PAPER • OPEN ACCESS

Limits of carbon micro/nano particles utilization to improve properties of polymer matrices in fibre reinforced composites

To cite this article: B Tomková et al 2018 IOP Conf. Ser.: Mater. Sci. Eng. 459 012024

View the article online for updates and enhancements.

You may also like

- <u>Capacity Fading Mechanisms on Cycling a</u> <u>High-Capacity Secondary Sulfur Cathode</u> Sang-Eun Cheon, Soo-Seok Choi, Ji-Seong Han et al.
- Insights on Relationship between Deterioration and Direct-Current Internal Resistance of Valve Regulated Lead-Acid Battery by Addition of Granular Carbon Additives under HRPSoC Duty Junxiong Wang, Jiakuan Yang, Jingping Hu et al.
- A Microstructurally Resolved Model for Li-S Batteries Assessing the Impact of the Cathode Design on the Discharge Performance Vigneshwaran Thangavel, Kan-Hao Xue, Youcef Mammeri et al.





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.136.97.64 on 04/05/2024 at 08:59

Limits of carbon micro/nano particles utilization to improve properties of polymer matrices in fibre reinforced composites

B Tomková, J Novotná, M Pechočiaková

Dept. of Material Engineering, Technical University, Liberec (Czech Rep.)

blanka.tomkova@tul.cz (Author)

Abstract. This work focuses on the changes in properties of epoxy resin filled with five carbon forms in several volumes (graphene nanopellets, carbon particles from acrylic waste, and 3 different types of recycled carbon fibres). Main purpose is to enhance knowledge in influence of various carbon forms and their volume on final matrix structure and properties, and their applicability in fibre reinforced composites. Current measurements show that all types of carbon particles influence matrix properties to a certain extent, as their presence activates overall structural changes in epoxy resins curing.

1. Introduction

The development of new composite materials is one of the fastest growing sectors in industrial research. As the textile reinforcements remain more or less the same except for development of "green" composites, many recent studies are focused on improvement of mechanical, thermal, electrical or wear properties using different combinations of nanofillers in polymer matrices [1-9]. The selection of the filler type depends, in the first place, on the property we aim to improve.

It is known that mechanical and thermal properties mainly depend on level of matrix cross-linking, and interface quality (optimized contact) between the matrix and applied nanoparticles [10-11], while transmission of electrical charges in polymer composites depends not only on quality of their structure but also on electrical properties of individual components [12].

For instance, if we mean to increase thermal/mechanical endurance along with electrical conductivity, we must consider the fact that most polymeric materials belong into category of insulators [13] with electrical conductivity lower than 10⁻¹⁴ S/m. To increase both, electrical conductivity, and thermal/mechanical properties, it is necessary to fill polymer matrix with electroconductive particles and/or nanoparticles, that concurrently support arrangement of matrix structure. From this viewpoint, electro-conductive carbon/graphite particles of various shapes and sizes seem like very promising material [14]. Their market offer is very wide [15], from chopped or milled carbon fibers, over graphen nanopellets, carbon black, multiwalled or singlewalled carbon nanotubes, to natural fullerens, and they can be variously combined. As such they are promising filling material for variety of technical applications. This study focuses on properties of epoxy resin filled with five carbon forms (graphene nanopellets, carbon particles from acrylic waste, and 3 different types of recycled carbon fibres). Aim was to study the influence of particles structure and volume on epoxy resin properties, and analyse its applicability for improvement of fibre reinforced plastic composites (FRPC) in perspective of appropriate balance between the cost of the production and required properties of final composites.

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

2. Experimental

2.1. Material

Epoxy specimens were made from Bisphenol A-based low viscosity epoxy resin MGS LR 285 [16], and cyklo-alifatic polyamine curing agent H 508 (mixing ratio 100:40 by weight). As fillers were used following carbon materials: graphene nanopellets (GNP, Figure 1, a) [17], milled carbon particles from acrylic waste (mCPAN, Figure 1, b) [18], commercially available Carbiso Milled Carbon Fibres (CMF, Figure 1, c) [19], milled Carbiso CF CMF (mCMF, Figure 1, d) [20], and milled recycled carbon fibre from epoxy resin composites (mRCF, Figure 1, e) [21].





nanopellets (GNP), b) Carbon particled from acrylic waste (mCPAN), c) Carbiso Fibres (CMF), d) Milled Carbiso (mCMF), e) Milled recycled CF (mRCF).



e)

One specimen was neat epoxy, the others were filled with carbon particles in following concentrations: 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt% respectively. Higher concentration was not used due to striking increase of resin viscosity in 3wt%, which means it is useless as a fiber bonding in FRPC.

2.2. Milling

Nanoparticles from Carbiso (mCMF), recycled CF (mRCF) and carbonized acrylic fibrous waste (mCPAN) were made by the dry pulverization using high energy planetary ball milling of Fritsch pulverisette 7, Germany. Carbon material was placed in 80 ml sintered corundum container and milled by zirconium balls (\emptyset 10 mm) for 30 minutes in dry state. Selected balls/material ratio was 10:1, rotation speed was set at 850 rpm. Samples of Carbiso Milled CF (CMF), and graphene nanopellets (GNP) were not milled.

2.3. Size of fillers

Parameters of Carbiso milled carbon fibres are specified by producer [19], who states average diameter about 7 μ m and average length about 100 μ m. Size of other samples was determined from

structural micrographs using image analysing software NIS Elements [22]. Micrographs were scanned

| Table 1. Structural geometry of used carbon micro/nano miers. | | | | | |
|---|------|-------|-----|------|------|
| Properties | GNP | mCPAN | CMF | mCMF | mRCF |
| Equivalent particle diameter [µm] | 0.36 | 0.62 | 7.0 | 3.2 | 1.51 |

Table 1. Structural geometry of used carbon micro/nano fillers

2.4. Methods of measurement

Alternating current (AC) conductivity

on SEM microscopes VEGA 3 TESCAN and VEGA TS 5130.

AC conductivity σAC [Sm⁻¹] of carbon filled specimen was measured using AGILENT 4294. The measurements were made in the frequency range 100 Hz–3MHz according to ASTM D150-98:2015. A precision analyzer was used to measure the sample capacitance C [F] and the loss tangent tan δ directly. The total conductivity σ_{AC} [Sm⁻¹] is calculated using following equation:

$$\sigma_{AC} = 2\pi f \varepsilon_0 \varepsilon''$$

where, f [Hz] is the measurement frequency and ϵ_0 [Fm⁻¹] is free space permittivity (the electric constant, approx. 8.85×10^{-12} Fm⁻¹). Imaginary part of permittivity ϵ ''[Fm⁻¹] is calculated using following relation:

$$\varepsilon'' = \varepsilon' tg\delta$$

where the real part of permittivity ε' is determined from the relation:

$$\varepsilon' = \frac{C.d}{\varepsilon_0 S}$$

d [m] is the sample thickness and S $[m^2]$ the sample cross-sectional area.

Charpy Impact test

Impact strength and energy were tested to analyse the influence of carbon nanofillers on epoxy matrix impact resistence. The test was run according to ISO 179-1:2010, where specimen is laid into horizontal position on Charpy's hammer struts. When the ram is released, the hammer freely falls into the center of the specimen between the supports, and the amount of energy, consumed for specimen breaking, is set in Joules. Impact strength is then determined from following relation:

$$a_{CN} = \frac{E_C}{h*b} * 1000$$

where, a_{CN} [kJ.m⁻²] is the Impact strength, E_C [J] is Impact energy, h [mm] is specimen thickness, and b [mm] is specimen width.

Analysis of thermo-mechanical and thermal properties

Differential Scanning Calorimeter DSC6 (Perkin Elmer) was used to analyse glass transition of analysed set of filled epoxy specimen. Samples of 10 mg weight were placed in aluminum pans and sealed. The specimens were heated in an inert nitrogen atmosphere from room temperature (25°C) up to presumed softening temperature of used epoxy resin [16] (120°C) at a heating rate of 10°C/min.

Using dynamic mechanical analysis DMA DX04T (RMI) in 3PB mode the changes of elastic/plastic properties were scanned. These changes indicate structural transformation of matrix due to carbon filling. The specimen has been loaded as free-fixed beam. The tests have been realized only up to 60°C (working temperature of used resin) at the heat rate of 3°C/min under the 1 Hz load frequency.

Heat transfer of epoxy specimens was tested with Isomet 2114 - Thermal Properties Analyser to estimate the progress of thermal conductivity due to carbon filling in epoxy. The amount of transferred heat may be distorted due to weak insulation of the device, and non-homogenity of material, so the final value of thermal conductivity serves only for monitoring, as it is not confirmed yet.

3. Results

The measurements of epoxy resin filled with various carbon forms proved, that increase of particles' volume changes the properties of epoxy resin, as shown in Table 2 (data for mCMF were selected).

| Properties of mCME | Neat Epoyy | 0.5wt% | 1wt% | 1.5wt | 2wt% | 2.5wt% |
|---|---------------|--------|-------|-------|-------|--------|
| | Ербху | | | | | |
| x 10^{-8} [S.m ⁻¹] at 10 kHz | 6.94 | 7.32 | 7.66 | 7.81 | 8.12 | 8.34 |
| Flexural Modulus [GPa] | 3.28 | 3.32 | 3.38 | 3.42 | 3.51 | 3.52 |
| Impact strength [kJ.m ⁻²] | 38.27 | 38.62 | 38.95 | 39.28 | 39.41 | 39.43 |
| Thermal conductivity [W.m ⁻¹ .K ⁻¹] | 0.101 | 0.159 | 0.183 | 0.199 | 0.201 | 0.208 |

Table 2. Properties of neat and mCMF filled epoxy.

As other carbon fillings showed more or less similar behavior, and with respect to processing requirements on low viscosity of resin used as a composite bonding, we suggested 2.5wt% carbon filling as an optimum combination for both property improvement and matrix processability, and further experiments were done only for this filling volume. A comprehensive overview of the results for 2.5wt% carbon filled epoxy resins is presented in Table 3 (in Discussion part).

Results for mechanical properties (see Figure 2) show remarkable effect only for CMF filling, which is standard short fiber carbon reinforcement (even in low concentration). Other particles filling have little or rather weakening effect, except for GNP in impact measurements. AC conductivity of specimens are in detail shown in Figure 3. It is obvious that only Carbiso filling remarkably shifted the AC conductivity of the resin. Other carbon particles show only slight improvement of epoxy no matter, what type of particle was used. DSC analysis showed, that all carbon fillers have plasticizing effect on used epoxy resin (see Figure 4). Same behavior also showed up on DMA analysis in 60°C. While neat epoxy is still stiff, filled specimen already show viscous behavior. As for thermal conductivity, all fillings increased the conductivity approx. twice.





IOP Publishing

IOP Conf. Series: Materials Science and Engineering 459 (2019) 012024 do

doi:10.1088/1757-899X/459/1/012024



4. Discussion

Experimental measurements showed that use of carbon micro/nanoparticles in the same volume (2.5wt%) influences matrix properties to a certain extent depending on the carbon particle morphology. Remarkable effect showed mainly CMF filling, which is standard short fiber carbon reinforcement (even in low concentration). Other particles' filling exhibit little influence on electrical properties, in case of thermal/mechanical properties it sometimes exhibits even weakening effect (e.g. mCPAN, or mRCF). Comprehensive overview of the results is presented in Table 3.

| Properties | Neat Epoxy | GNP | mCPAN | CMF | mCMF | mRCF |
|--|---------------|-------|-------|-------|-------|-------|
| AC conductivity x 10 ⁻⁸ [S.m ⁻¹] at 10 kHz | 6.94 | 9.12 | 7.55 | 18.2 | 8.34 | 8.51 |
| AC conductivity x 10 ⁻⁷ [S.m ⁻¹] at 100 kHz | 8.32 | 11.2 | 9.10 | 22.1 | 9.51 | 10.0 |
| AC conductivity x 10 ⁻⁵ [S.m ⁻¹] at 1000 kHz | 0.89 | 1.24 | 0.99 | 2.35 | 1.06 | 1.07 |
| Impact strength [kJ.m ⁻²] | 38.27 | 57.02 | 34.6 | 66.41 | 39.43 | 34.50 |
| Flexural modulus [GPa] | 3.28 | 3.45 | 3.31 | 3.78 | 3.52 | 3.33 |
| Tensile modulus [GPa] calculated from 3PB | 3.55 | 3.21 | 3.22 | 4.01 | 3.04 | 3.23 |
| Tg [°C] | 58.75 | 54.56 | 57.12 | 57.46 | 49.54 | 53.63 |
| Thermal conductivity λ [W.m ⁻¹ .K ⁻¹] | 0.101 | 0.215 | 0.195 | 0.203 | 0.208 | 0.192 |

| Table 3. Selected properties of neat and carbon particles filled ep | poxy resin. |
|--|-------------|
|--|-------------|

Achieved results show, that limits of carbon micro/nanoparticles utilization as matrix filling in FRPC are derived from processing parameters based on resin viscosity, and from morphology of carbon particles. The fibrous particles (2D) exhibits better influence comparing to bulk particles (3D). Significant is also market price of selected fillings, which points to milled recycled fibers (CMF) as not only cost-effective but also environmentally friendly filling prepared from recycled carbon fibre

wastes. Use of such material supports the ecological aspects in design, development, and processing of new fiber/polymer composites.

5. Conclusions

The aim of presented work was to find the use limits of carbon micro/nanoparticles, mainly those prepared from ground recycled carbon fibers, to improve electrical, thermal and/or mechanical properties of epoxy matrices. The use of such fillers incorporates processing of recycled carbon wastes, and may contribute to environmentally friendly development in engineering of FRP composites.

Achieved results show a good processing potential of milled recycled carbon fibers (CMF) but rather poor use of further reduction of carbon particles size. In the future work we would like to analyse this behavior more deeply, and we will also test selected fillers' influence on different types of resin systems, and incorporate achieved results in future design and development of novel fiber reinforced polymer composites. Finally we would like to transfer our findings into practical industrial applications. This is the main challenge for future work.

Acknowledgements

Authors are grateful for the financial support by the Ministry of Education, Youth and Sports of the Czech Republic and the European Union - European Structural and Investment Funds in the frames of Operational Programme Research, Development and Education - project Hybrid Materials for Hierarchical Structures (HyHi, Reg. No. CZ.02.1.01/0.0/0.0/16_019/0000843).

References

- [1] Kotsilkova R, Fragiadakis D and Pissis P 2005 J. of Polymer Science B 43(5) 522
- [2] Singh S, Srivastava VK and Prakash R 2015 Applied Nanoscience 5(3) 305
- [3] Zhou T, Wang X, et al. 2013 Polymer Letters 7 585
- [4] Safdari M, Al-Haik MS 2013 Carbon 64 111
- [5] Zhang K, Zhang Y, Wang S 2013 *Carbon* **65** 105
- [6] Guo M, et al. 2014 Comp. Sci. Technol. 97 27
- [7] Hussan SI 2012 Al-Mustansiriya J. of Science 23(3) 133
- [8] Du FP, Tang H, Huang DY 2013 Int. J. of Polymer Sci. 2013 1
- [9] Seiler J, Kindersberger J 2013 Proc. of 18. International Symposium on High Voltage Engineering (Seul, Korea) p 1297
- [10] Ellis B 1993 Chemistry and Technology of Epoxy Resins (Dordrecht: Springer Netherlands)
- [11] Fiedler B, et al. 2006 Composite Sci. Technol. 66 3115
- [12] Aneli JN, Khanasvili LM, Zaikov GE 1998 Structuring and Conductivity of Polymer Composites (NY, USA: Nova Science Publishers)
- [13] Peliskova M, Saha P 2012 Chem. Letters 106 1104
- [14] Burchell TD 1999 Carbon Materials for Advanced Technologies (Oxford, UK: Elsevier)
- [15] Delgado JL, et al. 2008 J. of Materials Chemistry 18 1417
- [16] EPIKOTETM 2017 www.swiss- composite.ch/pdf/t-Epoxyd-Harz-L-285-LF-e.pdf
- [17] KOH-I-NOR GRAFIT 2017 <u>http://www.grafitnetolice.cz/grafit_en.php</u>
- [18] Baheti V, et al. 2015 Fibers and Polymers 16(10) 2193
- [19] Carbiso 2017 <u>http://www.easycomposites.co.uk /#!/resin-gel-silicone-adhesive/filler-powders-and-additives/general-fillers-and-additives/milled-carbon-fibre-powder.html</u>
- [20] Novotna J, et al. 2017 Proc. of 9th Central European Conference (Liberec, Czech Rep.)
- [21] Tomkova B, Militky J 2010 World J. of Engineering 7(2) 232
- [22] Tomkova B, Grabmullerova J, Novakova, J 2013 Proc. of 5th International Conference on Experiments/Process/System Modeling/ Simulation/ Optimization (Athens, Greece, on CD)