1 Introduction

Epoxy resins are widely used in the aircraft industry because of their low density, high strength and low shrinkage during curing. Application of polymer matrix composites to aircraft structures leads to the significant weight reduction and as a result to reduced fuel consumption, as well as CO$_2$ emission and what is the most important to the higher flight comfort and safety. In order to withstand high loads transfer by components of aircraft structure usually polymers are strengthened by application of high tensile fibres, such as glass or nowadays carbon fibres. Composite structures applied in the aircraft industry besides high mechanical properties should also perform other important functions, especially high electrical conductivity. Although carbon fibres are conductive for electrical current, the electrical conductivity of epoxy - carbon fibres composites is still not sufficient for aircraft protection against light strike, what still limits their application in primary structures.

Among different nanofillers carbon nanotubes (CNTs) are the most promising, because they hold potential for the realization of conducting composite structure, delivering an overall weight saving. CNTs are characterized by high strength, as well as thermal and electrical conductivity. Moreover, they can conduct high density current, and are also resistant to high temperature. Even small amount of CNTs, much below 0.1 wt.% can increase electrical conductivity of the polymer matrix by a few orders of magnitude [1]. Possibility of carbon nanotubes application in the aircraft industry is connected mainly with the electromagnetic interference shielding, lightening strike protection and electrostatic discharge.

Nano-sized fillers exhibit strong tendency to form the agglomerates. It is a result of high surface area of nanofiller and interaction of van der Waals forces between particles. For that reason the crucial technological problem is to obtain uniform dispersion of nanofiller in the polymer matrix. In the literature different information about methods of nanofillers dispersion can be found. When the selection of mixing method is made not only the uniform dispersion should be taken into account but also its influence on degradation of the filler and the resin properties. The most often methods used for nanofiller dispersion are ultrasonication and three roll milling (calendaring) [2, 3], extrusion [4], mixing with application of solvents or combination of previous.

Among different dispersion techniques ultrasonication with or without solvents is widely used. Application of ultrasonic makes carbon nanotubes dispersion easier, but it can also bring nanotubes damage, what leads to decrease of electrical and mechanical properties. In the case of the resin with the high viscosity the significant temperature increase can be observed during ultrasonication, and therefore there is a necessity of mixture cooling [5, 6].

Mechanical mixing by three roll milling makes use of shear effect realized by the three rolls placed in one axis, each roll goes with different speed and direction. Two of them, the first and the last one turn in the same direction, while the central one goes in the opposite. Also speed and distance between rolls can be changed in control manner. The biggest advantage of this method is possibility to obtain polymer matrix with uniform CNTs dispersion without tubes damage [5]. Uniform dispersion
obtained with this method allows to decrease percolation threshold much below 0.1 wt. % of CNTs and increases thermal conductivity about 60% for 5 wt.% of CNTs [7].

Due to the effect of unbalanced polarization and defects forming by chemical modification or functionalization the decrease in electrical conductivity of nanocomposites occurs [8]. Functionalization reduces electrical and photonic properties because of introducing sp3 hybridization defects [9, 10].

In order to improve the carbon nanotubes dispersion in the polymer matrix solvents like acetone [11, 12], ethanol [13-15] or dimethylformamide (DMF) [16] are often used. The reduction of the functional groups amount in the polymer, as an effect of curing epoxy resin in the presence of different solvents can lead to the decrease in the mechanical and thermal properties [17]. Often, in order to obtain better dispersion of CNTs in the polymer matrix different surfactants are used [18].

Polymer matrix nanocomposites are widely studied and used in recent years. Nanofillers are introduced in much smaller weight fraction than micro-fillers and even small amount of them can significantly change the properties of composites. Unfortunately nano-sized particles have tendency to agglomerate. The main problem in nanocomposites manufacturing is to obtain the uniform dispersion in the polymer matrix. There is a lot of work concerning mixing methods of carbon nanotubes (CNT) into the polymer. In our work the focus is put on dispersion of CNT in the epoxy matrix cured at different temperature. The quantitative analysis was made to quantify the influence of different curing parameters on CNT dispersion, and correlation between electrical conductivity and degree of dispersion was found.

2 Materials, fabrication and testing methods

2.1 Materials

In this work epoxy resin EPON 862 supplied by Hexion was used. As curing agents EPICURE W for high temperature curing and TETA for room temperature curing were applied respectively. Two kind of CNTs supplied by Nanocyl were applied. CNTs characteristic is given in the table 1 and SEM and TEM images are shown in fig. 5.

2.2 Fabrication methods

Samples were fabricated using the same mixing method by milling on the three roll miller. Two different curing agents resulting in two different curing temperature: 130° and room temperature (RT) were applied. For curing at elevated temperature curing agent was mixed together with the resin by rollers, while for curing at room temperature it was added after mixing by rollers.

2.3 Testing methods

In this work scanning electron microscopy combined with image analysis methods were used for evaluation of carbon nanotubes distribution in the epoxy matrix. First, SEM images were transformed into digital ones and analysed using methods of image analysis. The imaged positions of CNTs have been used to define so-called Zones of Influence, ZI, by SKIZ method (see fig. 1). Coefficient of variation of the size of these regions, defined as the standard deviation divided by the average value, is a measure of uniformity in spatial dispersion of CNT. This coefficient is equal to zero, CV = 0, for CNT evenly spaced on the section of the composite. It increases with the increasing of non-homogeneity of their distribution [19].

Electrical conductivity was measured by Van der Pauw method. In this method square shaped electrode was used and the edges were covered with the silver electroconductive paste to ensure a good contact between the electrode and the sample. The current was released by two edges, while remaining two were used for the measurement of the voltage decrease. Conductivity was calculated from the Eq (1):

\[
\exp(-\pi \cdot t \cdot s \cdot RA) + \exp(-\pi \cdot t \cdot s \cdot RB) = 1,\ (1)
\]

where: t – sample thickens, s - conductivity,

\[
RA = (V34/I12 + V12/I34)/2 \ a
\]

\[
RB = (V41/I23 + V23/I41)/2
\]

In this study Keithly 6220DC was used as a source of electrical current, which was connected to Keithly 218A nanovoltmeter [20].
3 Results and discussion

In this work effect of curing parameters of nanocomposites on carbon nanotubes dispersion was determined. Results of image analysis as calculated coefficient of variation of Zones of Influence were summarized with the electrical conductivity and percolation threshold in table 2. In fig. 2 SEM images and the imaged positions of CNT so called Zones of Influence of composites cured in different parameters and with different type of CNT are shown. In figs. 3 and 4 comparison of histograms of equivalent diameter distribution and area for different curing parameters and different type of carbon nanotubes are presented.

It was found that better dispersion is observed for composites cured at room temperature (see fig. 3). However, higher electrical conductivity was found at higher temperature of curing. It is due to different type of curing agent and changes of crosslinking density.

For composites with carbon nanotubes modified with NH₂ groups distribution of Zones of Influence differs from non-modified CNTs. Better dispersion was obtained for composites cured at higher temperature, as well as higher electrical conductivity was observed. CNTs modified with amino groups seems to be better dispersed at 130°C because of the possible reaction of epoxy groups with epoxy groups in the high temperature. It helps to obtain uniform dispersion. However, higher electrical conductivity for this kind of CNT is caused not only due to better dispersion but also due to application of different curing agent.

4 Conclusions

The study shows that curing parameters of the epoxy resin have influence for both electrical conductivity and dispersion degree of nanofiller in the epoxy matrix. For improvement of electrical and mechanical properties not only kind of nanotubes or dispersion method are important, curing parameters are also meaningful and they can increase electrical conductivity in few order of magnitude.

5 Acknowledgements

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Fig. 1 Schematic explanation of SKIZ method.
Fig. 2 Scanning electron microscopy images and Zones of Influences of these regions for different curing parameters and different type of carbon nanotubes: a) 130°C/NC3100; b) RT/NC3100; c) 130°C/NC3152; d) RT/NC3152.
EFFECT OF CURRING PARAMETERS ON DISPERSION AND ELECTRICAL CONDUCTIVITY OF EPOXY/CNT COMPOSITES DEFINE BY IMAGE ANALYSIS

Fig. 3 Histogram of distribution of equivalent diameter (a) and surface area (b) of composites with non-modified carbon nanotubes.

Fig. 4 Histogram of distribution of equivalent diameter (a) and surface area (b) of composites with non-modified carbon nanotubes.
Fig. 5 Scanning electron microscopy and transmission electron microscopy images of carbon nanotubes a) non-modified; b) modified with NH$_2$ groups.
Fig. 6 Electrical conductivity of composites with different type of carbon nanotubees cured in different parameters.

Tab. 1 Carbon nanotubes characterization.

<table>
<thead>
<tr>
<th>Mark</th>
<th>Modification</th>
<th>Length [μm]</th>
<th>Diameter [nm]</th>
<th>Purity [%]</th>
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</thead>
<tbody>
<tr>
<td>NC3152</td>
<td>NH₂</td>
<td>1</td>
<td>9.5</td>
<td>&gt;95</td>
</tr>
<tr>
<td>NC3100</td>
<td>-</td>
<td>1.5</td>
<td>9.5</td>
<td>&gt;95</td>
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</table>

Tab. 2 Coefficient of variation of composites curing at different temperature.

<table>
<thead>
<tr>
<th>Curing/CNT</th>
<th>CV(A)</th>
<th>CV(d2)</th>
<th>σ[S/m]</th>
<th>p,</th>
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<tr>
<td>RT/NC3100</td>
<td>0.97</td>
<td>0.45</td>
<td>0.03</td>
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<tr>
<td>130°C/NC3100</td>
<td>1.02</td>
<td>0.53</td>
<td>1.87</td>
<td>0.033</td>
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<tr>
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<td>0.94</td>
<td>0.44</td>
<td>0.02</td>
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<tr>
<td>130°C/NC3152</td>
<td>0.84</td>
<td>0.42</td>
<td>1.11</td>
<td>0.04</td>
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</table>

References


