Highly conductive, flexible PU/PANI based conductive adhesives for flexible electronics

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***Abstract*—Composite matrix material based on polyurethane (PU) and polyaniline (PANI) were synthesized via a simple process. The composite material and the silver flakes were used as matrix and filler, respectively. Resistivity can be achieved as low as 3.8×10^{-5} Ω·cm at 70 wt.% loadings, suggesting good conductive properties. The conductivity of the electrical conductive adhesive sample was basically unchanged after 400 cycles of bending and 1000 cycles of twisting. The flexible electrical conductive adhesives (FECAs) possess not only good mechanical properties but superior electrical conductivity with good stability even under bending. These superior material properties combined with excellent performance and simple processing make it very promising for emerging flexible electronics.**

***Keywords*—matrix; electrical conductive adhesives; flexible electronics**

I. Introduction ,

As an interconnecting material, electrically conductive adhesives (ECAs) has been paid more and more attention to replace traditional Sn/Pb solder, because ECAs has many advantages, including more friendliness, simple processes, higher resolution [1-3]. Typical ECAs are usually composed of polymeric matrix and conductive fillers. Polymer matrix give a certain shape while electrically conductive fillers provide the electrical conductivity properties. Silver flakes with high electrical conductivity and oxidation resistance were chosen as a primary filler[4, 5]. Among various polymers matrix, PU is the best choose with high tensile strength, chemical resistance, processability, and mechanical properties. PU comprises hard and soft segments which proportion can be adjusted according to the reality[6, 7]. These features make PU important candidates in the field of foams, furniture, paints, fibers, adhesives[8], and coatings[9].

However, in some special circumstances PU can not give satisfactory performance. We are trying to find a material able to provide good services even under harsh environmental conditions[10]. PANI is a kind of conducting polymer. In the characterization of PANI filled in PU/PMMA interpenetrating network system, Wang et al. mentioned that the hydrogen bonding formation between NH of PANI and NHCOO group of PU/PMMA polymer network had some effect on the physical, mechanical, electrical as well as thermal properties of the conductive IPN[11, 12]. In PANI/PU composites, PANI was usually used as a filler, there is no good conductivity[13]. The tensile strength of the PANI graft WBPU sample has been improved. However, this reaction process is complex and requires high requirements[14].

Here, we report a novel design to prepare AgMFs/PANI/PU flexible electrical conductive adhesives. The PANI/PU composite as matrix, while AgMFs as electrically conductive filler. The AgMFs/PANI/PU flexible electrical conductive adhesives tested at 400 cycles of bending.

II. EXPERIMENTAL SECTION

A. Materials

Aniline monomer (Tianjin Baishi Chemical Co., Ltd.. Tianjin, China). Polyethylene glycol (PEG, number average molecular weight (Mn) = 400, 1000g/mol, Aladdin, Shanghai, China). Isophorone diisocyanate (IPDI, Aladdin, Shanghai, China), ditin butyl dilaurate(DBTDL, Aladdin, Shanghai, China) and amines(JH-280, Junhe Chemical Co., Ltd.. Shanghai, China). Ag microflakes (Tianjin) Medical Chemical Co., Ltd.. (Tianjin Chain), and dodecyl benzenesulfonic acid (DBSA, Aladdin, Shanghai, China).

B. Synthesis of ECAs

PU was made by PEG and IPDI, then mixed a certain quality of PU with aniline monomer doping with DBSA. After two hours of reaction, AgMFs was added to the PANI/PU mixture. Two hours later of high temperature curing in the mold ECAs films were get.

III. RESULTS AND DISCUSSION

AgMFs was shown in Fig. 1. It can be seen the two dimensional flaky structure, which is almost all single or small, with a diameter of about 10 microns. Structure decision performance, uniform 2 D structure is conductive to silver piece distributed in the matrix. There is a tendency to achieve low thresholds and excellent electrical performance.

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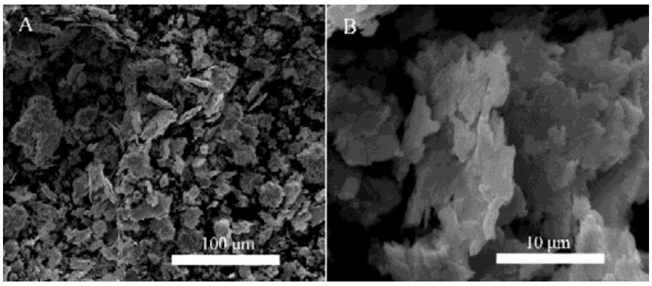

Fig. 1. SEM images of AgMFs.

Fourier Transform Infrared Spectrometer is an important tool to characterize the interaction between two or more components in a polymer[15]. Fig. 2 shows the FTIR spectra of the water-borne PU prepolymer and PANI/PU prepolymer. In line A, the characteristic absorption peak at 3324 cm^{-1} and 1712 cm^{-1} confirm the structure of the N–H stretching vibration and the carbonyl C=O stretching vibration. They were due to the urethane-urea groups in water-borne PU[16, 17]. The characteristic absorption peaks at 1538 cm^{-1} which was come from the vibration of -NH- amino group[18]. In line B, at 3296 cm^{-1}, there was an obvious absorption peak, which was migrated by the -N-H absorption peak at 3324 cm^{-1}. The strongly interaction reduces the interaction between the -C=O and -N-H of polyurethane itself. As a result, the absorption peak of 3324 cm^{-1} migrated to the low-frequency direction.

From the above results, it can be confirmed the PANI/PU of chemical crosslinking were successfully synthesized.

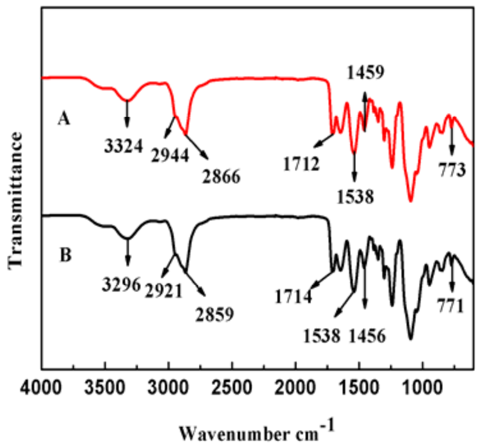

Fig. 2. FTIR spectra of (A) the water-borne PU prepolymer and (B) PANI/PU prepolymer.

A series of AgMFs/PANI/PU splines were prepared and it was found that when the amount of AgMFs was added to 70%, the resistivity was the smallest was 3.8×10^{-5} Ω·cm. The threshold was reached.

With a bending radius of 30 cm, the AgMFs40/PANI0.6/PU59.4 film has been subjected to 400 bending cycles, and a series of resistance values were obtained during the cycle. The resistance value of the relaxation film is R_0, real time resistance is R. Set the bending times to the X-axis, while the R/R_0 as Y-axis. We can see from Fig. 3, in the 400 cycles of bending, the R/R_0 changed with regular vibration between 0.995 and 1.005.

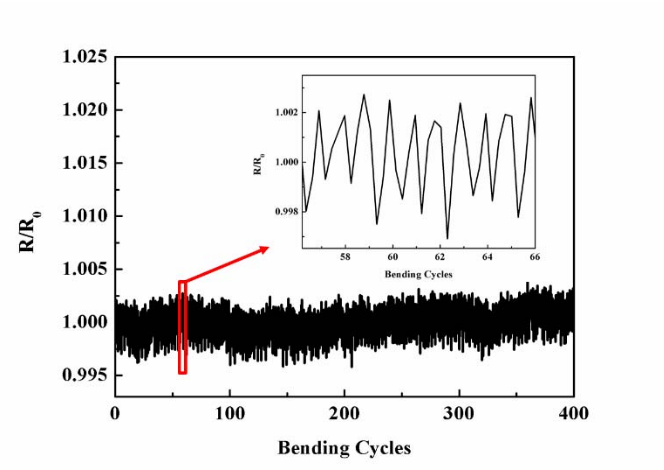

Fig. 3. The electrical resistance changes (R/R_0) of AgMFs/PANI/PU flexible electrical conductive adhesives film under mechanical deformation of bending.

In Fig. 4, the AgMFs40/PANI0.6/PU59.4 film is twisted like a hemp flower at 30 degrees. Repeated uniform changes were made 1000 times, with the horizontal coordinate as the change in time and the vertical coordinate as the change rate of resistance value. It is obvious that during the deformation process of 1000 times, the resistance value changes regularly with good repeatability and visibility of every detail.

We can draw a conclusion, that the AgMFs/PANI/PU film maintains excellent electrical performance in curved and twisty environment, great advantages in the application of flexible electronic device packaging.

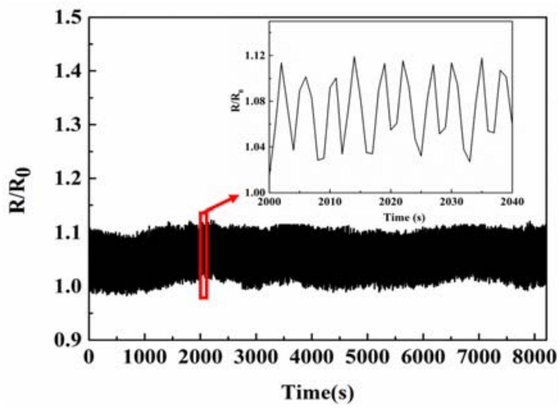

Fig. 4. The electrical resistance changes (R/R_0) of AgMFs/PANI/PU flexible electrical conductive adhesives film under mechanical deformation of bending twisting.

IV. CONCLUSION

In summary, composite matrix material based on PU and PANI were successfully synthesized via a simple process. The structure was demonstrated by FTIR. The excellent flexibility comes from PANI/PU composite matrix, and the excellent electrical performance comes from AgMFs conductive filler. Resistivity can be achieved as low as 3.8×10^{-5} Ω·cm at 70 wt.% loadings, suggesting good conductive properties. Even in bending and twisting environment, it still has stable electrical performance. Good flexibility and electrical properties make it great advantage in the application of flexible electronic device packaging.

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