

STUDY OF THE CONDUCTIVITY OF VARIOUS SIZE FORMS CARBON PARTICLES USED AS FILLERS OF EPOXY POLYMER COMPOSITES

Jana Novotná¹, Jana Salačová¹, Blanka Tomková¹, Jana Müllerová²

¹Technical University of Liberec, Dep. Of Material Engineering, Studentská 2, 461 17 Liberec, Czech Republic

Email: jana.novotna3@tul.cz , Web Page: <http://www.ft.tul.cz/en/departments/department-of-material-engineering.cz>

Email: jana.salacova@tul.cz , Web Page: <http://www.ft.tul.cz/en/departments/department-of-material-engineering.cz>

Email: blanka.tomkova@tul.cz , Web Page: <http://www.ft.tul.cz/en/departments/department-of-material-engineering.cz>

² Technical University of Liberec, Institute for Nanomaterials, Advanced Technology and Innovation, Studentská 2, 461 17 Liberec, Czech Republic

Email: jana.mullerova@tul.cz, Web Page: <http://cxi.tul.cz>

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Abstract

The electrical conductivity of a polymer can be increased by the addition of a conductive material in particulate or fibrillar form [4]. There are a lot of possibilities of conducting additives composites, for example chopped or milled carbon fibers (CMF), over multiwalled or singlewalled carbon nanotubes (CNT), graphite, graphene nanopellets and carbon black (CB) or fullerenes [3]. The advantages of milled carbon fibers are affordability of starting materials. Presented work is focused on influence of size of short and small carbon fibers and fillers at changes AC conductivity of epoxy composites. The electrical properties for the matrix do not have significant effect on the electrical properties for the composite [2].

1. Introduction

In the previous articles we deal with composites filled with 0.5-4% volume fraction of Carbiso Milled Carbon Fibers [10]. On the basis of the results of previous measurements, the concentration of 2.5%wt was determined to be the most interesting for conductivity comparison. Various types of recycled carbon fiber were selected as composites fillers, and non-milled fillers, samples A and F (Carbiso CMF and Graphite) were used for comparison. Milling was used to reduce fiber particles from micro (sample A) to nano dimensions (sample F). Therefore, there are compared different tips of carbon fillers for each other. The aim of the work is to determine which fillers are suitable for the better electrical properties of epoxy composites. All data were statistically tested for statistical significance and their interdependencies.

2. EXPERIMENT

2.1. Material

The used epoxy resin system, MGS LR 285 (epoxy)/ H 508 (hardener), mixing ratio 100:40 by weight [14]. As fillers were used the following materials: Carbiso Milled Carbon Fiber [2], 5min. milled Carbiso Milled Carbon Fiber, 30min. milled Carbiso Milled Carbon Fiber, 30min. milled Carbon Recycled Fiber, 30 min. milled Carbonized Acrylic Fibrous Wastes [9] and Graphite, see Figure1. All particles were added in 2.5wt% concentrations.

2.2 Milling

Preparation of particles samples B-E by the dry pulverization was carried out using high energy planetary ball milling of Fritsch pulverisette 7. The sintered corundum container of 80 ml capacity and zirconium balls of 10 mm diameter were chosen for 5min. or 30min. of dry milling. The source material is crushed and ground by grinding balls in a grinding bowl. The centrifugal forces from the rotation of the grinding bowls around their own axis and from the rotating support disc have an effect on the contents of the grinding bowl, consisting of material to be ground and grinding balls.

Samples A and F (Carbiso CMF and Graphite) were not milled.

2.3. Size of fillers

Sample A: have average diameter about 7 μm and average length 100 μm [15]. Samples B-F: fillers geometry was characterized by means of digital image processing, using software NIS elements. Particle size was determined based on the SEM pictures from VEGA 3 TESCAN and VEGA TS 5130, see Table 1.

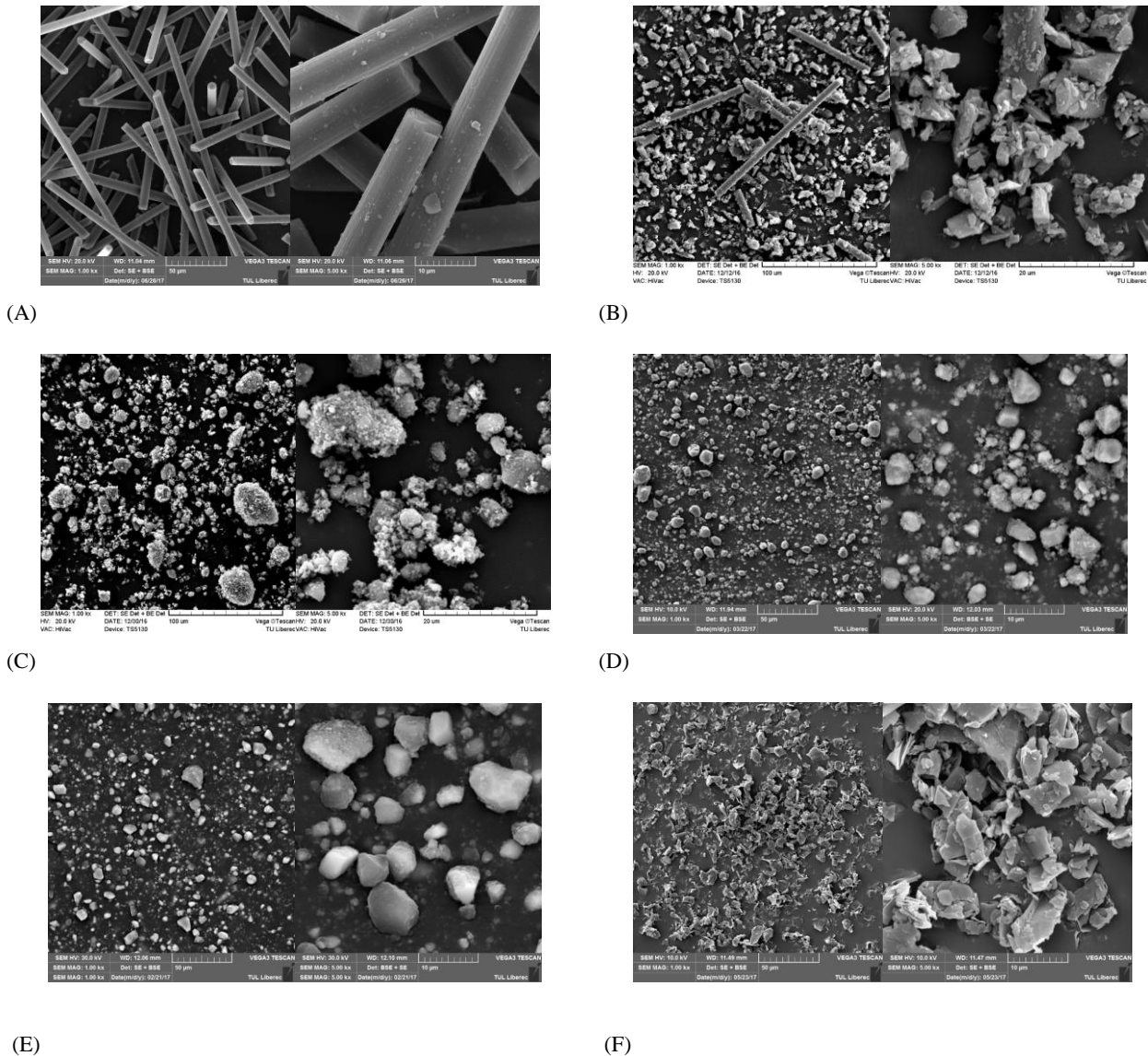


Figure 1. Sample A - Carbiso Milled Carbon Fiber (CMF), Sample B - 5 min. milled CMF, Sample C - 30min. milled CMF, Sample D - 30min. milled recycled CF, Sample E – 30min. milled carbonized acrylic fibrous wastes, Sample F - Graphite.

2.4. Methods of measurement

AC conductivity was measured using AGILENT 4294. The measurements were carried out in the frequency range 100 Hz – 3MHz according to ASTM D150-98 [1]. A precision analyzer was used to measure the sample capacitance C and the loss tangent $\tan \delta$ directly. The total conductivity σ_{AC} was calculated from the equation:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon'' \quad (1)$$

where, f is the frequency and ε_0 free space permittivity. Imaginary part of permittivity ε'' was calculated from the relation:

$$\varepsilon'' = \varepsilon' \tan \delta \quad (2)$$

The real part of permittivity ε' was calculated using the relation

$$\varepsilon' = \frac{Cd}{\varepsilon_0 S} \quad (3)$$

where, d is the sample thickness and S the sample cross-sectional area.

2.5. Data analysis

Data have been provided statistical algorithms and tools for organizing, analysing and modelling. Firstly, it has been applied assumption of random statistical selection.

Then it has been used statistical plot histogram, descriptive statistics, analysis of variance (ANOVA2N) and regression analysis [13].

- Statistical plot histogram

Histogram has been used for statistical visualization to convey essence and to allow for further processing. Distribution plots with histogram help to identify an appropriate distribution together with the fitted distribution. The histogram has a similar shape to the random numbers generated using the Weibull distribution.

- Descriptive statistics

Descriptive statistics is available to summarize large, complex data sets—both numerically and visually—to measures of central tendency locate a distribution of data along an appropriate scale, to calculate average, standard deviation, variability, modus, median, confidence interval, kurtosis, skewness, quantiles and percentiles.

- Linear Regression analysis and data fitting

A data model explicitly describes a relationship between predictor and response variables. Predictor is size of particles and responds is AC conductivity. We use Linear regression fits a data model that is linear in the model coefficients and least-squares fit with polynomials.

- Analysis of Variance (ANOVA2N)

The purpose of two-way ANOVA is to find out whether data from several groups have a common mean. The two-way ANOVA form of the model is:

$$y_{ijk} = \mu + \alpha_j + \beta_i + \gamma_{ij} + \varepsilon_{ijk} \quad (4)$$

where,

y_{ijk} is a matrix of our observations (with row index i , column index j , and repetition index k),

μ is a constant matrix of the overall mean,

$\alpha_{.j}$ is a matrix whose columns are variables,

β_i is a matrix whose rows are the deviations of each variables,

γ_{ij} is a matrix of interactions [12].

Hypothesis tests of mean values agreement is used to quantify decisions. There are two predictors, frequencies and size of particles, to explain

2.5. Results, Related discussion

The AC conductivities (samples B-F) of the individual fillers have by the same frequency comparable values, see Figure3. The average area particle size range is different, see Table1. By comparing the average area with the modulus area in samples B and C, it can be concluded by more milling (CMF) particles and that their size surface is unified.

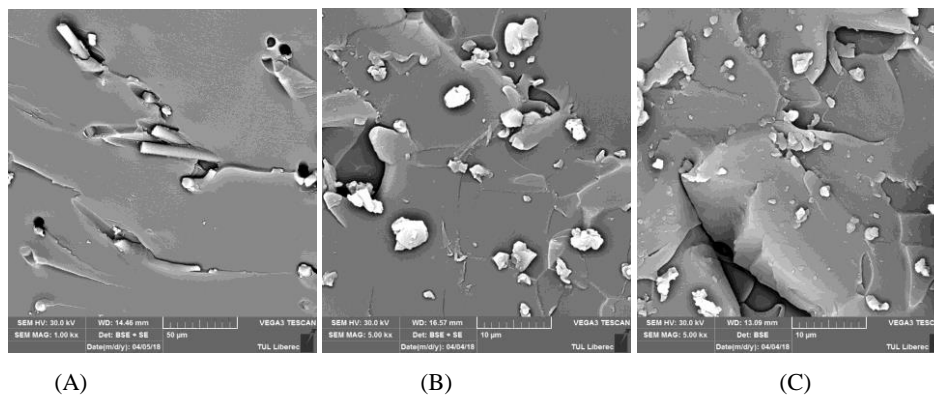


Figure 2. Internal structure of composites: Sample A - Carbiso Milled Carbon Fiber (CMF), Sample B - 5 min. milled CMF, Sample C - 30min. milled CMF

Short fibers with small aspect ratios are usually randomly oriented in all directions and give thus isotropic composites structure, while long fibers are mostly oriented in defined directions, and give therefore anisotropic composites and they are better conductors. This corresponds to our results, sample A (Carbiso CMF) reaches the highest conductivity values. Unfortunately, they do not achieve the CNT or GNP filled composites conductivity values, referred to in the literature [6-8]. But the structure of these fillers is completely different. However, our results are comparable to the CB fillers, whose structure is very similar, see in [5]. Additionally, the high anisotropic conductivity explains the absence of a frequency dependence as expected when assuming the occurrence of a highly interconnected fiber network with almost an absence of electrical barriers [4], see Figure 2.

Table 1 Measured data of average areas

Typ of fillers	A	B	C	D	E	F
Milling time	-	5min.	30min.	30min.	30min.	-
Equivalent particle diameter [μm]	7,01	6,5	3,20	1,51	0,62	0,36

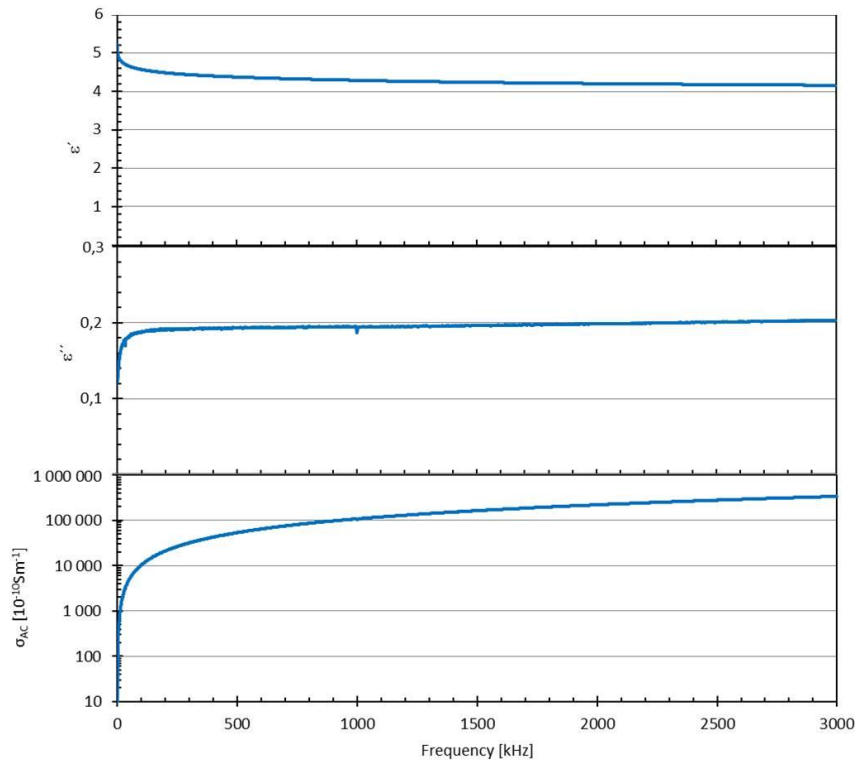


Figure 3. Typical dielectric properties of composites; real permittivity, imaginary permittivity, and AC electrical conductivity (Sample A)

Further, the higher the frequency the more conductivity is more invariable with particle size order keeping. This implies that it is important to find a regression dependency of conductivity at a higher frequency, see Figure 3.

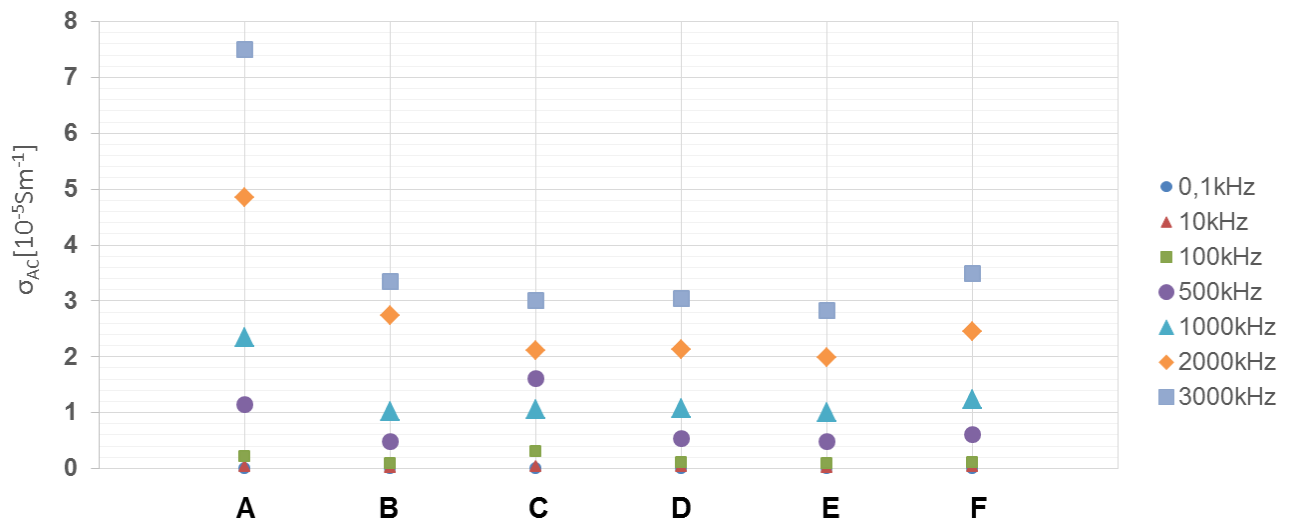


Figure 4
 Measured data of AC conductivity

In terms of statistical analysis, the goal was to determine how conductivity statistical depends on frequency and particles' size.

Firstly, high variation coefficients and high data kurtosis may lead to the view that the data do not approximate to the normal distribution, by to statistical plot histograms. According to this facts data could be organizing by tools of exploratory data analysis.

Table 2 ANOVA 2N for AC conductivity

Source	SS	dif.	MS	F	P - value	F - critic
<i>rows</i>	7,21E+06	6	1,20E+06	1	4,37E-01	2,4
<i>collums</i>	1,91E+08	6	3,19E+07	27	7,28E-12	2,4
<i>error</i>	4,30E+07	36	1,20E+06			
total	2,42E+08	48				

Further, according to ANOVA2 results, see Tab. 2 (the assumption of mean values agreement of all frequency levels), null hypothesis for frequency was not reject and the effect of the frequency on conductivity to be considered statistically insignificant. Other, null hypothesis for particle size was not reject, at least one of the particle levels is statistically significant. For this reason, it was proceed to regression analysis.

3. Conclusions

Experimental measurements have shown that all types of carbon composites particles, depends on frequency, exhibit similar increase in electrical conductivity. The milling of carbon particles does not increase the conductivity of the composites, on the contrary it decreases slightly. More comparative studies with a higher than 2.5%wt concentration of carbon recycled fillers are needed. Another possible way is a combination carbon fillers into composites [5].

Carbon fiber composites have higher recycling potential due to a higher material value. If we compare the average areas of our additives with their modus, see Table 1, we can say that repetition or milling lead to more even data of average sizes (sample C-E). Such material has a very good potential for further industrial processing. By recycling or repeated recycling of carbon fibers, possibly by using of the carbonized acrylic fibrous wastes by means of further milling, new one is emerging an affordable composite fillers with a good AC conductivity. Further, it seems that the influence of particle size on AC conductivity is increasing with increasing frequency.

Statistical analysis ANOVA demonstrated that they are statistically significant, therefore it is advisable to continue in a more detailed statistical testing, e.g. multiple comparisons.

Finally, in all samples the conductivity exhibits a frequency dependence which becomes stronger as average areas increases.

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