, which is in the stage of 110°C.

By studying the temperature resistance of the sensor before and after curing, it was found that the temperature resistance of the sensor increased with the addition of bisphenol a-type diether dianhydride. The estimated critical temperature of flexible pressure sensors with $r = 0$ and $r = 0.16$ increases from 65°C to 110°C under constant pressure of 5 N.

6. CONCLUSIONS

This study systematically reports the preparation and performance of a kind of printable flexible pressure sensor functional material, as well as the structure design and preparation technology of this full printed flexible pressure sensor and other basic issues. The emphasis is on the selection of resin matrix, conductive particles and curing agent used in flexible pressure sensor, and the influence of curing agent on material properties and device properties. Finally, a printable flexible pressure sensor and its materials with good temperature resistance and creep resistance are obtained, which can overcome the limitations of region and domain. Moreover, the whole preparation process of this sensor, no matter from the electrode or the functional materials, or to packaging glue, is all obtained by screen printing, which greatly simplifies the process. Through layer upon layer overprinting, rapid and large-area industrial production of such high performance flexible sensors can be realized.

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