STIFFNESS-MODIFIABLE COMPOSITE FOR PEDESTRIAN PROTECTION

A. Bachinger[a*], E. Marklund[a,b], J. Rössler, P. Hellström[a], L. E. Asp[a,c]

[a]*Composite Structures, Swerea SICOMP AB, Argongatan 30, SE-431 22 Mölndal, Sweden.*
[b] *Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE-971 87 Luleå, Sweden.*
[c] *Applied Mechanics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden.*
**angelika.bachinger@swerea.se*

Keywords: fibre/matrix interface, stiffness-variable composite, pedestrian protection.

Abstract

A novel functional material allowing stiffness-reduction upon external stimulation was developed. Implementation of such technology in the design of a car front has high potential to result in increased protection of vulnerable road users (VRUs). The composite material is obtained by coating carbon fibres with a thermoplastic polymer in a continuous process, followed by infusion with an epoxy resin. The process is scalable for industrial use. The coating process was optimized regarding coating efficiency, energy consumption, risks involved for operating personnel and environment, and tailored to gain the optimal coating thickness obtained from numerical calculations. A drastic decrease in transversal stiffness could be detected for the composite material by dynamic mechanical thermal analysis (DMTA), when the temperature was increased above the glass transition temperature of the thermoplastic interphase. The ability of the material to achieve such temperature and associated reduction in stiffness by the application of current was verified using a special 3-point bending setup developed for this task.

1. Introduction

The current work addresses the development of a new stiffness-variable composite material aimed to be employed in a car front structure for increased protection of pedestrians.
According to the European statistics, 6000 VRUs were killed in road accidents in the EU in 2010 [1]. The European Injury Database (EU IDB) estimates that about 4.2 million road injuries per year have to be treated in European hospitals and almost two thirds of these road injury victims are VRUs [2]. The most frequent areas of injuries in pedestrian fatalities are the head and the lower extremities, and the vehicle area causing these injuries is usually the car front [2]. It has been shown in investigations performed at Chalmers University of Technology that the head injury severity of VRUs upon car front impact depends mainly on impact speed and car front stiffness [3].
Recently, Tridech developed a technique to prepare a composite material that softens by application of an electric current through the fibre reinforcement [4]. The material was studied for use in morphing wing concepts for unmanned aircraft. In the spirit of Tridech, a novel type of stiffness-modifiable composite material for use in hoods and other parts of the front structure of future electric cars is reported in the present work. Allowing parts of the car front

to soften on impact will decrease the deceleration by increasing the distance over which the head or other body parts decelerate.
The aimed functional material is achieved by introducing a thermoplastic interphase in carbon fibre reinforced thermoset composites. The stiffness-reduction in this material can be triggered by applying current through the carbon fibres. Thereby, the thermoplastic coating is heated above its glass transition temperature, which leads to softening of the interphase and hence decreased load transfer between the matrix and the fibre reinforcement.

A promising method to achieve organic coatings on conductive surfaces is electrocoating. The cathodic electropolymerization at constant potential has been studied extensively for the application of polymer coatings on metal surfaces [5]. Electrocoating at constant potential does, however, usually result in extremely thin layers in a slow process and requires inert atmosphere and is therefore industrially applied exclusively for highly advanced products.
It is assumed that the application of higher current densities might accelerate the process and make it less sensitive by supplying an excess of active species (electrons). This assumption is supported by earlier studies by Bismarck and his group, who showed that electrocoating of carbon fibres at constant current is possible at ambient conditions [4, 6]. In the mentioned publications, continuous coating of carbon fibres with Poly(acrylamide) (PAAm) [4] and batch coating with Poly(methyl methacrylate) (PMMA) [6] was reported.
Investigations on improving the electrocoating process in the present work focus mainly on (i) increasing control over the system and reducing the required energy by using electropolymerization at constant potential rather than constant current, alternatively by using lower current densities and (ii) possibilities to avoid the carcinogenic monomer Acrylamide (AAm, required for PAAm coatings). Moreover, a continuous coating process is developed and optimized regarding coating efficiency and coating thickness.
Material models are employed to simulate the properties of a material reinforced with such coated fibres. In order to support the material development, the influence of the coating thickness on the mechanical properties at different temperatures is simulated. The stiffness-variable properties of the material are verified by DMTA measurements and 3-point-bending tests with applied current.

2. Description of experiments and analysis

2.1. Material development

Electrocoating experiments were performed in a set-up that allowed the continuous coating of carbon fibres in a bundle as shown in Figure 1. Constant potential (reduction potential of the monomer i.e. -1.5 V vs. Pt) or constant current (between -0.2 and -2.4 mA/cm^2, corresponding to -0.1 and -1.2 A) was applied between the carbon fibres and the stainless steel tube.

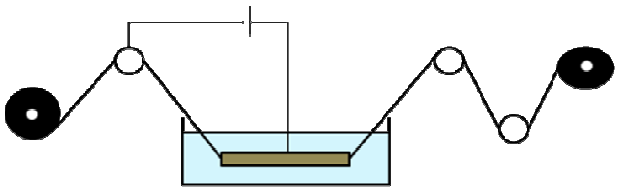

Figure 1: Set-up for continuous coating of carbon fibres.

Application and control of current was achieved using a Gamry Reference 3000 potentiostat and the potential was measured against a platinum pseudo-reference electrode.

The set-up shown in Figure 1 allows the continuous coating of fibre bundles by pulling unsized carbon fibre bundles (Hexcel® HexTow™ AS4D) through the electrocoating rig by a motorized rotating spool.

Electrocoating experiments were performed in N,N-Dimethylformamide (DMF, 98%) containing 0.75-10 mol/L Methyl methacrylate (MMA, 99% with ≤30 ppm inhibitor) and 0.25 mol/L Lithium perchlorate ($LiClO_4$, ≥98%) at a constant temperature of 65°C. Static coating was performed by applying constant potential or current for 70 s, while continuous coating was performed at a fibre pulling speed of 3 mm/s (corresponding to 70 s in bath). All coating experiments were performed at ambient conditions. The coated fibres were washed with DMF and dried overnight at 100°C under reduced pressure. The quality and thickness of the coating was characterized by TGA, optical microscopy and SEM.
Optical microscopy was performed on an OLYMPUS BH2-UMA microscope with MSPLAN and MDPLAN objective lenses providing different magnifications between 2.5 and 50x. The images were further enlarged digitally using Analysis imaging software. The evaluation of optical microscopy images was performed with the help of a rough system judging the coating success between:

Mark	***Description***
1	Discontinuous or powder-like coating or continuous film on some fibres
2	Film covering a considerable portion of the fibre surface or continuous film on most fibres
3	Continuous film covering complete fibre surface

Table 1. Description of the system for evaluating optical microscopy images.

SEM micrographs were recorded on a Hitachi S4800 scanning electron microscope at the Royal University of Technology in Stockholm (KTH). TGA experiments were performed on a Mettler TGA/DSC1 instrument in air at a heating rate of 10°C/min. The results were evaluated using Mettler StarE software. The amount of polymer coating present on the fibre surface was calculated from the mass loss between 160 and 350°C.
The composites reinforced with unidirectional coated fibres and commercial sized carbon fibres (Hexcel® HexTow AS4D - for the reference sample) were prepared by filament winding followed by vacuum infusion of epoxy resin (Araldite LY556 with hardener Aradur HY914 and accelerator DY070).

2.2. Material modelling

The effect of temperature on the stiffness of the described material was modelled using the concentric cylinder assembly model [7]. The model is a straightforward generalization of Hashin's concentric cylinder assembly model and Christensen's generalized self-consistent approach. It was shown that all engineering constants for the composite cylinder may be calculated (with required accuracy) from knowledge of the constituent (phase) properties by setting up and solving a system of linear equations using appropriate continuity and interfacial conditions [7]. The coated composite is considered as a three-phase system: carbon fibre surrounded by PMMA coating embedded in the epoxy matrix.

2.3. Validation

2.3.1. DMTA

DMTA analysis of the material was performed to verify the ability of the material to reduce its stiffness at temperatures above the glass transition temperature of the polymer coating. DMTA measurements were performed on a Rheometric Scientific DMTA 4 analyzer in single cantilever bending mode. The free distance between the clamp and the drive shaft was 14 mm. Rectangular samples with dimensions 30x10x1.5 mm were heated from room temperature to 155°C with a heating rate of 5°C/min. The tests were performed in strain controlled mode with a frequency of 1 Hz (according to ASTM-D7028-07) and with a maximum strain of 0.1%. The specimen were clamped to the frame with an initial clamp torque of 30cNm.

2.3.2. Testing with applied current

The stiffness-modifiable properties of the material were verified by 3-point bending tests with applied current. A special 3-point bending rig was developed in order to enable safe handling even if high current or potential is applied to the specimen. The load is thereby applied via a weight exhibiting no contact to other parts of the setup. As seen from the schematic image of the setup presented in Figure 2, an electrically isolating material (Teflon) is used for the ground plate. The whole rig can be placed inside a Faradayan cage for experiments where high current is handled.

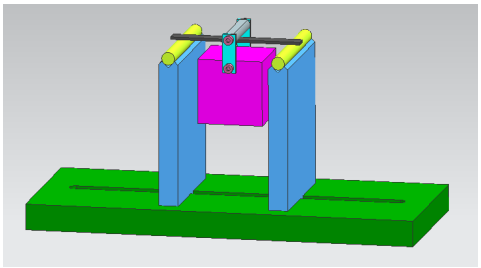

Figure 2. Schematic representation of the 3-point bending rig for tests with applied current.

Electrical current was applied to the specimen by a Oltronix B32-10R power supply with a maximum output of 10A/32V. In order to assure efficient current transfer to the carbon fibres in the specimen, the ends were polished with a rough polishing paper and silver paint was applied to the polished ends before covering them with aluminium foil. A laser beam was used to measure the displacement of the sample and the temperature of the specimen was measured by taping a thermoelement to the specimen's surface.

3. Results and Discussion

3.1 Material development

The experiments and results regarding coating efficiency and coating thickness are summarized in Table 2. For the evaluation of the polymer coating, optical microscopy proved to be a useful tool. The colourful appearance of the polymer in the optical microscope (see Figure 3) facilitated the evaluation of the coating regarding the uniformity of its distribution on the fibre surface.

	Experimental details				*Results*		
Constant Potential	**Exp.**	**[MMA]**	**Potential**	**Comments**	**Mass loss 160-350°C**	**Coating thickness***	**Microscopy (mark)**
	EP1	0.75 M	-1.5 V	static	0.6%	15nm	1
	EP2	1.5 M	-1.5 V	static	0.65%	17nm	1
	EP3	5.0 M	-1.5 V	static	0.8%	20nm	2
	EP4	10.0 M	-1.5 V	static	0.2%	5nm	1
Constant Current	**Exp.**	**[MMA]**	**Current density**	**Comments**	**Mass loss 160-350°C**	**Coating thickness***	**Microscopy (mark)**
	EC1_1	5.0 M	-0.2 mA/cm^2	static	1%	25nm	1
	EC1_2	5.0 M	-0.4 mA/cm^2	static	1.3%	33nm	2
	EC1_4	5.0 M	-0.8 mA/cm^2	static	2.5%	65nm	2
	EC1_5	5.0 M	-1.2 mA/cm^2	static	3.7%	96nm	3
	EC1_6	5.0 M	-2.4 mA/cm^{2**}	static	3.2%	83nm	3
	EC2	7.0 M	-1.2 mA/cm^{2**}	static	3.1%	80nm	2
	EC3	10.0 M	-0.8 mA/cm^{2**}	static	0.5%	13nm	1
	EC4	5.0 M	-1.2 mA/cm^2	dynamic	1.7%	43nm	3

Table 2. Experimental details and results for electrocoating experiments.

*As calculated from the mass loss measured by TGA
** The potential limit of the potentiostat used for the application of current was reached. The current was therefore reduced automatically to a value corresponding to maximum possible potential.

As seen from experiments EP1 – EP4 (Table 2), no complete coverage of carbon fibres with the polymer coating could be obtained for electropolymerization at constant potential (see Figure 3, left image). Increasing the monomer concentration did not improve the coating efficiency significantly.

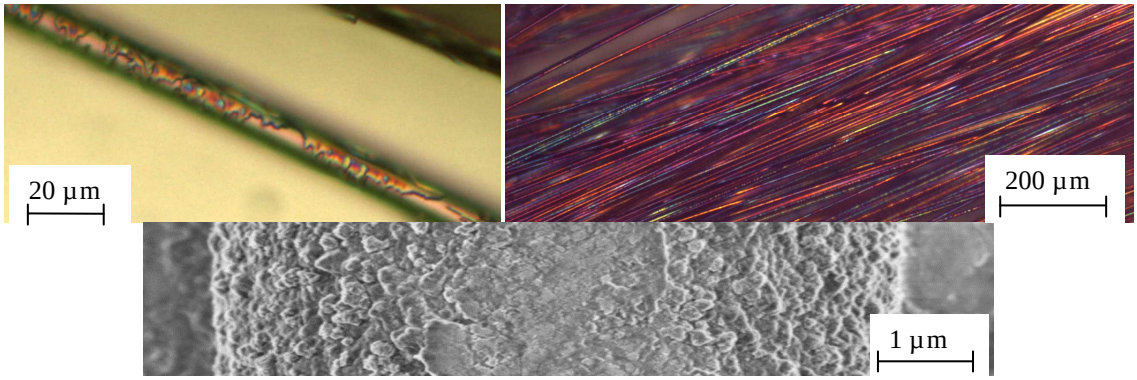

Figure 3. Left image: Optical microscope image of EP3: best coating achievable at constant potential. **Right image:** typical optical microscope image of carbon fibres continuously coated with PMMA (EC4). **Lower image:** typical SEM image of coated carbon fibres (here: EC1_5).

Unfortunately, no simulation tools are available to identify the required polymer coverage of carbon fibres for efficient adhesion to the matrix. However, in order to achieve a high effect of stiffness-reduction, complete coverage of the carbon fibres was aimed in the present work.

Comparing experiments EP and EC presented in Table 2, it is seen that the coating efficiency can be increased by using controlled current electrocoating (as compared to controlled potential electrocoating). It has been explained above that higher current density may be able to accelerate the reaction. This technique has proven to be successful and a perfect coating of

single carbon fibres with about 80 to 100 nm thickness can be obtained even if the coating process is performed on a carbon fibre bundle of 12,000 fibres.
It is seen from the TGA and microscopy results presented in Table 2 that the coating efficiency increases with increasing current density up to -1.2 mA/cm^2 and cannot be further improved if the current density is increased above this value.
Monomer concentrations above 5 M have been found to result in less efficient coating. This finding is assigned to a higher electrical resistance of the electrolyte for such cases, which limits the current density achievable in the system. This is because the potentiostat used for the application of current had a limited potential output, which means that the limit for the potential was reached already for moderate current densities in such system. Hence, the current was automatically reduced by the device to values where the corresponding potential does not exceed the maximum output.
Hence, the most promising experiment was EC1_5. This experiment was therefore performed in a continuous way, thus pulling the fibres through the electrocoating system at a speed of 3 mm/s. As seen from Figure 3 (right image), such experiment (EC4) resulted in a bundle of carbon fibres where every fibre was completely covered with a PMMA layer. SEM measurements revealed a continuous coating of carbon fibres with a cauliflower-like appearance (see Figure 3 – lower image). This observation is in concordance with coating morphologies observed in literature for electrocoating at constant potential [8].

3.3 Validation

3.3.1. Modelling of the stiffness reduction and validation by DMTA

The CCA-model has been used to calculate the possible influence of coating thickness on the stiffness change of UD composites with increased temperature. Predictions were based on the assumed properties of carbon fibre, see Table 3, and softening behaviour of LY556 and PMMA, see Figure 4 (left). Results are shown in Figure 4 (right) for the transverse modulus assuming a fibre volume fraction of 60% for the uncoated fibre composite and 45% for the coated fibre composite. Due to the different fibre content the results are compared in terms of normalized modulus.

Property	*Carbon fibre*	*PMMA coating*	*LY556 matrix*
E_1 (GPa)	233	2.9	3.2
E_2 (GPa)	23	2.9	3.2
G_{12} (GPa)	20	1.0	1.2
ν_{12}	0.2	0.4	0.34
ν_{23}	0.2	0.4	0.34

Table 3. Fibre and matrix properties (at RT) in the micromechanical study.

It is clear from these results that the apparent glass transition temperature (T_g) of the composite can be decreased efficiently by a thin thermoplastic interphase and that this influence of the interphase obviously depends on its thickness. It is, however, also noticed that even a very thin thermoplastic film of 50 nm allows significant reduction of the T_g. These results are promising with regard to the rather thin coatings that have been obtained from our electrocoating experiments, as described above.

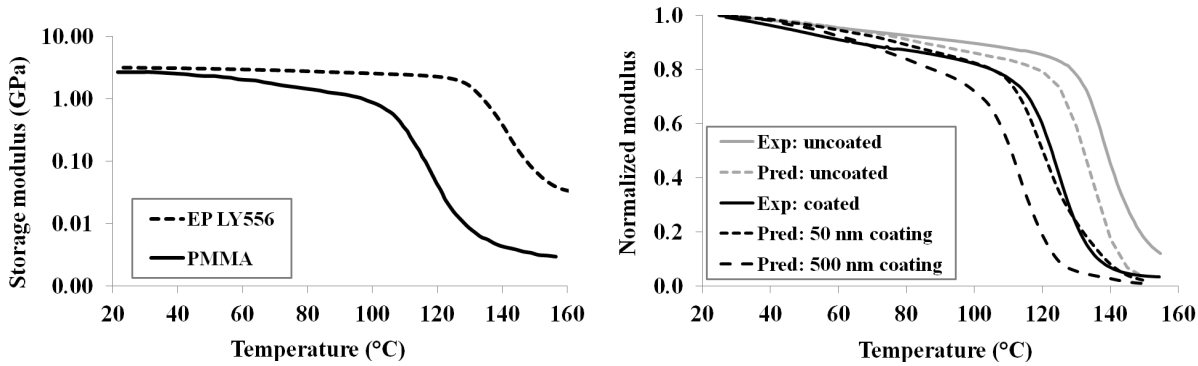

Figure 4. Left image: Measured storage modulus for neat epoxy LY556 and assumed curve for PMMA, recreated from [9]. **Right image:** Normalized transverse storage modulus for coated/uncoated fibre composite and predictions using the CCA-model.

The experimental results obtained from DMTA are presented as unbroken curves in Figure 4 (grey: uncoated fibres, black: fibres exhibiting a 43 nm thermoplastic film). It can be seen that experimental results are in reasonable agreement with the micromechanical predictions. Furthermore, it is obvious from these results that the apparent T_g could be reduced successfully by introducing a thermoplastic interphase.

3.3.2. Testing with applied current

In Figure 5 the displacement measured at different temperatures during 3-point-bending tests with applied current is presented for a composite reinforced with coated fibres and a reference material reinforced with uncoated fibres. It is obvious that the thermoplastic coating has a significant effect on the displacement that is observed at elevated temperatures. The corresponding reduction in bending stiffness was calculated to be 71% for the composite reinforced with coated fibres and 33% for the reference sample respectively.
Hence, it was proven that stiffness-reduction of such composite can be achieved by application of current through the composite.

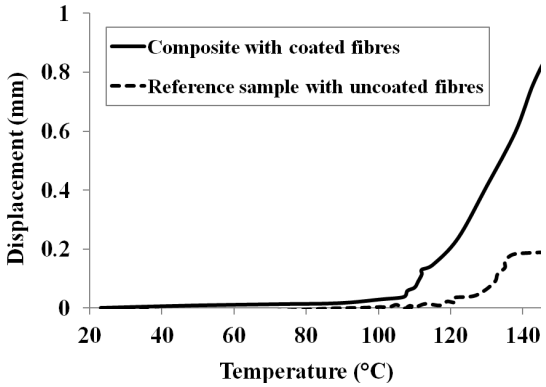

Figure 5. Typical results obtained for the displacement in relation to the temperature from 3-point bending tests with applied current.

4. Conclusions

Optimization of the electrocoating process focused on (i) avoiding the highly carcinogenic Acrylamide, (ii) investigations on electrocoating at constant potential (alternatively lower

current densities), which would provide increased control over the system and (iii) optimization of the process considering industrial implementation.
Investigations on performing electrocoating at constant potential (in contrast to constant current electrocoating as performed by Bismarck and his group [4,6]) in order to increase the control over the process were of limited success. The coating efficiency was found to increase slightly with increasing monomer concentration (up to 5 M), but coverage of the entire fibre surface could not be achieved.
By using electropolymerization at constant current, however, successful coating with PMMA could be achieved and implemented in a continuous process. The process is scalable for industrial implementation. The coating efficiency could be optimized with the support of material simulation and the required current density could be reduced by 50% (1.2 mA/cm^2 as compared to 2.4 mA/cm^2 as used by Tridech [4]) without reducing coating efficiency. The process thus provides increased control and requires less energy compared to previously reported electrocoating processes at ambient conditions [4,6].
A composite material reinforced with the thus achieved coated carbon fibres was obtained by filament winding and infusion with epoxy. The resulting material could be shown to reduce its stiffness at elevated temperatures and upon application of current.

5. Acknowledgements

The authors like to express their gratitude to Mr. Runar Långström and Dr. Tony Carlson for assistance with the manufacture and test. The presented work was funded by the European Commission within the project ENLIGHT (Grant agreement No: 314567).

References

[1] Traffic Safety Basic Facts 2012 – Pedestrians. http://ec.europa.eu/transport/road_safety/pdf/statistics/dacota/bfs2012_dacota-intras-pedestrians.pdf.
[2] European Injury Dabase (IDB) report 2013, page 19. http://ec.europa.eu/health/data_collection/docs/idb_report_2013_en.pdf.
[3] J. Yao, J. Yang, D. Otte. Head Injuries in Child Pedestrian Accidents—In-Depth Case Analysis and Reconstructions. *Traffic Injury Prevention* 8:94-100, 2007.
[4] C. Tridech, H.A. Maples, P. Robinson, A. Bismarck. High Performance Composites with Active Stiffness Control. *Applied Materials & Interfaces* 5:9111-9119, 2013.
[5] S. Palacin, C. Bureau, J. Charlier, G. Deniau, B. Mouanda, P. Viel. Molecule-to-Metal Bonds: Electrografting Polymers on Conducting Surfaces. *ChemPhysChem* 5:1468-1481, 2004.
[6] A. Bismarck, A.F. Lee, A.S. Sarac, E. Schulz, K. Wilson. Electrocoating of carbon fibres: A route for interface control in carbon fibre reinforced poly methylmethacrylate? *Composites Science and Technology* 65:1564–1573, 2005.
[7] E. Marklund, J. Varna, R.C. Neagu, E.K. Gamstedt. Stiffness of Aligned Wood Fiber Composites: Effect of Microstructure and Phase Properties. *Journal of Composite Materials*, 42(22):2377-2405, 2008.
[8] M. Mertens, C. Calberg, L. Martinot, R. Jerome. The Electroreduction of Acrylonitrile: A New Insight into the Mechanism. *Macromolecules 29:*4910-4918, 1996.
[9] Meneghetti P, Qutubuddin S. Synthesis, thermal properties and applications of polymer-clay nanocomposites. *Thermochimica Acta* 442:74–77, 2006.