Development of a Colored GFRP with Antistatic Properties

Hauke Meeuw[1, a)], Markus Radek[1] and Bodo Fiedler[1]

[1]Institute of Polymer Composites, Hamburg University of Technology, Denickestraße 15, D-21073 Hamburg, Germany

[a)]*Corresponding author: hauke.meeuw@tuhh.de*

Abstract. This study shows that a modification with ultralow filler content of novel single wall carbon nanotubes (SWCNT) converts an intrinsic insulating GFRP into one with antistatic properties. These properties remain even by adding pigments for customizing without affecting the wanted bright coloring (e.g. signal color). We developed a bright colored and antistatic glass fiber reinforced polymer (GFRP) by addition of carbon nanoparticle and pigments. Novel, in industrial scale available SWCNT dispersed in polyester resin with low content of volatile organic compounds (VOC) show an ultra-low percolation threshold of 0.005wt.%. This ultralow filler content leads to the required conductivity as well as a given transparency of the nano composite. In a next step, we transferred these properties into a GFRP, manufactured by infusion process. The addition of pigments lead to the individual coloring of the GFRP. Both, the SWCNT modified and SWCNT colorized GFRP fulfilled the required electrical resistances for ESD protection.

INTRODUCTION

The development of novel multifunctional materials, in particular by modification of polymers with carbon-based nanoparticles, became one of the main research topics in the last decades. Especial interest lays on SWCNT due to their unique material properties. By adding this filler type, the intrinsic insulating polymer becomes electrical conductive. This modification provides the possibility for industrial applications requiring electrostatic discharge. In the 1880s, the topic of electrostatic discharge began to attract attention, when nearly 80 explosions occurred in German laundries due to electric discharge [1]. Recent statistics published in Europe and the USA show that, even today, electrical discharges are the cause for explosions in 35% of all cases [2]. In general, charge formation occurs due to body separation. There are three typical cases to distinguish [3]:

1. Two bodies in contact are separated by sliding each other (e.g. unwinding tape)
2. Repetitive separation (e.g. walking on a carpet)
3. Quasi-continuous contact and separation (e.g. flow of liquids in pipes)

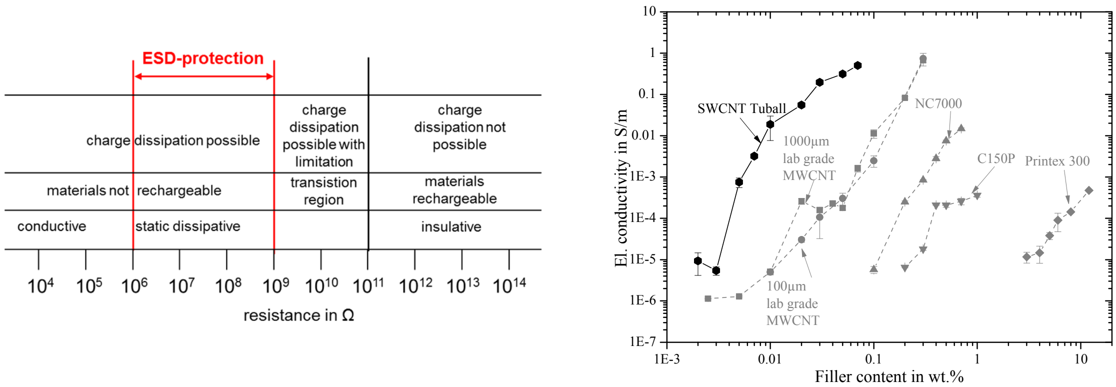
The possibility of static electricity to be a source of ignition rises, if following conditions occur [4]:

- Charge generation is higher than dissipation rate
- Discharge occurs in ignitable atmosphere and exceeds ignition energy

Following equation calculates the discharge energy W in dependence of the generated potential U and the capacity C of the material:

$$W = \frac{1}{2} C_{HB} U^2 \tag{1}$$

A person walking across a carpet generates a potential of about 15kV. According to human body model, the capacity of the human body C_{HB} differs between 100pF to 300pF [5]. This leads to a generated energy dissipation of 10mJ up to 35mJ. Britton et al. classified the discharge energies according to the human reaction, whereby more than 15mJ leads to an unpleasant shock [4]. In comparison, the generated energy exceeds the lowest minimum ignition energy by a factor 100 for common vaporous solvents (e.g. 0.19 for acetone at a concentration of 4.97vol.% in air) [6]. The dissipation of generated charge avoids high charge formations. Antistatic materials provide an electrical conductivity that is sufficient to dissipate the charge in short time at accompanying hazard-free electrical current flow preventing a generation of a sparks. For handling electrostatic sensitive devices (ESD), three types of resistances influence the charge dissipation: The Surface resistance, measured between two electrodes, the volume resistance measured between top and bottom surface and the dissipation resistance, measured between top surface and ground. According to ASTM F 150-06 the static dissipative region lays between 1MΩ (safe dissipation) to 1GΩ (sufficient fast dissipation) [7]. Figure 1a sums up the classification of conductors and insulators in respect to their surface resistance. By incorporation of carbon nano fillers, e.g. SWCNT, into an intrinsic insulating polymer it becomes electrical conductive. We described in 2016 the possibility to adjust the electrical properties of carbon filled epoxy systems. Figure 1b shows the dependency of filler content on the electrical conductivity for different carbon fillers [8].



(a) (b)

FIGURE 1. a) Classification of materials in respect to their surface resistance in style of [9] b) Dependency of filler content on the electrical conductivity for different carbon fillers (SWCNT results were generated in this study) [8]

The fact of adjustable electrical properties combined with the outstanding mechanical properties normalized on fiber-reinforced carbon nano filler modified polymers' density leads to promising novel industrial applications and opens further markets. Furthermore, possibility of coloring fulfills the customers' demands for individualized products. In the past carbon black was mostly utilized to achieve conductivity in polymers. If color was a requirement, then the addition of carbon-based fillers cannot be used. With the development of next generation carbon nanotubes, especial SWCNT, ultra-low filler addition leads a sufficient conductivity of the polymer (fig. 1b). The aim of this work is the development of a signal colored and at the same time ESD protective GFRP flooring by utilization of ultra-low filler addition of SWCNT and color pigments.

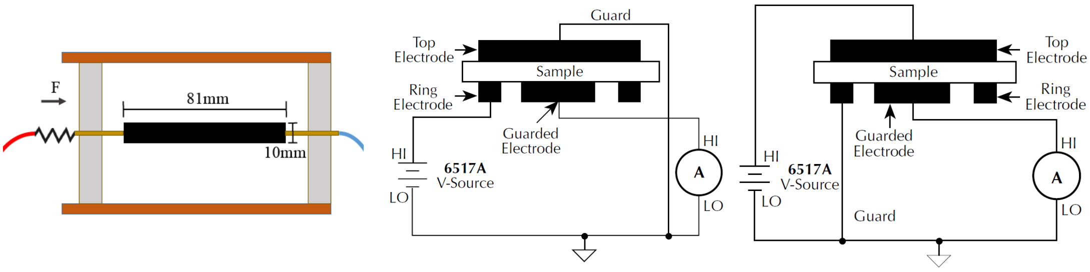
MATERIALS AND METHODES

Unsaturated polyester resin AROPOL FS7993M-25, in combination with a cobalt accelerator and a peroxide catalyst ME50LY, Romar Voss, Netherlands, was used as polymer matrix. This resin provides a low volatile content. Dicyclopentadiene serves as replacement for styrene for environmental safety purpose, flame-retardation and improved fiber wetting [10]. A low viscosity of 100-150mPas makes it suitable for vacuum infusion processing [11]. Incorporation of SWCNT Tuball, OCSiAl, Russia, enables the required electrical conductivity for ESD protection of the material. They feature a SWCNT content of more than 75wt.%, nearly no amorphous carbon (less than 1wt.%), a G/D ratio over 70, diameter of 1.8nm, a length of 5µm and a market price at industrial scale 50 times lower compared to other SWCNT suppliers [12]. Addition of coloring paste PU5011 lemon yellow provided by Altropol, Germany, leads to signal color of the composite. It contains of organic pigments yellow PY74, a hydrocarbon based binder and a disperse agent based on alkylammonium salt and silicic acid to stabilize the dispersion. For manufacturing of GFRP by infusion processing unidirectional non-crimp glass fiber fabric (91%warp, 9%weft, 600g/m²) in $[0]_6$ configuration was used. In a first step, the percolation behavior of the SWCNT/polyster resin composite (without coloring and glass fiber) was investigated. Incorporation of SWCNT into the polymer by three-roll milling process with parameters listed in **tab.1** leads to homogenous dispersion. After dispersion 1wt.% catalyst and 0.5wt.% accelerator were added, the dispersion stirred under vacuum and vacuum infused into a mold (170mm x 81mm x4mm).

TABLE 1. Process parameters for dispersion via three-roll mill

Steps	Gap sizes [µm]	Roll speed [rpm]
1	13/5	300/100/33
2	13/5	300/100/33
3-5	5/5	300/100/33

After curing for 25h at 30°C, rectangular specimens (80mm x 10mm x4mm) were cut and electrical contacts applied on the edges. The DC resistance was measured with source meter Keithley 2606 according to DIN EN ISO 3915 [13] (referring fig. 2a). Chosen source voltage was 10V. With the gained results the most adequate filler content out of the percolation curve was picked for vacuum assisted infusion process of the SWCNT modified GFRP plate aswell as the colored SWCNT modified GFRP plate. Six areas were cut out from the manufactured plates and the volume and surface resistance was determined according to ASTM D257-07 [14] with combination of Keithley resistivity test fixture 8009 and Keithley source meter 2606 (fig. 2b and c), respectively. Accompanying analysis of the dispersion quality via light microscopy as well as determining the influence of particle modification on glass transition temperature via differential scanning calorimetry were conducted.

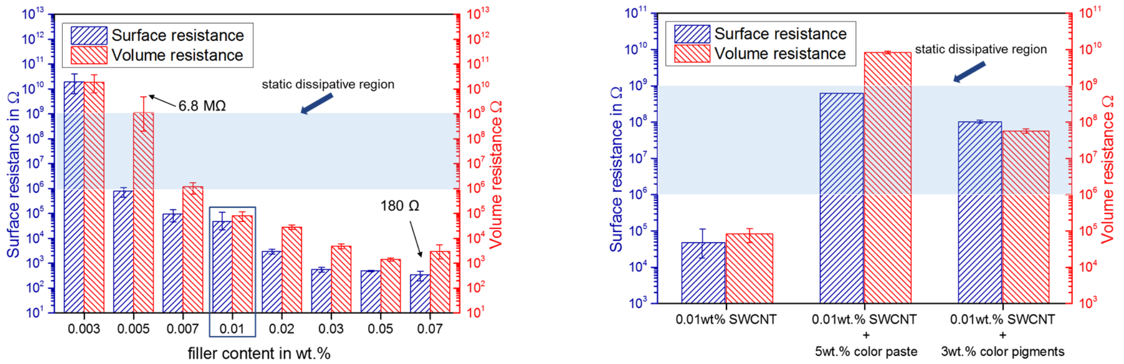


(a) (b) (c)

FIGURE 2. Measuring setup according to: a) volume resistance DIN EN ISO 3915; b) surface and c) volume resistance ASTM D257-07 [15]

RESULTS AND DISCUSSION

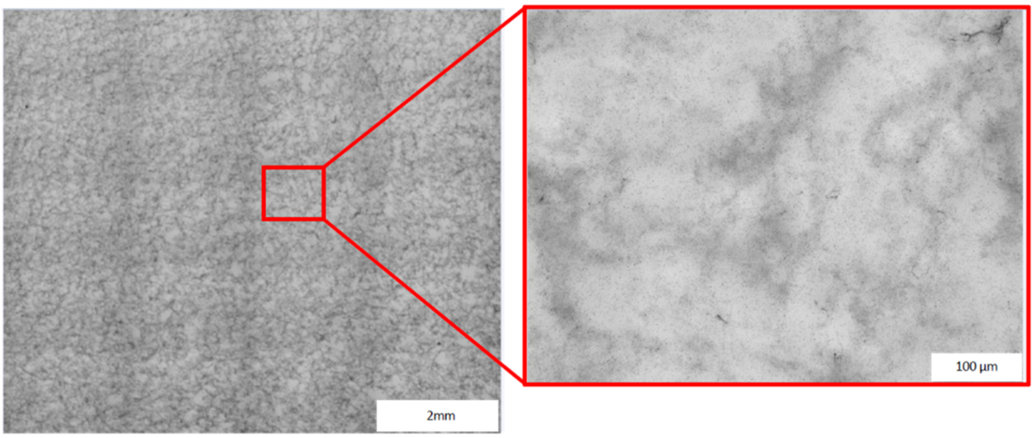
The SWCNT/resin composite shows an expected decrease of the resistance with increasing filler content (see fig 3a**)**. Starting with a filler content of 0.007wt.% the material fulfills the requirements for ESD protection. For the further material development a filler content of 0.01wt.% was chosen, because an increase of resistance results from addition of coloring paste and color pigments. Figure 3b visualizes the influence of either 5wt%. coloring paste or 3wt.% color pigment addition on the electrical resistance.



(a) (b)

FIGURE 3. a) Dependency of the surface and volume resistance on filler content and b) influence of color additives on the resistances

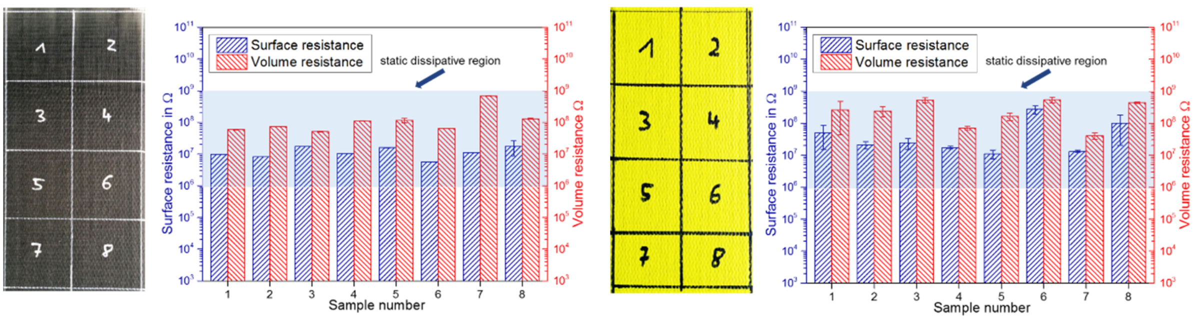
As expected, the resistance increases with the addition of both materials. Pigment addition fulfils the required demands. For the coloring paste addition, the increase in resistance exceeds the for ESD application required range. Conducted DSC measurements show, that color paste lowers the glass transition temperature slightly. Sumfleth [16] as well as Ma et al. [17] investigated the influence of multi filler systems on the electrical resistance change of epoxy resin dispersions. Globular, high conductive carbon black shows a synergetic effect in combination with CNT regarding the electrical properties. Carbon black particles settle at the free ends of the CNT. There they function as bridges between the CNT and benefit the formation of the percolating electrical network by reducing tunneling distances. Transferred to this study, the globular color pigments settle as well at the free ends of the SWCNT. These intrinsic electrical isolative pigments disturb the tunnel mechanism and therefore the electrical resistance. Taken micrographs show a homogeneous distribution of particles and no percolating network (see fig. 4).



(a) (b)

FIGURE 4. Micrograph of polyester resin modified with 0.01wt.% SWCNT and 5wt.% PU5011 lemon yellow

Alkylammonium salt and silicic acid act as stabilizers and disturb the formation of the percolating network. Ma et al. [17] and Yue et al. [18] concluded that additional particle stabilize dispersions. Different particle geometries prevent re-agglomeration. The composition of the of the coloring paste results in significant higher resistances compared to the addition of pristine pigments. Thus, the SWCNT modified resin with the pristine pigment features ESD protection these parameters are transferred into the GFRP. Figure 5 shows the results for the only SWCNT modified (a) as reference and for the colored GFRP (b).



(a) (b)

FIGURE 5. Surface and volume resistances for a) 0.01wt.% SWCNT and b) 0.01wt.% SWCNT and 3wt.% color pigment yellow PY74

In comparison, there occurs a slight increase in volume resistance for the colored GFRP, but the developed GFRP fulfills the requirements for ESD protection.

CONCLUSION

In this study we demonstrated, that the new generation SWNT feature an electrical percolating network at ultra-low filler loadings (0.01wt.%). Within the development process, ESD protection in the nano composite was achieved. Transferring the used modification parameters into the fiber composite leads to the desired antistatic properties. Even with coloring, the GFRP does not lose the ESD protective properties. Ultra-low filler addition SWCNT allow even of signal coloring.

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