

# Evaluation of the morphology of metal particles in intrinsic conductive polymer dispersions

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**Abstract.** For the production of smart textiles the resistivity of prints and coatings with intrinsic conductive polymers is often too high and the performance properties not sufficient. The addition of metal components enhances many characteristics, however the choice of type of metal, morphology and application method influence results to great extend.

## 1. Introduction

Flexible and wearable electronic devices are in increasing demand due to simple interaction with the human body. Advantages of textile structures are combined with electronic functions, such as sensors and actuators, creating numerous smart textiles [1]. The use of intrinsic electrically conductive polymers (ICP) has been investigated for a number of years, but in many cases the conductivity of such polymers applied to textile base materials is not sufficient [2, 3]. Currently, manufacturer claim, that PEDOT:PSS dispersions reach resistivity as low as 0,01 to 0,1 Ohm sq. [4]. However, those effects can only be obtained with coatings on 2D surfaces such as glass or film. Increasingly prone 3D structured textile surfaces reduce conductivity substantially [5, 6, 7].

Alternatively, carbon and metal components have been used in combination with polymer binders to produce conductive textiles. However, those materials often lead to insufficient wash- and wear behaviour, high weight add-on, enormous cost addition, undesirable colour, questionable ecology etc. [8, 9]. Over and above those negative effects, most particle-based dispersions cannot easily be printed with digital printers as they block the nozzles within very short time [10, 11]. Therefore, in this work initially, dispersions were blended for coating processes to define general properties and allow conclusions towards the requirements for inkjet printing.

## 2. Experimental

In this work, the influence of differences in morphology of metal components insulating and conductive polymer dispersions was investigated. Various types of metal particles, based on copper, silver, glass and aluminium with and without silver coatings, ranging in average size from 4 to 40 µm were evaluated in combination with a typical textile coating dispersion based on polyacrylate (PAC) and with a dispersion based on the currently most advanced ICP, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS).

Commercially available PAC as well as PEDOT:PSS dispersions were blended with metal substances of different morphology. The influence of type of metal, size, shape, surface and aggregation state of the particles was specifically analyzed. Due to the specialty of 3D surfaces, particles of different size were blended in one dispersion to optimize the coating layers. The change of



the initial particle characteristics after blending with PAc or PEDOT:PSS was evaluated. Furthermore the effect of kind of application to textiles was considered. In focus were electrical conductivity, weight add-on as well as elasticity and evenness of coating on 3D textile surfaces. In addition, mean height, increase of surface area and orientation of the particles in the coating was determined.

## 2.1. Materials

**2.1.1 Textile materials.** Plain-woven polyester fabric with a weight of 210 g/ m<sup>2</sup> and with 18 warp and 36 weft threads was used. Prior to the coating trials the fabric was treated with fluorocarbon auxiliaries and optical brighteners and fixed at 190°C for 60 s. Subsequently the fabric was coated with polyurethane, fixed at 130°C for 90 s and calandered. The total weight before coating with conductive dispersions was 270 g/ m<sup>2</sup>.

**2.1.2 Coating materials.** The coatings were produced with commercially available binder dispersions and metal micro-particles. All chemicals were used as received without further purification. Polymer materials were obtained from CHT R. Beitlich, Tübingen, Germany and Heraeus Precious Metals GmbH & Co. KG. *Germany*. The polyacrylate is an aqueous dispersion, with 12,5% solid content, a density of 1,00 g/cm<sup>3</sup> and a pH of 7,5-9,0. The poly-3,4-ethylene-dioxythiophen:Polystyrene sulfonic acid is also an aqueous dispersion with approx. 1% solid content, a density of 1,0058 g/cm<sup>3</sup> and a pH of 1,5. The metal particles came from Eckart GmbH and Doduco GmbH. The details of such particles are described in Table 1:

**Table 1:** Metal particles

Material	Particle size D50 [µm]	Main content	Ag-content [wt.-%]	Shape	Density* [g/m <sup>3</sup> ]
CuAg 4	4	Cu	25	Flake	9,31
CuAg 10	10	Cu	20	Flake	9,23
CuAg 40	40	Cu	5	Flake	8,99
Cu	5	Cu	0	Flake	8,92
Ag	5	Ag	100	Flake	10,49
GlassAg	17	Glass	50	Flake	6,49
AlAg 18	18	Al	15	Granular	3,87
AlAg 23	23	Al	30	Granular	5,04

\* The density was calculated according to wt.-% of components

**2.1.3 Dispersions.** All dispersions were mixed with 80 wt.-% polymer dispersion and 20 wt.-% metal particles. As there are differently sized silver coated copper flakes, not only blends with one single size particle were produced, but also blends mixing 4 µm with 10 µm, 4 µm with 40 µm and 10 µm with 40 µm particles at 10 wt.-% each as well as all three particle sizes mixed at 6,67 wt.-%.

## 2.2. Methods

**2.2.1 Sample preparation.** The coating dispersions were prepared by mixing the polymers, thickener, water and metal pigments with a VMA-Getzmann Dispermat LC30. The coating dispersions were applied to the fabric manually with Erichsen K-Hand-Coater for 50, 100 and 200 µm wet film. After coating the samples were dried at 120 °C in a Heraeus Dryer.

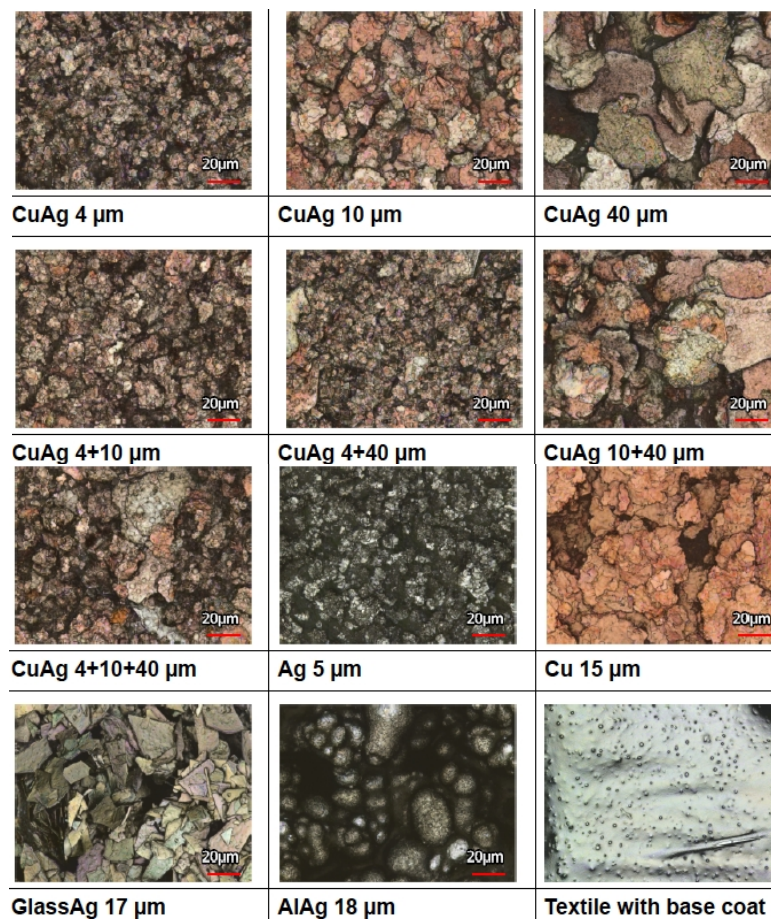
**2.2.2 Analytical methods.** The coated textile samples were evaluated as to physical and conductive properties, structure and morphology. Samples were always conditioned at 20°C and 65% relative humidity for 24h before analysis.

The sheet resistivity was measured with a portable Schuetz MR 1 surface resistance meter with a special 4-pole contact probe with smooth surface for textiles.

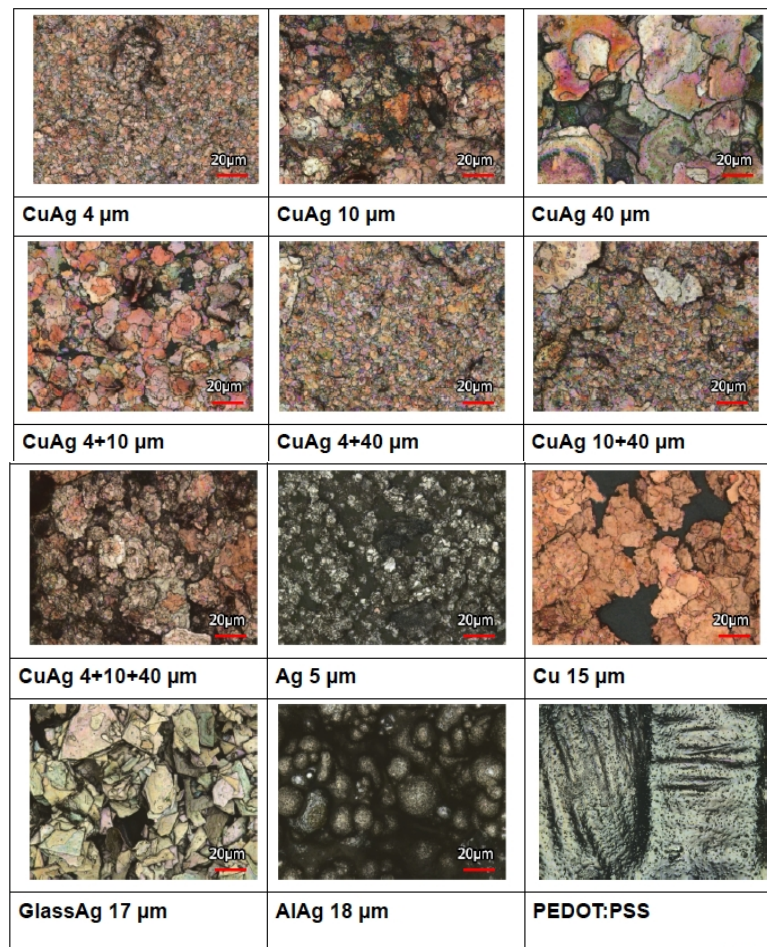
With the Keyence laser microscope the topography of the coatings on the textile surface was analysed. The distribution of the coating dispersion and in particular the metal particles was investigated by images 10 and 100 times magnified. Furthermore arithmetic mean heights as well as maximum height differences, increase of surface area and aspect ratio of orientation were identified with the special software of the laser microscope.

### 3. Results and Discussion

The size and shape of metal particles as well as the kind of binder system and its solid content have a substantial influence on layer formation on textiles surfaces. Figure 1 illustrates the laser micrographs at 100 x magnification of the 200 µm wet film, while figure 2 shows the same layers produced with PEDOT:PSS dispersions.

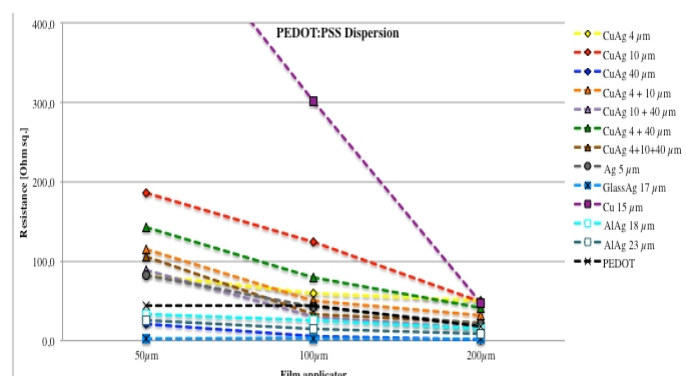


**Figure 1:** Laser microscope images of different particles in PAc dispersion



**Figure 2:** Laser microscope images of different particles in PEDOT:PSS dispersion

The images show, that the coatings with PAC cover the 3D surface much more even than coatings with PEDOT:PSS. The particles form a smooth surface when embedded in PAC. The larger particles are predominantly on the surface; most particles are well in contact. In the PEDOT:PSS film the particles almost seem to aggregate in islands and smaller particles are found more often on the upper surface. The textile structure is clearly visible with those coatings, which is mostly due to the lower solid content in this dispersion.

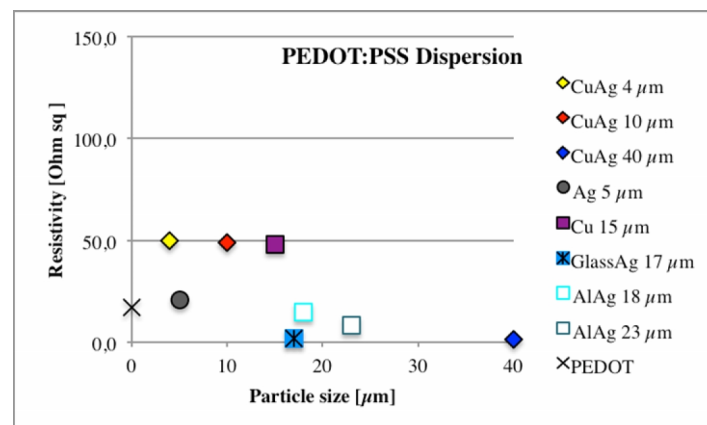


**Figure 3:** Sheet resistance of coatings with PEDOT:PSS dispersions and metal particles



The sheet resistance of almost all coatings is much lower with PAc dispersions than PEDOT:PSS. In figure 3 it is demonstrated, that in the 200  $\mu\text{m}$  wet film the values range as little as 1.90 to 49.00 Ohm in PEDOT:PSS, while 0.15 to 1.10 Ohm in PAc. The differences between the two dispersions are similar also in 50  $\mu\text{m}$  and 100  $\mu\text{m}$  wet film thickness. As seen in the microscopic images the PAc film is much more solid and denser which keeps the particles embedded and yet on the upper surface. In the PEDOT:PSS dispersion the overall surface has increased as the small solid content of the base dispersion does not cover the particles as solid film well enough. Furthermore the particles seem to form small islands in the depth of the 3D textile structure. These two factors increase the surface, which increases the sheet resistance by almost two decimal powers. The resistance of CuAg 40 and GlassAg 17 is much lower than all other metal particles, even than pure silver Ag 5. In PAc dispersion those two showed values two to three times lower than all others. There was even no resistance measurable with AlAg 18 and with AlAg 23, only at 200  $\mu\text{m}$  wet film results came up to the same values as all other metal particles. In PEDOT:PSS dispersions the differences of all metal particles were not so strong, also the influence of wet film thickness had not as much impact on sheet resistance as in PAc. Interestingly, the pure PEDOT:PSS dispersion resulted in better resistance than blends with CuAg 4 and 10 as well as mix of different sized CuAg particles. This is probably due to the fact that the surface area is increased so drastically by the particles.

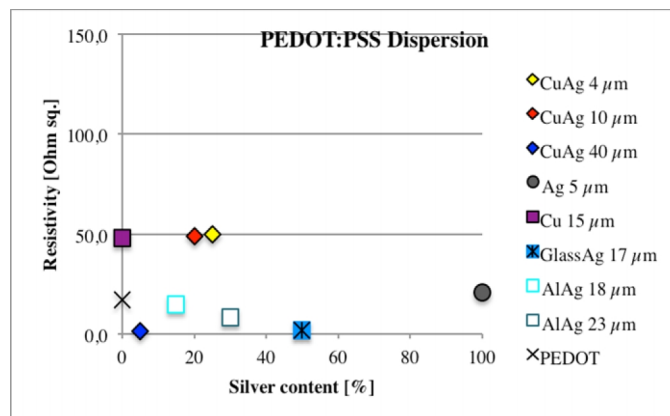
As expected the particle size has an enormous influence on the conductivity of the coatings, as demonstrated in figure 4. Although it was estimated, that the larger particles could not so easily form a closed layer on the 3D textile surface, the results were best with 40  $\mu\text{m}$ , 23  $\mu\text{m}$ , 18  $\mu\text{m}$  and 17  $\mu\text{m}$  particles in PEDOT:PSS, while in PAc only CuAg 40 and GlassAg 17 performed outstandingly (all at 200  $\mu\text{m}$  wet film thickness).



**Figure 4:** Influence of particle size on sheet resistance of 200  $\mu\text{m}$  coatings with PEDOT:PSS

The influence of silver content in the various metal particles on sheet resistance of the coatings was further investigated. Although silver generally resembles the highest conductivity compared to the metals used in this work, the coatings with the large silver coated copper particle and the silver coated glass showed much better results than pure silver particles in PAc. In addition the large silver coated aluminium particle was similarly good in PEDOT:PSS (figure 5).

A third aspect was evaluated regarding the sheet resistance in relation to the add-on weight from the coatings. All coatings with PEDOT:PSS had much lower weight add-on, as the solid content of the base polymer is only 1 % compared to PAc with 12,5 %. Although the density of the two AlAg particles and GlassAg is the lowest, the impact is not substantial in the coating. The sheet resistance drops in the same way as the add-on increases due to thicker wet films.



**Figure 5:** Influence of silver content on sheet resistance of 200 µm coatings with PEDOT:PSS

With laser microscope the surface increase was calculated and the coatings' orientation was determined. The surface increase was largest with the smallest particle CuAg 4 with 7,35 % in PAc and 8,12 % in PEDOT:PSS and smallest with granular AlAg 23 particle with 3,04 % and 3,25 %. The orientation of the metal coatings is regarded optimum at 1 and none existing at 0. All coatings exhibited values between 0,57 and 0,87. The coating with the blend of all three CuAg particles in PAc was best with 0,57 followed by GlassAg in PAc with 0,61. The results in PEDOT:PSS were all slightly less as the polymer does not cover the layer as much as PAc with higher solid content.

#### 4. Conclusions

Depending on application, required conductivity and performance characteristics the morphology of metal components in polymer dispersions must be considered. The size of particles is a major contributor to differences in conductivity. Furthermore, the shape substantially influences the conductivity, as well as the orientation of the coating, spheric or plate forms behave differently to round or longitudinal forms. The type of metal does not impose as much a difference, at least not at a concentration of 20 wt.-%. The polymer, whether insulating or intrinsically conductive is required to fix the metal particles to the textile surface. The solid content as well as the chemistry itself determines the film further and also plays a great role in wash and wear behavior in use.

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