

# ELECTRICALLY CONDUCTIVE TEXTILES UNDER CONSIDERATION OF PERCOLATION THRESHOLD AND POLYMER CRYSTALLINITY

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## ABSTRACT

For the production of smart textiles often electrically conductive coatings or prints are required. Using polymeric binders in combination with micro particles based on metal can achieve good results once a critical concentration – the percolation threshold – is exceeded. The shape and size of the filler particles as well as the crystallinity of the polymer have a major influence on conductivity. In addition to conductive properties of the coatings also other textile characters such as weight and flexibility have to be considered when choosing fillers as well as binders.

**Key words:** Percolation threshold, surface resistivity, filler particles

## 1. THEORETICAL BACKGROUND

Electrically conductive coatings on textile surfaces can be achieved using inherently conductive polymers such as commercially available poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) dispersions for coating or printing. Alternatively, non-conductive polymeric dispersions are filled with conductive particles based on metal or carbon as the electrical resistivity of insulating polymers can be decreased by dispersing such conductive fillers in the polymer matrix. However, a critical (minimal) volume of filler is necessary to build up a continuous conductive network, in this case the transition between conductive and non-conductive states takes place at percolation threshold [1]. There are a number of factors inherent with the fillers affecting the percolation threshold, such as the basic conductivity of the filler particles, the filler volume fraction, the distribution and packing factor of the fillers as well as the general characteristics of the fillers such as size, shape, surface area, morphology and orientation [2]. Additionally, the polymer matrix has a major influence on the conductivity of the two-phase system, especially the interparticle filler spacing and the crystallinity of the polymer [3]. Differences in percolation threshold concentration can be caused by different crystallinity of the matrix, because in highly crystalline polymers the formation of a continuous conductive path of metal or carbon particles is easier, as the particles are forced to move to the outside of the crystallites. The higher amorphous portion in the matrix results in more homogeneous distribution of filler particles without concentrating on path formation. The crystallinity of the matrix is basically not influenced by particles [4]. However, high temperature from annealing of thermoplastic binders increases polymer diffusion and entanglement, which leads to blocking some of the conductive particle paths resulting in the increase in resistivity [5]. Within the polymeric matrix the packing factor is highly relevant. Statistically, the highest possible filler volume can be calculated to 64% for monodispersed spherical particles. In the case of mixing different sized particles the packing factor increases above 64%, as the smaller particles fill the gaps between the larger ones without increasing conductivity. However, the factor can be reduced well below 64%, when either using skeleton forming particles or anisotropic fillers shaped with a length larger than the diameter. ( $l/d > 1$ ) [6]

Amongst others, cost, added weight and loss of flexibility using metal pigments in such two-phase systems directly correlate with the concentration of the fillers [7].

## 2. EXPERIMENTAL WORK

For this research work, various two-phase systems were studied, with special focus on the influencing factors of binder type and percolation threshold. The polymer matrices were based on a polyurethane dispersion with 15% solid content as well as a polyacrylate dispersion at the same solid content. As conductive fillers different particles based on copper, aluminum and glass, all silver-coated, in different size and shape were blended at increasing concentrations with the polymer dispersions. The blends were applied to polyester woven textile material and subsequently dried only at low temperature as well as additionally thermoset at higher temperature. The metal-filled polymer dispersions were analyzed with respect to viscosity and crystallinity, the resulting coatings were investigated for thickness, particle distribution and orientation, added weight and surface resistivity.

### 2.1. Materials

**Textile materials:** Plain-woven polyester fabric, weight 210 g/m<sup>2</sup>, 18 warp and 36 weft threads. Prior to the coating trials 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>.

**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. The polyacrylate is an aqueous dispersion, with 60% solid content, a density of 1,08 g/cm<sup>3</sup> (at 20°C) and a pH of 6,0-7,8. The polyurethane is also an aqueous dispersion with 60% solid content, a density of 1,10 g/cm<sup>3</sup> (at 20°C) and a pH of 7,0-9,0. The metal particles were obtained from Eckart GmbH. The silver-coated copper flakes show an average size D50 of 34 µm and a density of 8,99 g/m<sup>3</sup> and contain 95% Cu and 5% Ag. D50 of silver-coated glass flake is 17 µm with a density of 6,49 g/m<sup>3</sup>, and a silver content of 50%. The silver-coated aluminum pigments are granular with a more or less round shape with a silver content of 30%, D50 is 23 µm and the density 5,04 g/m<sup>3</sup>.

### 2.2. Methods

**Preparation of dispersions:** The coating dispersions were prepared by mixing the polymers with water for a base solid content of 15%. The various metal pigments were blended in with a VMA-Getzmann Dispermat LC30.

**Coatings on textile:** The coating dispersions were applied to the fabric manually with an Erichsen K-Hand-Coater 100 µm wet film. After coating the samples were dried at 80°C for 120 s in a Heraeus Dryer, half of the sample was annealed at 150°C for 180 s.

**Analytical methods for dispersions:** The viscosity was determined with Haake Viscotester, Spindel 2. A defined volume of dispersion was dried only on glass plates at 80° for 600 s and also annealed at 150°C for 600 s.

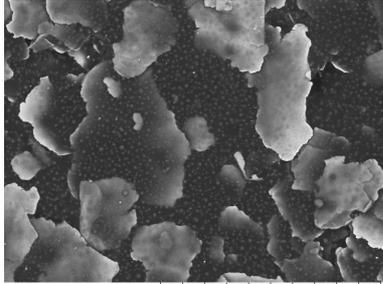
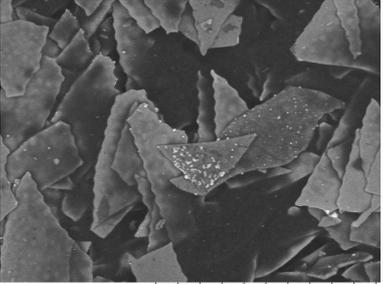
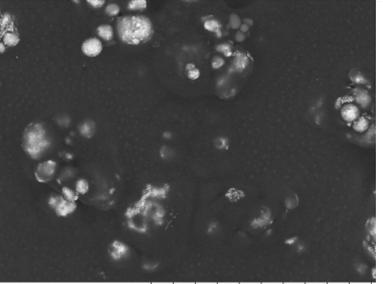
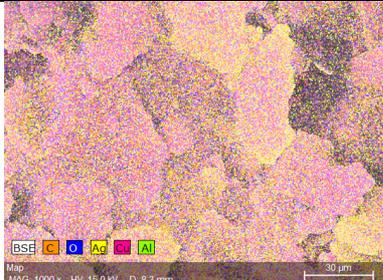
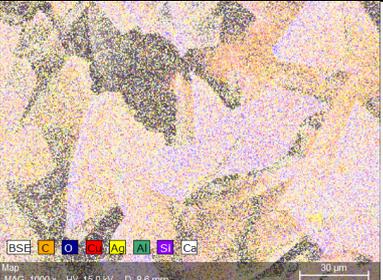
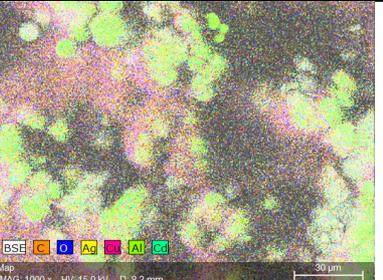
**Analytical methods for coatings:** The coated textile samples were evaluated for conductive properties, conditioned at 20°C and 65% relative humidity for 24h before analysis. The sheet resistivity was measured in mOhm sq. with a portable Schuetz MR 1 surface resistance meter with a special 4-pole contact probe with smooth surface for textiles.

With the Hitachi SEM the distribution of the coating dispersion and in particular the metal particles were investigated by images magnified in various steps. Furthermore, EDS was obtained and the mass of the relevant elements was calculated. Lastly, the weight add-on of the coating itself was determined in g/m<sup>3</sup>.

### 3. RESULTS

Via SEM the shape of the particles was determined for all concentrations and blends. The images at 20% particle in PU-dispersion, dried at 80°C are shown in table 1. The copper particles are flakes with irregular contours with an average size D50 of 34µm. The particles expand almost the same in length and width, however the flakes are basically quite flat. The glass particles exhibit very sharp/ straight edges and most of them a rather dimensioned longitudinal with an average length D50 of 17µm and very flat (broken glass fragments). In contrast to those two, the aluminum particles are spherical granules with an average size D50 of 23µm. In EDS the main element found with the copper particle is Cu, as the silver coating is minimal with only 5% (pink). The glass particle shows as major elements Si in purple as well as Ag in yellow due to 50% silver coating. With the aluminum particle almost only Al in green is visible, although the silver coating amounts to 30%.

**Table 1: SEM images and EDS of coatings with 20% particles in PU-dispersion dried at 80°C**

| 20% CuAg in PU 80°C   | 20% GlassAg in PU 80°C  | 20% AlAg in PU 80°C   |
|---|---|---|
|   |   |   |
| VR12_CuAg<br>80°C<br>HL D8,3 x1,0k 100 µm   | VR12_Glas<br>80°C<br>HL D8,6 x1,0k 100 µm   | VR12_Al<br>150°C<br>HL D8,2 x1,0k 100 µm  |
|  |  |  |
| Map<br>BSE C O Ag Cu Al<br>MAG: 1000x HV: 15.0 kV D: 8.3 mm 30 µm                   | Map<br>BSE C O Ag Al Si Cu<br>MAG: 1000x HV: 15.0 kV D: 8.6 mm 30 µm                | Map<br>BSE C O Ag Al Cu<br>MAG: 1000x HV: 15.0 kV D: 8.2 mm 30 µm                     |

The surface resistivity of the coatings on PES-fabric was determined and is shown in figure 1. The percolation threshold of the glass particle was found at 15% in PU as well as PAC, however there is no significant reduction of resistivity above 25%. The threshold for the copper particle is a little higher, which can be attributed to the rather longitudinal shape of the glass particle. However, resistivity is further reduced substantially with increasing concentration and reaches much lower values than glass. The reason can be pointed to the fact, that the copper flakes are much larger and the copper center is conductive compared to the glass. In comparison, for the aluminum particle the threshold was detected at 35% and the resulting surface resistivity is way higher than with glass or copper. This is caused by the fact, that the aluminum pigments are spherical. Much larger concentration of round pigments is required for the same packing factor than with flakes, particularly long flakes.

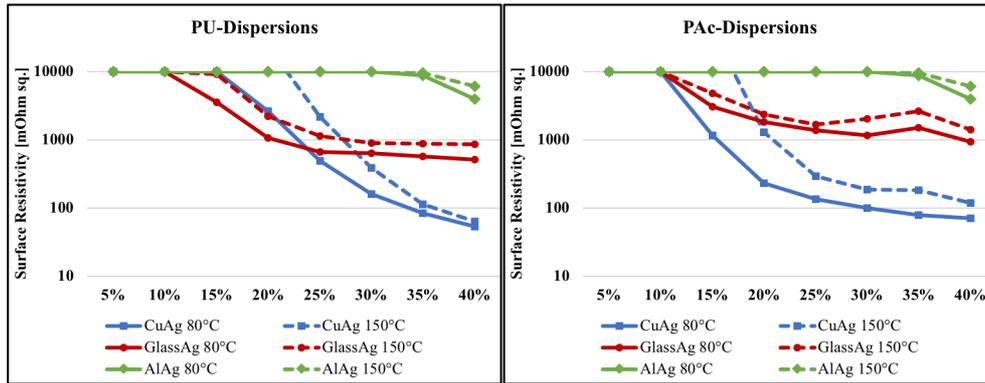
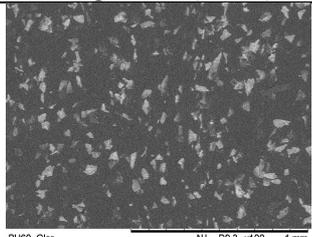
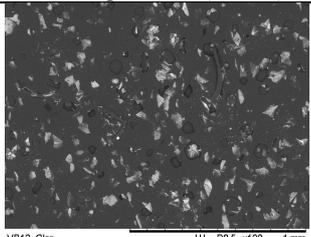
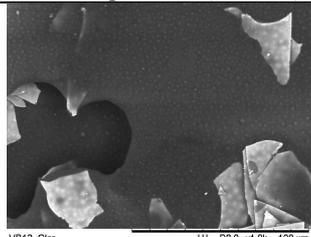
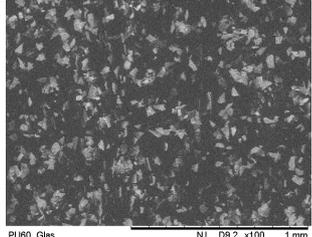
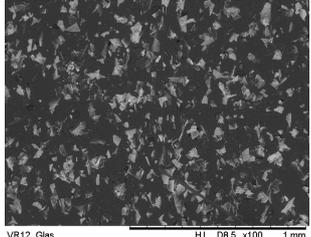
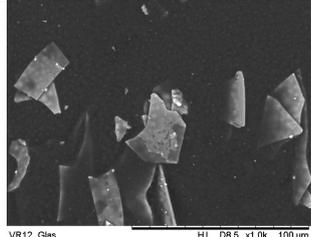
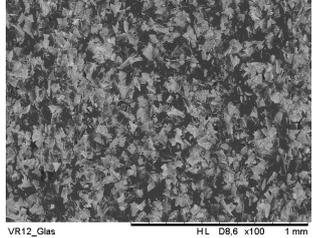
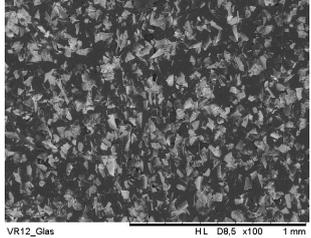
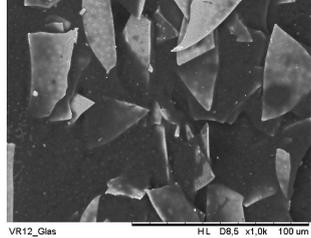
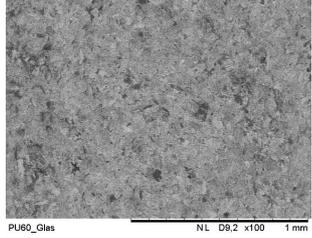
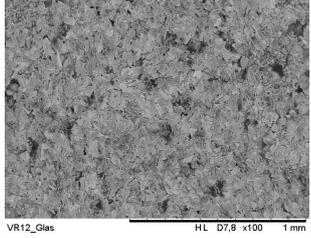
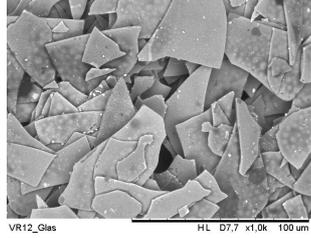


Figure 1: Influence of type of particle and concentration in PU- and PAC-Dispersions on surface resistivity

The SEM images in table 2 also identify the missing path formation/ contacting between particles within the coating, when magnified x 100 as overview and in particular at larger magnification of x 1000.

Table 2: SEM images of coatings with GlassAg in PU- and PAC-dispersions dried at 80°C

| %  | PU-Dispersion (x 100)   | PAC-Dispersion (x 100)  | PAC-Dispersion (x 1000)   |
|----|---|---|---|
| 5  |   |   |   |
| 10 |  |  |  |
| 15 |  |  |  |
| 40 |  |  |  |

The drying temperature influences the surface resistivity of the coatings, as demonstrated in figure 2. Above percolation threshold, the resistivity is always less after drying at 80°C than at 150°C. The temperature has rather little influence on coatings with glass or aluminum particles, however the results differ more obviously when using copper particles. At 80°C as well as at 150°C the resistivity is less when using PAc as polymer, at 150°C it is slightly less with PU. The reason for this can be seen in the fact, that more humidity is present in the coatings when dried at 80°C. In addition, when the polymer binders are fully cross-linked, less humidity can be picked up, hence the conductivity is less. The PAc-binder used in this work is particularly designed to pick-up moisture, which is why the resistivity is less than in the chosen PU.

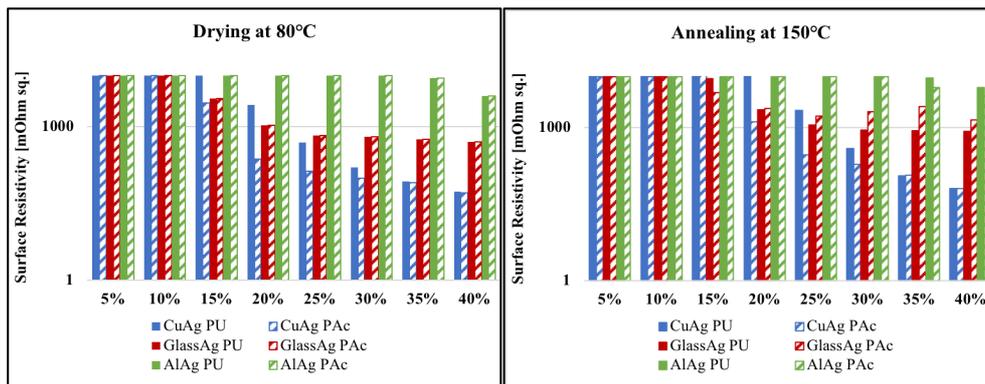


Figure 2: Influence of drying temperature for particles in PU- and PAc-dispersions on surface resistivity

The weight add-on increases almost linear with the increase of particle concentration as expected. Overall, the add-on is higher in PAc- than in PU-dispersions. However, the weight of the coatings with copper particles increases even more when drying at 150°C. This is probably caused by progressive formation of copper oxide, particularly in the PAc-formulation (higher moisture up-take as mentioned above).

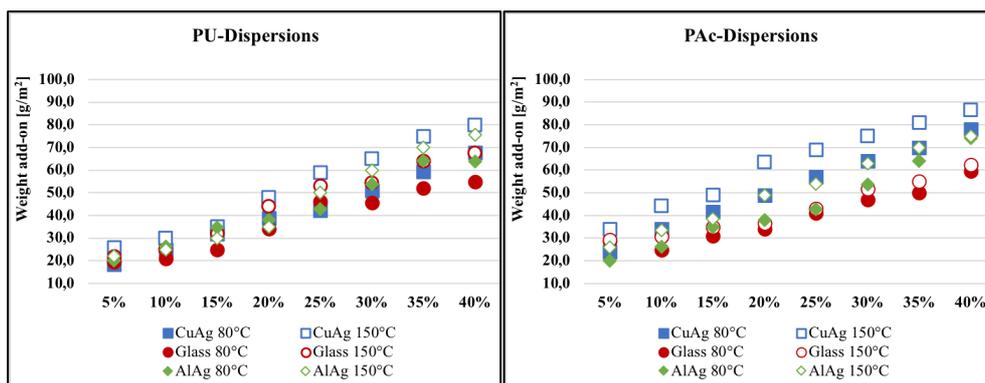


Figure 3: Correlation of weight add-on and concentration of particles in PU- and PAc-dispersions

#### 4. DISCUSSION

By choosing the appropriate matrix polymers as well as optimum shape and size of metal particles the percolation threshold can be reasonably low and the prints or coatings perform

best for the production of smart textiles. The results with silver-coated copper particles in polyacrylate dispersions were superior to all other pigments tested, with a threshold at 15% and a minimum resistivity of less than 100 mOhm sq. above 30% concentration. The threshold of the copper particle in polyurethane was higher at around 20%, but with increasing concentration the lowest resistivity was achieved. With the silver-coated glass particles, threshold is lower, which is mostly contributed by the longitudinal shape of the particle as this affects the packing factor positively. But overall the resistivity is higher by the power of one than with copper particles. However, the weight add-on using the glass particle is less than with copper and the influence of temperature is also less. In addition, corrosion of the copper particle was observed, particularly in the PAC-dispersion, which would lead to difficulties in bulk production.

### **ACKNOWLEDGEMENT**

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