Hierarchical design of structural composite materials down to the nanoscale via experimentation and modelling

L. Gorbatikh1*, Q. Liu1, V. Romanov1, M. Mehdikhanî1, A. Matveeva1, O. Shishkina1, A. Aravand1, B. Wardle2, I. Verpoest1, S. V. Lomov1
1Department of Materials Engineering, KU Leuven, Kasteelpark Arenberg 44, B-3001 Leuven, Belgium
2Department of Aeronautics and Astronautics, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA

* Larissa.Gorbatikh@kuleuven.be

Abstract. We envision the next generation composite materials as hierarchically structured down to the nanoscale. The importance of nanoscale features has been long recognized from studies of naturally occurring composites. Thanks to their hierarchical organization spanning through multiple scales they show exemplary resilience to failure combined with a plethora of different functions. In man-made composites, nanostructure can be introduced through modifications of the matrix, interfaces and fibers. Here we review our research efforts in the field of nano-engineered composites, focusing on the mechanical performance of fiber-reinforced plastics modified with carbon nanotubes. Our research is a combination of experimental and computational studies.

1. Introduction

There has been immense interest in the use of carbon nanomaterials for reinforcement of plastics and their composites. Figure 1 shows evolution of the number of articles referring to carbon nanotubes (CNTs), graphene and composites in the last three decades. The number of articles published in 2017 on a combined topic of “carbon nanotubes” and “composites” is close to 10 000, and the one on “graphene” and “composites” is 14 000 (source: Web of Science). There has been an accelerated growth in graphene research related to composites triggered in the year of 2010. We like to believe that this remarkable productivity in research results is linked to the prior knowledge acquired on CNTs that is now being transferred to studies of graphene based composites.

The focus of this brief review is a special class of composite plastics that combine reinforcing components of two scales (microscopic fibers and nanotubes) and are known as hierarchical composite materials [1]. These materials have a complex structure with several levels of organization and distinguishable macroscopic, mesoscopic, microscopic, and nanoscopic features. Figure 2 illustrates these structural levels on an example of a nano-engineered alumina fiber/epoxy composite. One can distinguish layers of a woven fabric on the meso-level, individual fibers inside yarns of the fabric and CNT bundles grown on the fibers on the micro-level. By zooming in to the nanoscale one could examine internal structure of the CNT bundles (not shown on the figure) and even structure of individual nanotubes.
2. Nano-engineering of fiber-reinforced polymer composites

Different routes can be followed for introduction of CNTs in fiber-reinforced plastics. For example, CNTs can be dispersed in the matrix, added in fiber sizing/coatings, directly grown on fibers/fabrics (as shown in Figure 2) or integrated in interleaves between plies. Benefits for the mechanical performance and challenges in processing for these strategies have been a subject of many reviews [1, 2]. Direct growth of CNTs on fibers is a promising route considering that it allows to bypass typical problems of CNT agglomeration and filtration in approaches based on CNT dispersion.

![Graph showing the number of journal articles per year in composites research with reference to carbon nanotubes and graphene.](image)

**Figure 1.** The number of journal articles per year in composites research with reference to carbon nanotubes and graphene.

![Diagram illustrating structural levels in hierarchical composites: meso-level - a micro-CT image resolving textile structure; micro-level - SEM images distinguishing individual fibers with aligned nanotube growth; nano-level - a TEM image of a multi-wall nanotube grown on the fiber.](image)

**Figure 2.** Structural levels in hierarchical composites: meso-level - a micro-CT image resolving textile structure [3]; micro-level - SEM images distinguishing individual fibers with aligned nanotube growth [4]; nano-level - a TEM image of a multi-wall nanotube grown on the fiber [5].
Moreover, the route of CNT grafting provides additional benefits such as control of CNT alignment and possibility to achieve a high CNT content in the composite. Composites with these CNT grafted fibers (also known as ‘fuzzy’ fibers) show improved mechanical performance (fiber–matrix interface strength, interlaminar toughness, bearing strength, [5, 6]). In earlier days researchers working in this direction had to face a serious challenge: CNT growth on carbon fibers was detrimental to the fiber strength, but in the meantime this challenge has been successfully addressed [7].

Processing of the fuzzy fiber composites with vacuum infusion, light RTM and autoclave manufacturing needs, in some cases, adjustment of processing parameters. The fibre volume fraction in composites produced with these techniques is controlled by compressibility of the fibre reinforcement. Since the presence of grown CNT decreases compressibility of dry fibres/fabrics [8, 9], it is likely to lead to a lower fiber volume fraction in the composite. Internal geometry of fuzzy fabrics and their composites is also different: yarns are typically swelled due to the CNT grafting leading to a laminate thickness increase [3]. Changes in the material microstructure may alter the process of damage development and final failure of the composite. Thus it is a combined effect of the nanoscale reinforcement and microstructural changes that is responsible for the changes in the mechanical performance.

3. Modelling of fiber-reinforced composites with carbon nanotubes

Modelling approaches have been indispensable in helping to understand the mechanical behavior of such complex materials as nano-engineered composites. The number of design parameters is so large that it is not feasible to investigate them all experimentally. In [10-12] we proposed a computational approach to predict the effect of CNTs on stresses in hierarchical composites (Figure 3). The approach is based on the mesh superposition technique in the framework of the finite element analysis.

![Figure 3. Geometrical models of the composites with different CNT assemblies and corresponding stress fields in the matrix and CNTs [10].](image)
It allows modelling of composites with a large variety of CNT assemblies: CNTs that are dispersed in the matrix with different degrees of agglomeration, CNTs that are grown on fibres with different degrees of alignment and CNTs that are concentrated in the interphase region mimicking fibre sizings or coatings (Figure 3). The models have shown that CNTs introduce strong heterogeneity in stress and strain fields at the microscale. This heterogeneity is closely linked to the morphology of the CNT distribution [10-13].

Strains predicted by the models are consistent with the strain maps obtained experimentally using digital image correlation in combination with SEM [4] (Figure 4). Both experimental and modelling studies confirmed that aligned CNT forests constrain tensile deformation in their longitudinal direction (Figure 4). The strain in the transverse direction, on the other hand, is not constrained. Thus, an impregnated CNT bundle behaves as a quasi-unidirectional nanocomposite, transverse properties of which are dominated by the matrix behavior.

![Figure 4. Comparison of the strain maps measured using digital image correlation (a) and maps predicted by the two scale FEM analysis (b); and comparison of the measured and predicted strain profiles along paths a and b (c,d) [4].](image)

Recently we extended capabilities of our models towards predictions of the strength and toughness [14], by accounting for three damage mechanisms: 1) fibre/matrix debonding, 2) CNT/matrix debonding and 3) damage in the matrix. Computational experiments showed that damage diffusion (crack branching) is the major toughening mechanism in composites with CNT grafted fibres, while debonding of CNTs and that of the fibers play secondary roles. Figure 5 shows microscopic damage in the CNT-modified composite and the reference case (pristine composite without CNTs) at the time of composite failure. When CNTs are absent, damage starts at the fibre/matrix interface and then kinks into the matrix, resulting in a very localized fracture. In the case of fuzzy fibers we see significant damage diffusion in resin rich zones between CNT forests, which is accompanied by CNT debonding. The latter also consumes energy and further toughens the material. All this leads to a dramatic improvement of the transverse strength and toughness (Figure 5d).
Figure 5. Damage in (a) the pristine composite without CNTs and (b) the composite with fuzzy fibers; (c) zoom in view on the interfacial damage in the composite with CNTs; (d) predicted stress–strain curves for the two composite types [14].

4. Outlook

Research in the field of hierarchical structural composites is in its very beginning. More research is needed to better understand interdependent effects of nano- and micro-structures on composite properties as well as to proceed to more material combinations and hierarchical levels as we see it in nature. Although not discussed here, the emergence of carbon nanomaterials is presenting us with unique opportunities not only to develop light, strong and tough composites but also smart composites that could self-manufacture, self-sense, self-heal and perform many other practical functions ([15-17]).

Acknowledgments

The authors acknowledge the support from C24/16/021 project, funded by KU Leuven Research Council. S.V. Lomov holds the Toray Chair for Composite Materials at KU Leuven.

References

[1] Gorbatikh L, Wardle BL, Lomov SV, Hierarchical lightweight composite materials for structural applications. 2016 MRS Bulletin 41(9) 672
[2] Gorbatikh L and Lomov SV 2018 2.15 Damage in Architectured Composites. In: Beaumont, P.W.R. and Zweben, C.H. (eds.) Comprehensive Composite Materials II. vol. 2, 291–306. Oxford: Academic Press.
[3] Aravand MA, Shishkina O, Straumit I, Liotta AH, Wicks SS, Wardle B, Lomov SV, Gorbatikh L 2016 Internal geometry of woven composite laminates with “fuzzy” carbon nanotube grafted fibers. Composites Part A 88 295–304
[4] Mehdikhani, M, Matveeva A., Aravand A, Wardle B., Lomov SV, Gorbatikh L 2016 Strain mapping at the micro-scale in hierarchical polymer composites with aligned carbon nanotube grafted fibres. Composites Science and Technology 137 24–34
[5] Garcia EJ, Wardle BL, Hart AJ, Yamamoto N 2008 Fabrication and multifunctional properties of a hybrid laminate with aligned carbon nanotubes grown in situ. Composites Science and Technology 68 2034–2041
[6] Wicks SS, Wang W, Williams MR., Wardle BL 2014 Multi-scale interlaminar fracture mechanisms in woven composite laminates reinforced with aligned carbon nanotubes. Composites Science and Technology 100 128–135
[7] Li R, Lachman N, Florin P, Wagner HD, Wardle BL 2015 Hierarchical carbon nanotube carbon fibre unidirectional composites with preserved tensile and interfacial properties. Composites Science and Technology 117 139–145
[8] Lomov SV, Wicks S, Gorbatikh L, Verpoest I, Wardle BL 2014 Compressibility of nanofibre grafted alumina fabric and yarns: aligned carbon nanotube forests. Composites Science and Technology 90 57–66

[9] Lomov SV, Gorbatikh L, Verpoest I 2011 A model for the compression of a random assembly of carbon nanotubes, Carbon 49 2079–2091

[10] Romanov VS, Lomov SV, Verpoest I, Gorbatikh L 2015 Modelling evidence of stress concentration mitigation at the micro-scale in polymer composites by the addition of carbon nanotubes. Carbon 82 184

[11] Romanov VS, Lomov SV, Verpoest I, Gorbatikh L 2015 Inter-fiber stresses in composites with carbon nanotube grafted and coated fibers. Composites Science and Technology 114 79–86

[12] Romanov VS, Lomov SV, Verpoest I, Gorbatikh L 2014 Can carbon nanotubes grown on fibers fundamentally change stress distribution in a composite? Composites: Part A 63 32–34

[13] Romanov VS, Lomov SV, Verpoest I, Gorbatikh L 2015 Stress magnification due to carbon nanotube agglomeration in composites. Composite Structures 133 246–256

[14] Liu Q, Lomov S.V., Gorbatikh L, Carbon nanotubes grafted on fibers diffuse damage in composites leading to their improved toughness at the micro-scale. Proceeding of ECCM18 - 18th European Conference on Composite Materials, Athens, Greece, 24-28th June 2018

[15] Buschhorn ST, Kessler SS, Lachmann N, Gavin J, Thomas G, Wardle BL, Electrothermal icing protection of aerosurfaces using conductive polymer nanocomposites. 54th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference, Structures, Structural Dynamics, and Materials and Co-located Conferences (AIAA 2013-1729)

[16] Lee J, Ni X, Daso F, Xiao X, King D, Sánchez Gómez J, Varela TB, Kessler SS, Wardle BL 2018 Advanced carbon fiber composite out-of-autoclave laminate manufacture via nanostructured out-of-oven conductive curing. Composites Science and Technology (in print)

[17] Lee J, Stein IY, Kessler SS and Wardle BL 2015 Aligned Carbon Nanotube Film Enables Thermally Induced State Transformations in Layered Polymeric Materials. ACS Appl. Mater. Interfaces 7 (16) 8900–8905