HIERARCHICAL COMPOSITES WITH SECONDARY CNT NANOREINFORCEMENT: COMPUTATIONAL MODELLING

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ABSTRACT

The effect of distribution of carbon nanotubes in hybrid and carbon fiber reinforced composites on their strength and fatigue resistance is investigated with the use of computational experiments. 3D microstructure-based unit cell models, the automatic script based model generation, multiscale modelling and other advanced computational techniques are employed to analyze the effects of hybrid structures, interface properties, nanostructural reinforcements on the strength and fatigue resistance of composites. It was shown that secondary nanoreinforcement can drastically increase the fatigue lifetime of composites. The feasibility of the application of CNT reinforced composites for wind turbine blades is discussed.

1 INTRODUCTION

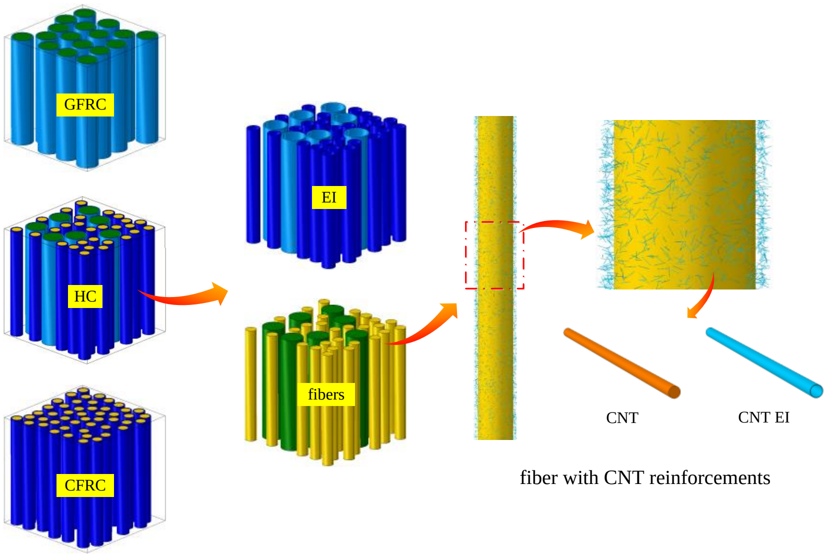
Unidirectional polymer composites are used in many areas of industry. The important task in the materials development is the enhancement of strength and fatigue resistance of these materials [1]. It has been observed in many studies that the introduction of small amount of nanoparticles (e.g. graphene, carbon nanotubes/CNT, clay particles with high aspect ratios) into fiber reinforced composites can be used to improve composite properties [1]-[15]. According to [5], matrix-dominated properties (flexural and interlaminar shear strength) are drastically improved by the CNT additions to fiber-reinforced thermoplastic composites, while fiber-controlled properties (such as tensile strength and stiffness) are improved only slightly. In [6]-[8], the authors observed that the crack initiation toughness increases (by 10% if CNTs in sizing and by 25% if in matrix) and the crack propagation toughness decreases (by 30…50%) when CNTs are placed in sizing [7]. However, in the system with carbon fibers, both crack initiation and propagation energies were improved by CNT addition in matrix [8], what is related with CNT bridging and other toughening mechanisms (crack deflection, blocking). 45% increase in shear strength is achieved by adding 0.015 wt% nanotubes into glass fiber reinforced vinyl ester composite [9]. 30% enhancement of the interlaminar shear strength was achieved by deposition of multi and single walled CNT on woven carbon fabric fibers in epoxy matrix [13], [14].

In this paper, computational studies of the effect of secondary CNT reinforcement on strength, fracture and fatigue of nanoreinforced hybrid and carbon fiber reinforced composites, carried out at the Department of Wind Energy, Technical University of Denmark, are presented.

2 UNIT CELL MODELLING OF HYBRID AND HIERARCHICAL COMPOSITES: UNIT CELL MODELS

For the computational testing of different generic and real structures of composites, a set of programs for the automatic generation of 3D multiscale unit cell finite element models of composite was developed [16]-[19]. The programs generate command files for the commercial FE software ABAQUS. The unit cell structures are divided into two levels. The macro (upper level) unit cells contain three phases: the matrix, fibers and “third phase” interface layers (which characterizes the interface roughness, interphases [17][18]). The fibers in the unit cells are placed randomly, using the RSA (random sequential absorption) algorithm [17]. Both matrix and the interface layer might contain nanoreinforcements. The microscale (lower level) unit cell includes the nanoreinforcement in matrix and/or interfaces, polymer matrix as well as the “effective interface layers” [20]. The macro-model analysis saves the time-dependent values of variables (i.e. stress and displacement field) of the “seed nodes” which located on the boundary between macro model and micro model after the macro-level analysis. The micro-model inherits these data as the initial boundary condition and together with other added boundary condition (if needed) to go on the analysis. The mechanical properties and strength of fibers and epoxy were taken from [1], [16], [21]. The mechanical properties of the “effective interface layer” between CNTs and epoxy in the micromodel were taken from inverse simulations in [22] (assuming that the “effective interfaces” between graphene and epoxy, and CNT and epoxy are similar). For simplicity, the carbon nanotubes were represented as cylinders.

A number of 3D multiscale unit cell models of CNT and fiber reinforced composites have been generated automatically, and used for the computational testing of structures of composites [17]. Figure 1 shows an example of a unit cell model.



GFRC: glass fiber reinforced composite HC: hybrid composite CFRC: carbon fiber reinforced composite
EI: effective interface

Figure 1. Example of unit cell model of CNT reinforced hybrid composite. Reprinted from [3] with kind permission of Elsevier

3 DAMAGE AND FATIGUE BEHAVIOUR OF CNT REINFORCED CARBON AND HYBRID COMPOSITES

In order to analyse the effect of CNT reinforcement on the fatigue strength of carbone fiber and hybrod reinforced composites, a number of computational experiments were carried out using the macro-micro multiple-step modeling strategy [1][3][16]. The aspect ratio of CNTs was 1000, and they were distributed In the sizing of the fibers. The volume fraction of the CNT reinforcement is 0.46%.

The model was subject to cyclic compression-tension loading. In order to simulate the fatigue damage evolution, two step procedure was employed. Initial defects (with the sizes of the order of one…two finite elements) were introduced into the macro-scale model by subjecting the unit cell to a quasi-static load before the cyclic loading. After the initial defects are formed, the fatigue modeling for macro-scale model is carried out. Both the crack growth onset and crack propagation are described using the Paris law The crack propagation analysis is carried out in the framework of the linear elastic fracture mechanics (LEFM) approach and is based on the extended-FEM method. The Virtual Crack Closure Technique (VCCT) is employed to calculate the strain energy release rate at the crack tip.

Figure 2 shows the S-N curves of composites (under tension-compression loading with R=-1) with pure glass, pure carbon and hybrid (1:1) fibers, reinforced by CNTs located in fiber sizing, and some examples of the unit cells. The vertical axis is normalized by the initial maximum stress of 1:1 hybrid fiber reinforced composite without CNT reinforcement under this loading (274.82MPa). One can see that the CNT enhances the fatigue performance (maximum stress and lifetime) in all considered composites. For the very low cycle loading, the CNT reinforcement leads to 25%...43% increase in the stress, while for the millions of cycles, the CNT effect increases the stress by 64…120%.

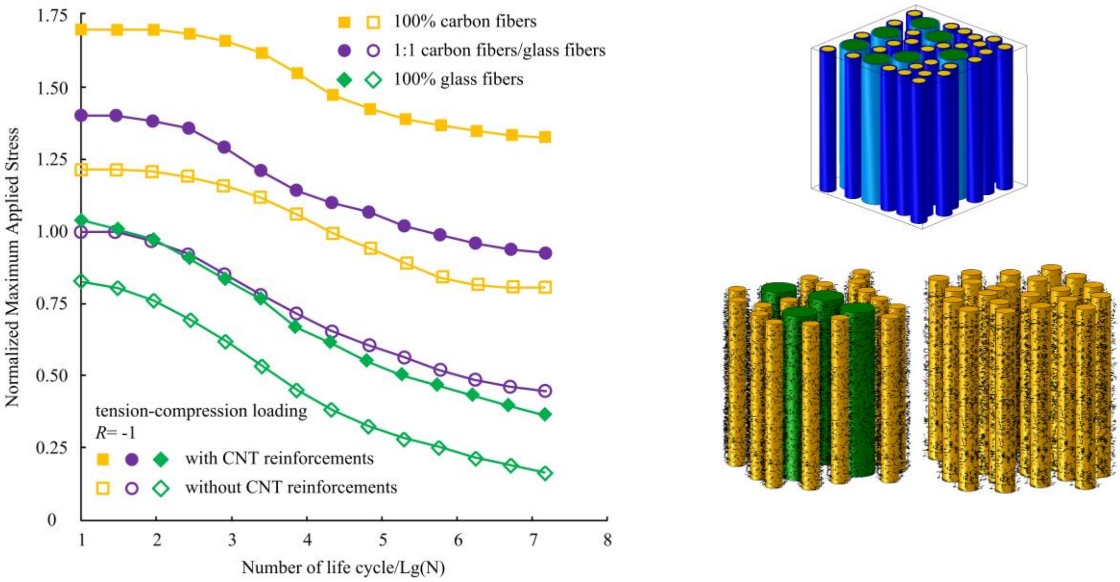
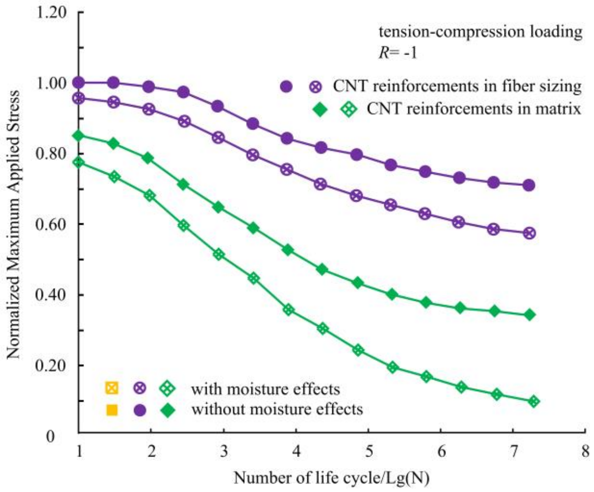


Figure 2. S-N curves for hybrid composites under pure mechanical cyclic loading (tension-compression) with CNT reinforcement (left) and examples of unit cells (right) (hybrid without CNT, hybrid with CNT, and pure carbon reinforced with CNT composites) [3]

4 EFFECT OF CNT DISTRIBUTION ON THE FATIGUE RESISTANCE

In order to analyze the effect of the CNT distribution/location on the fatigue resistance of the composites, we consider the cases of hybrid composites with CNTs localized either in the fiber sizing or distributed in the matrix. The total number of CNTs in the model ($9.450 * 10^5$) is fixed and the same in both cases. Apparently, the content of CTts in the sizing is therefore much higher than in the matrix (0.02% is the model with nanoreinforced sizing, and 0.005% in the model with CNTs in the matrix). All the CNTs are random arranged in either fiber sizing or matrix. Fig. 3 shows S-N curves of hybrid composite with secondary CNT reinforcements in fiber sizing or in matrix, subject to the mechanical cycling loading with and without high humidity. One can see that the composite with CNT reinforcements in fiber sizing show the better fatigue performance than those with the CNT reinforcements in matrix, both in dry and high humidity conditions.

The observation about the higher efficiency of nanoreinforcement localized in the fiber/matrix interfaces as compared with the randomly spread over the matrix corresponds to the observation in [23] about the nanostructuring interfaces and weak sites as a most promising way of the material properties enhancement.



A.

Figure 3. S-N curves of hybrid composite with secondary CNT reinforcements in fiber sizing or in matrix [3]

5 HUMIDITY EFFECT ON THE PERFORMANCES OF NANOREINFORCED COMPOSITES

Off-shore wind turbines, as well as other lightweight materials for difficult service conditions represent a promising area of application of strong reliable composites. For these cases, the effect of environmental loading (first of all, humidity) in combination with mechanical loading is of critical importance. In order to estimate the effect of humidity on the fatigue lifetime of the CNT reinforced composites, a series of computational studies has been carried out [3]. Literature data on the humidity effect on the mechanical properties and strength of the composite phases have been reviewed and collected. Due to the expected off-shore location of wind turbines, we considered the effect of seawater on the phase properties, with the relative air humidity 60% . Moisture absorption causes plasticization and swelling of epoxy matrix, and that weakens the interfacial strength between epoxy and reinforcements, degradation of crosslinks and segments rigidity [24]. Under the seawater 60% humidity conditions, Young modulus of epoxy is reduced by 5% and tensile strength is reduced by 15…18% [25]. Carbon fiber' mechanical properties don't change due to moisture. However, the maximum applied stress before the fiber fracture is reduced in seawater by 1.33 times (after 60 hours)…2 times (after 230 hours) [25]. The tensile strength of glass fibers can be reduced up to 20% if the moisture content is above 1% [26]. The maximum applied stress before the interfacial failure is reduced by 1.9 times after 60 hours in seawater [25]. The epoxy/carbon interface strength is reduced by 10% at high temperature under the humidity effect [27]. The ILSS (interlaminar shear stress) of both carbon and glass /epoxy interfaces are reduced by 1.5 times [28]. The detailed overview and other parameters are references are given elsewhere [3].

Using these values as input data, we carried out FE simulations of fatigue degradation of the composites. Fig. 4 shows the S-N curves of 50/50 glass/carbon fiber reinforced hybrid composites with secondary CNT reinforcement under cyclic fatigue under high humidity conditions. One can see that the moisture effect on the CNT reinforced glass composites is weaker than on pure glass composites: the stress is only 3.5 times higher for mechanical high cycle loading and 35% higher for mechanical low cycle fatigue than for combined mechanical + environmental loading (compared with 5 times higher for non-CNT high cycle case) and 65% higher for low cycle case). For pure carbon composites, the CNT reinforcement doesn't have visible effect of the moisture resistance.

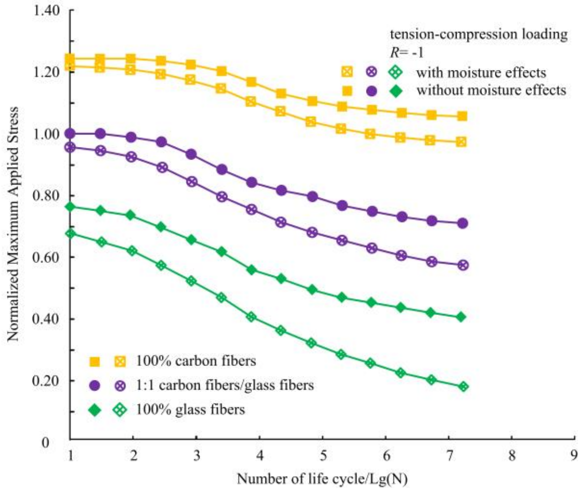


Figure 4. S-N curves for hybrid composites under high humidity + mechanical cyclic loading (tension-compression) with CNT reinforcement [3]

5 APPLICABILITY TO WIND TURBINE BLADE MATERIALS

Let us evaluate the feasibility of using hybrid and nanoreinforced composites in wind blades. The important requirement toward wind blade materials is their economic efficiency, i.e. the gains in strength and lifetime should overweight the additional costs. Let us make a rough estimation of the economic feasibility of new materials for wind energy applications.

The cost of energy over whole lifetime of the wind turbine can be estimated using the following formula [29]:

$$CoE_{total} = \frac{C * FCR + M}{P_{Avg} T} \tag{1}$$

where P_{Avg} – average power generation per hour, T – lifetime in hours, FCR – fixed charge rate (taken in as 10%), M – maintenance costs (taken as 2% installed capital costs), C – capital investment for a turbine, which is calculated as [30]: $C = cP_{rat}$, P_{rat} – rated (maximum) turbine power, c – coefficient, c=1100 €/kW (land based) or 1500…2000 €/kW (off-shore turbine). U – undisturbed wind speed, f(U) – wind speed probability density given by Weilbul distribution with shape factor 2, Uin and Uout – start and stop wind speeds of the wind turbine, P(U) – power at the wind speed U, P(U) can be calculated as $C_p \rho AU3/2$, C_p – power coefficient (≤0.59), ρ- air density, A –rotor swept area, $A=\pi R^2$, R- turbine radius. C_p can be taken 0.45 [30]. Using the very simplified analytical equation from [31], linking the lifetime of a turbine component to the wind speed and materials fatigue properties, one can define the allowable upper limit for the C_{nano} (cost increase , as a result of using nanoengineered materials) as a relative increase of the lifetime of blade from each material as compared with basic cases (here, glass fiber epoxy composite):

$$C_{nano}^{\max} < \frac{CoE_2}{CoE_1} = \frac{C_2 (K_2)^{b_2} (1 - S_m / S_{u1})^{-b1}}{C_1 (K_1)^{b1} (1 - S_m / S_{u2})^{-b_2}} \frac{\left(\frac{b_2}{2}\right)! \left(\frac{b_2}{\alpha}\right)!}{\left(\frac{b_1}{2}\right)! \left(\frac{b_1}{\alpha}\right)!} \tag{2}$$

where C and b – coefficient and power coefficient of S-N curve of the material, $N = C\sigma^{-b}$, f0 – average frequency, Sm, Su are mean stress and ultimate strength of WT material, Vm – mean wind speed, α – parameter of Rayleigh law distribution for wind speed variation, K – stress concentration factor, indices 1 and 2 refer to the basic case (here, glass fibers) and considered case of a composite with modified structure, respectively.

Let us estimate how the materials modifications considered above influence the wind blade lifetime. Table 1 shows the coefficients b and C determined in above simulations. Using these values, we can calculate that 0.5% CNT nanoreinforcements (in fiber sizing) increase the lifetime by 16% (if the fibers are still from glass) or even 86% (if the fibers are replaced by carbon fibers). Thus, one can state that the gains in the lifetime of the composites do justify some additional investments to produce the wind turbine blades from hybrid and nanoreinforced composites, with the investments in the range between 12 and 86% of the current costs. The justifiability of these investments becomes even more apparent when considering the blades which should work in off-shore conditions.

Case	**Pure glass reinforced composite (GRC)**	**Carbon RC**	**50/50 glass/carbon hybrid**
C, $*10^{10}$	2.405	3.188	2.703
b	0.542	0.333	0.463
CNT reinforcement			
Case	**Glass RC**	**Carbon RC**	**50/50 glass/carbon hybrid**
C, $*10^{10}$	2.804	4.455	3.704
b	0.486	0.318	0.408

Table 1: Proportionality and power coefficient of S-N curve of the considered model materials [3]

6 CONCLUSIONS

. The secondary CNT reinforcement ensures a much higher lifetime of composites. The lifetime of composites depends strongly on the humidity conditions, and the glass fiber composites are most sensitive to humidity, while the carbon composites are least sensitive to it The CNT reinforced glass fiber composites show lower humidity sensitivity than pure glass reinforced composites; yet, this effect is much weaker for carbon fiber composites. Also, hybrid carbon/glass composites with the secondary CNT reinforcement have a high potential to replace the common composites, with sufficient improvement of the materials performances.

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REFERENCES

[1] L. Mishnaevsky Jr., P. Brøndsted , R. Nijssen, D. J. Lekou and T. P. Philippidis, Materials of large wind turbine blades: Recent results in testing and modelling, *Wind Energy*, Vol. 15, No.1, pp, 83–97, 2012

[2] L. Mishnaevsky Jr., G.Dai, Hybrid and hierarchical nanoreinforced polymer composites: Computational modelling of structure-properties relationships, *Composite Structures*, **117** (2014) 156–168

[3] G.M. Dai, L. Mishnaevsky Jr , Carbone nanotube reinforced hybrid composites: computational modelling of environmental fatigue and their usability for wind blades, *Composites B,* 10.1016/j.compositesb.2015.03.073

[4] L. Mishnaevsky Jr., Micromechanics of hierarchical materials: a brief overview, *Reviews on Advanced Materials Science,* 30 (2012) 60-72

[5] A. M. Díez-Pascual et al, Multiscale fiber-reinforced thermoplastic composites incorporating carbon nanotubes: A review, *Current Opinion in Solid State and Materials Science,* 18, 2014, 62-80

[6] N. De Greef et al, The effect of carbon nanotubes on the damage development in carbon fiber/epoxy composites. *Carbon* Vol.49, Issue 14, 2011, Pages 4650-4664

[7] A. Godara et al, Interfacial shear strength of a glass fiber/epoxy bonding in composites modified with carbon nanotubes, *Composites Science and Technology,* Volume 70, Issue 9, 2010, Pages 1346-1352

[8] A. Godara et al., Influence of carbon nanotube reinforcement on the processing and the mechanical behaviour of carbon fiber/epoxy composites, *Carbon,* Vol.47, 12, 2009, pp. 2914-2923

[9] J. Zhu et al., Processing a glass fiber reinforced vinyl ester composite with nanotube enhancement of interlaminar shear strength, Compos Sci Technol 67 (7–8) (2007), 1509–1517

[10] P.C. Ma, Y. Zhang, Perspectives of carbon nanotubes/polymer nanocomposites for wind blade materials, *Renewable and Sustainable Energy Reviews*, 30, 2014, pp. 651-660

[11] L. Merugula, V. Khanna, B.R. Bakshi,. Reinforced wind turbine blades--an environmental life cycle evaluation, *Environ Sci Technol.* 2012 Sep 4;46(17):9785-92..

[12] L. Merugula, V. Khanna, B.R. Bakshi Comparative life cycle assessment:reinforcing wind turbine blades with carbon nanofibres. In: Sustainable Systems and Technology (ISSST), 2010 IEEE Symposium on Sustainable Systems and Technology, Washington, D.C., May 17-19, 2010, pp. 1-6.

[13] E. Bekyarova et al., Functionalized single-walled carbon nanotubes for carbon fiber-epoxy composites. *J Phys Chem C* 111 (2007), pp. 17865–17871

[14] E. Bekyarova, et al, Multiscale carbon nanotube-carbon fiber reinforcement for advanced epoxy composites. *Langmuir* 23 (7) (2007), pp. 3970–3974. E.

[15] S.S. Wicks et al, Interlaminar and intralaminar reinforcement of composite laminates with aligned carbon nanotubes, Composites Science and Technology, Vol 70, No 1, 2010, pp 20-28

[16] G.M. Dai, L. Mishnaevsky Jr., Fatigue of multiscale composites with secondary nanoplatelet reinforcement: 3D computational analysis, *Composites Science and Technology,* Vol. 91, 2014, pp. 71-81

[17] L. Mishnaevsky Jr and P. Brøndsted, Micromechanisms of damage in unidirectional fiber reinforced composites: 3D computational analysis, *Composites Science and Technology*, Vol. 69, No.7-8, 2009, pp. 1036-1044

[18] L. Mishnaevsky Jr, *Computational Mesomechanics of Composites*, John Wiley, 2007, 280 pp.

[19] H. Qing, and L. Mishnaevsky Jr, Unidirectional high fiber content composites: Automatic 3D FE model generation and damage simulation, *Computational Materials Science,* Vol. 47, 2, 2009, pp. 548-555

[20] H.W. Wang et al, Nanoreinforced polymer composites: 3D FEM modeling with effective interface concept, *Composites Science and Technology,* Vol. 71, No. 7, 2011, pp- 980-988

[21] L. Mishnaevsky Jr., G.M. Dai, Hybrid carbon/glass fiber composites: Micromechanical analysis of structure-damage resistance relationship, *Computational Materials Science*, Vol. 81, 2014, pp. 630-640

[22] G.M. Dai, L. Mishnaevsky Jr., Graphene monolayer nanocomposites: 3D simulation of damage and fracture, *Computational Materials Science,* Vol. 95, 2014, pp. 684–692

[23] L. Mishnaevsky Jr., Nanostructured interfaces for enhancing mechanical properties of materials: Computational micromechanical studies, *Composites B*, Vol. 68, 2015, pp. 75–84

[24] K.Y. Rhee, S.R. Ha, S.J. Park, H.J. Kim, D.H. Jung. Fracture behavior of seawater-absorbed carbon/epoxy laminated composites in the hydrostatic pressure condition, *Mater. Sci. Eng. A*, 419 (2006), pp. 209–213

[25] A. Zafar, et al. Investigation of the long term effects of moisture on carbon fibre and epoxy matrix composites, *Composites Science and Technology*, 72 (2012), pp. 656–666

[26] Mei Li, Temperature and moisture effects on composite materials for wind turbine blades. PhD thesis, Montana state university, Bozeman, Montana, 2000

[27] J.S. van der Wal. Water resistance of glass fibre reinforced epoxy (GFRP) and carbon fibre reinforced epoxy (CFRP) Composite. Diffusion-polumers.com, Netherlands, 2006

[28] B.C. Ray, Temperature effect during humid ageing on interfaces of glass and carbon fibers reinforced epoxy composites, *J Colloid and Interface Science*, 298 (2006), pp. 111–117

[29] J.F. Manwell, J G. McGowan, A. L. Rogers , *Wind energy explained: Theory, design and application*

[30] D. Veldkamp, Chances in Wind Energy. A Probabilistic Approach to Wind Turbine Fatigue Design, PhD thesis, 2006, DUWIND Delft University Wind Energy Research Institute, 290 pp.

[31] P. S. Veers H. J. Sutherland T. D. Ashwill, Fatigue life variability and reliability analysis of a wind turbine blade., 1991, 5p, Sandia National Labs., Albuquerque, NM.