PAPER • OPEN ACCESS

Influence of microwave plasma treatment on the surface properties of carbon fibers and their adhesion in a polypropylene matrix

To cite this article: C Scheffler *et al* 2016 *IOP Conf. Ser.: Mater. Sci. Eng.* **139** 012046

View the article online for updates and enhancements.

Influence of microwave plasma treatment on the surface properties of carbon fibers and their adhesion in a polypropylene matrix

C Scheffler,[1,3] E Wölfel[1], T Förster [1], C Poitzsch[1], L Kotte[2] and G Mäder[2]

[1]Leibniz Institut für Polymerforschung e.V. (IPF), Department Composite Materials, Hohe Straße 6, 01069 Dresden, Germany
[2]Fraunhofer Institut für Werkstoff- und Strahltechnik (IWS), Department Chemical Surface and Reaction Technology, Winterbergstraße 28, 01277 Dresden, Germany

[3]Corresponding author: scheffler@ipfdd.de

Abstract. A commercially available carbon fiber (CF) with an epoxy-based sizing (EP-sized CF) and an unsized CF have been plasma treated to study the effect on the fiber-matrix adhesion towards a polypropylene matrix. The EP-sized fiber was chosen because of its predictable low adhesion in a polypropylene (PP) matrix. The fibers have been modified using a microwave low-pressure $O_2/CO_2/N_2$-gas plasma source (Cyrannus®) developed at IWS in a batch process. One aim of this study was the evaluation of parameters using high energies and short time periods in the plasma chamber to see the effect on mechanical performance of CF. These results will be the fundamental work for a planned continuous plasma modification line. The CF surface was characterized by determining the surface energies, single fiber tensile strength and XPS analysis. The adhesion behavior before and after plasma treatment was studied by single fiber pull-out test (SFPO) and scanning electron microscopy (SEM). It was shown that the CO_2- and O_2-plasma increases the number of functional groups on the fiber surface during short time plasma treatment of 30 s. Carboxylic groups on the unsized CF surface resulting from O_2-plasma treatment lead to an enhanced fiber-matrix adhesion, whereas the fiber strength was merely reduced.

1. Introduction

The excellent properties of carbon fibers (CF), such as high specific strength and stiffness, performance to weight ratio, high thermal and chemical resistance and also conductivity, make them applicable in various fields of mechanical engineering, automotive and air transport industries [1][2][3]. However, the poor interfacial adhesion between reinforcing CF surface and the polymer matrix limits the crucial properties of the composites toughness as well as longitudinal and transverse strength. To solve these critical issue researchers followed different ways that are summarized by Sharma et al. [4] to two main approaches: "wet" and "dry" surface modification methods. The wet chemical approaches include: (i) the application of polymer finish to CF surface (sizing), (ii) acidic medication, (iii) electrochemical modification and (iv) electro-polymer coating. Surface modification of CF by dry methods are (i) high energy irradiation modification, (ii) nickel surface coating, (iii) thermal modifications, (iv) miscellaneous dry treatments and (v) surface modification in "multi-scales" by nano particle modification and nanotube coating using for example chemical vapour deposition or electrophoretic deposition. Plasma surface modification, also a dry method, changes the

fiber surface layer physicochemically by introducing functional groups without affecting the layers underneath. For plasma modification inert (Ar, N_2) [13]-[17] and reactive gases (O_2, CO_2, air, CF_4) [18]-[23] or mixtures of both are applied. Summarizing the literature, it can be concluded that all gases and process parameters during plasma treatment lead to more or less improved wetting behavior. The damage of the filament surface is more severe by application of reactive compared to inert gases and increases with treatment time, especially in the case of O_2. Also a higher surface roughness arises under all conditions. Based on XPS measurements it is stated [18][19][22], that using O_2-plasma, as pure gas as well as in a gas mixture, increases the [O]:[C]-ratio significantly. Mainly OH^--groups are generated, which lead to higher polarity and surface energy. In the most studies very long treatment times up to 30 min combined with low energies were chosen for the modification. In this work, the focus was set on low treatment times of 30 s, since short treatment times are a precondition for potential continuous modification processes. However, in this study the surface tension was determined over a time period up to 180 s to gain basic process knowledge. A maleic anhydride grafted PP was used as a matrix to investigate changes of the adhesion behavior.

2. Experimental

2.1. Materials

A commercially available PAN-based CF roving (50 k) with an epoxy-(EP)-based sizing (sizing content 1 wt.-% according to manufacture specification) and an unsized (electrochemically activated) PAN-based CF roving (50 k) were selected for the treatment by microwave plasma. The filament diameter was 7.2 ± 0.3 µm for EP-sized CF and 6.9 ± 0.4 µm for unsized CF, respectively. The EP-sized fiber was chosen because of its predictable low adhesion in a polypropylene matrix since EP-sizing is applicable in epoxy-based matrix systems. The EP-sized fiber serves as control fiber since it is expected that the EP-sizing will be removed during plasma treatment and this effect will be clearly seen during all testing methods.

As a matrix system for single fiber pull-out test (SFPO) an isotactic polypropylene (PP, HG455FB, Borealis) was used being modified by 2 wt.-% of maleic anhydride grafted PP. Before using the PP for manufacturing the single fiber model composites the PP was dried for four hours in the vacuum oven at 80°C to avoid any effect of moisture, although the moisture uptake of PP is known to be small.

2.2 Methods

2.2.1. Plasma modification. For surface modification of CF the microwave plasma equipment (developed at Fraunhofer IWS Dresden) was used, which works discontinuously in a batch process. The plasma chamber is a cylindrical 6 inch Cyrannus® plasma source and single 10 cm pieces of a 50K filament yarn have been introduced for each plasma treatment. The following parameters were used during treatment of CF: purging the chamber with argon for 5 min, pressure 5-210 mbar, O_2- and CO_2-plasma gas with 1000-5000 sccm.

2.2.2. X-ray photoelectron spectroscopy (XPS). X-ray photoelectron spectroscopy (XPS) studies were carried out by means of an Axis Ultra photoelectron spectrometer (Kratos Analytical, Manchester, UK) equipped with a monochromatic Al Kα (hν = 1486.6 eV) X-ray source of 300 W at 20 mA. The kinetic energy of the photoelectrons was determined with a hemispheric analyzer set to pass energy of 160 eV for wide scan spectra and 20 eV for high-resolution spectra, respectively. Quantitative elemental compositions were determined from peak areas using experimentally determined sensitivity factors and the spectrometer transmission function.

2.2.3. Single fiber tensile test. The tensile tests on the carbon filaments before and after plasma treatment were carried out on the testing machine FAVIGRAPH ME (Textechno, Germany) with a 20 cN force cell. The testing velocity was 25 mm/min at a gauge length of 50 mm. The fineness of each single filament was measured using a vibroscopical testing method according to ASTM D 1577. The filament strength and strain were measured in compliance with DIN ISO 5079. The distribution of failure stresses for each treatment condition is based on 50 measurements. The failure stresses were evaluated by Weibull distribution function as described in [12]. The scale parameter σ_o represents the stress at which 63.2 % of the filaments break $(P(\sigma_o) = 0{,}6321)$. The shape parameter m (also Weibull modulus) describes the distribution of the failure stress. A higher value of m indicates that the filaments fail in a narrower range of failure stresses. Weibull parameter are determined by plotting $\ln(-\ln(1-P))$ against $\ln(\sigma)$. Thereby, m is equal to slope of generated curve and σ_0 equates to the interception with $\ln(-\ln(1-P)) = 0$.

2.2.4. Wetting behavior. The surface energy measurement was made using a Krüss K14 tensiometer (Krüss GmbH, Germany) in water, ethylene glycol and n-hexane. One end of a single fiber was attached to the hook of an electro micro-balance (sensitivity $\pm$ 0.1 µg). The free end of the fiber was immersed into the liquid (final depth of immersion 2 mm, rate 6 mm/min, mean of 20 measurements) [5]. From the test, the force versus position loop was recorded and the force was converted to the contact angle (θ) using the Wilhelmy equation. The surface tension (γ_F) and its two components (non-polar or dispersive part, γ^d and the polar part, γ^p) of the fiber were then calculated to evaluate the wetting behavior of the fiber surfaces.

2.2.5. Single fiber pull out. The interfacial adhesion strength was evaluated by single fiber pull out test [6][7]. Using an embedding equipment designed and constructed at the Leibniz Institute, the model micro-composites were prepared by accurately embedding one end of the single fiber in the matrix perpendicularly with a pre-selected embedding length l_e ($l_e = 300$ µm) and an embedding temperature of 210 °C at controlled atmosphere and temperature. The pull out test was carried out on a self-made pull-out apparatus with force accuracy of 1 mN, displacement accuracy of 0.07 µm and a loading rate of 0.01 µm/s at ambient conditions.

The force- displacement curves were detected and the maximum force, F_{max}, required for pulling the fiber out of the matrix was measured. After testing, the fiber diameter, d_f was measured by optical microscopy. The adhesion bond strength between the fiber and the matrix was characterized by the values of the apparent interfacial shear strength $(\tau_{app} = F_{max}/2\pi*d_f*l_e.)$. Each fiber/matrix combination was evaluated in about 15-20 single tests.

3. Results

3.1. Surface energy

The surface energies of CF depending on the time of plasma treatment are summarized in Fig. 1. Comparing the results of O_2- and CO_2-plasma treatment shows that the O_2-plasma leads to a decreased polar fraction for EP-sized CF after 30 s. Additional testing by FTIR (not included in this paper) proved that this was due to the removal of the sizing. By further plasma treatment the surface tension and polar fraction increases again leading to a value of γ_F=28.4 mN/m after 60 s in O_2-plasma. In contrast, the highest polar fraction during this investigation was found for CO_2-plasma treated unsized CF after 60 s.
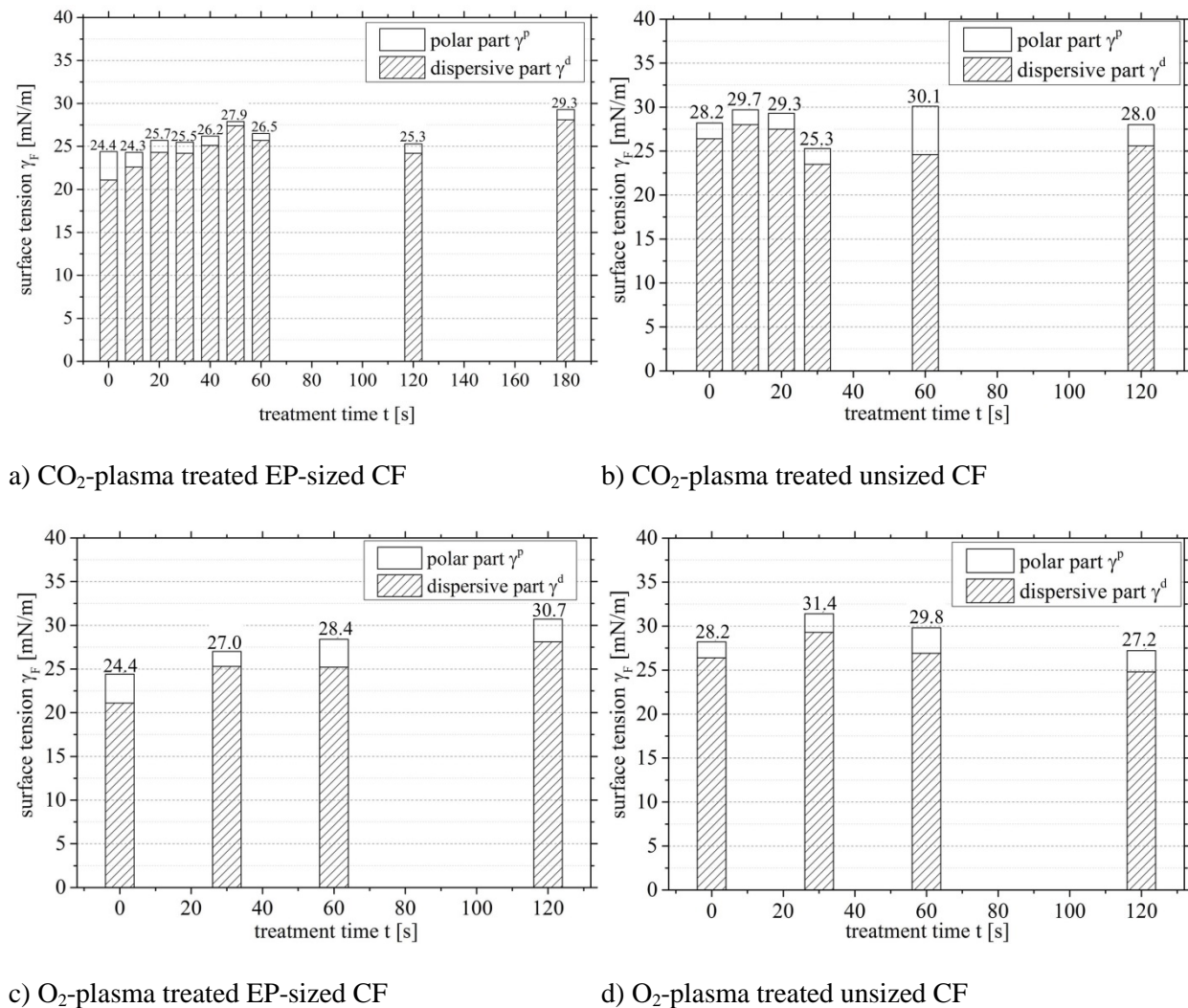
a) CO_2-plasma treated EP-sized CF

b) CO_2-plasma treated unsized CF

c) O_2-plasma treated EP-sized CF

d) O_2-plasma treated unsized CF

Fig. 1. Surface tension of CO_2-plasma treated a) EP-sized CF, b) unsized CF and O_2-plasma treated c) EP-sized CF, d) unsized CF vs. treatment time.

3.2. XPS

In the literature the carboxylic groups –COOH and –C=O have been discussed for the improvement of fiber-matrix adhesion as well as hydroxyl groups –C-OH for increasing the polarity of the fiber surface [8]. To avoid additional effects by sizing only unsized CF were analyzed by XPS after a plasma treatment time of 30 s. During the plasma treatment the [O]:[C]-ratio was increased by CO_2-plasma from 0.061 to 0.281, but also O_2-plasma treatment lead to a slightly increased [O]:[C]-ratio from 0.061 to 0.096.
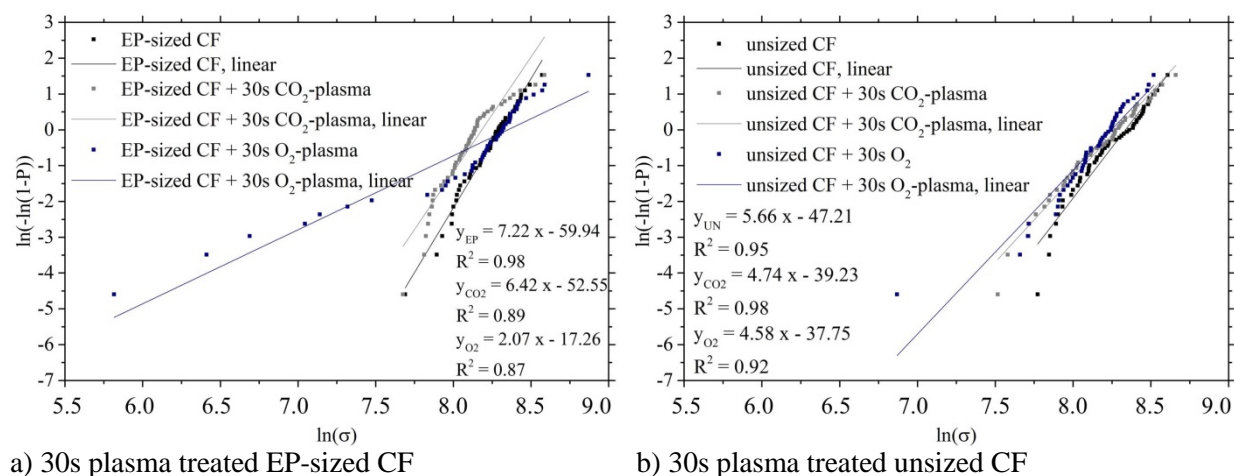
By deconvolution of C1s peaks the bonding characteristics and oxidation state, respectively, can be concluded by resolving in component peaks and their functionalities [11], see Table 1. Compared to the initial state of unsized CF, a slightly increased number of OH-groups after CO_2-plasma treatment and of HO-C=O-/ O-C=O-groups after O_2-plasma treatment was detected.

Table 1. XPS bonding characteristics of unsized CF compared to plasma-treated CF.

Peak	Unsized CF	CO_2, 30 s	O_2, 30 s
	Component [at.-%]		
Unsaturated –C=C- or =C-C= bondings	66.78	63.19	64.66
Saturated hydrocarbons C_xH_z	7.28	8.60	7.08
C-N-bondings of amines, C=N-bondings of imines, C≡N-bondings of nitrils	3.41	2.28	2.59
C-O-bondings of alcoholic and phenolic groups C-OH-groups	2.61	3.87	2.56
Carbonyl carbon atoms (C=O) of ketons or quinones	1.79	1.47	1.57
Carbonyl carbon atoms of carbonic acid groups (HO-C=O) or their carboxylates (⁻O-C=O)	0.07	0.37	0.82

3.3. Filament tensile strength

The tensile failure stresses for CF in the unsized and sized state are subjected to high scatter. The heterogeneity of CF seems to be based on a not homogeneous degree of graphitization of the single fibers [10]. Additionally, the distribution homogeneity of sizings contributes to the extent of scatter for failure stresses. The Weibull distribution function was used to derive the probability of failure. As shown in Fig. 2 and Table 2 the Weibull-modulus of EP-sized CF is decreased during 30 s plasma treatment with CO_2- and O_2-plasma. As already arises from the determination of the surface energies, the sizing is removed during the plasma treatment. This leads to reduced values of the Weibull-modulus, changing from m = 7.22 to m = 2.07 for O_2-plasma treatment. If EP-sized CF is exposed to longer treatment times of 120 s the failure stress is significantly reduced. Compared to the EP-sized CF no reduced failure stresses due to plasma treatment could be detected for unsized CF, nor for 30 s and neither after 120 s of treatment. It seems that the removal of sizing during plasma treatment is accompanied by effects that lead to severe damage of the CF surface, which do not occur on the unsized carbon surface.
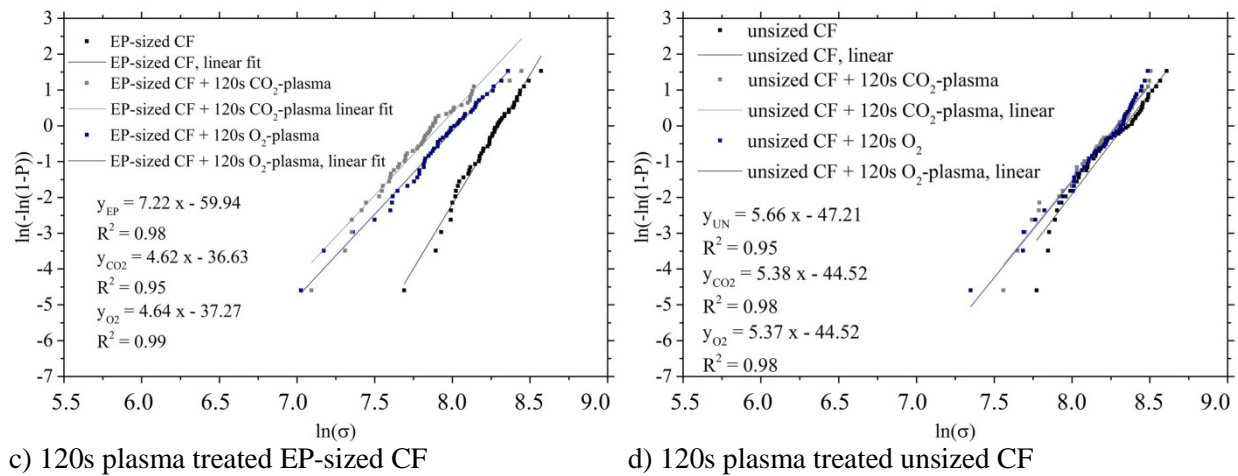

a) 30s plasma treated EP-sized CF   b) 30s plasma treated unsized CF

c) 120s plasma treated EP-sized CF   d) 120s plasma treated unsized CF

Fig. 2. Weibull plot of the 30 s plasma treated a) EP-sized CF, b) unsized CF and 120 s plasma treated c) EP-sized CF, d) unsized CF.

Table 2. Weibull modulus and characteristic strength of untreated and plasma treated CF.

	scale parameter σ_0 [MPa]	Weibull modulus m	scale parameter σ_0 [MPa]	Weibull modulus m
EP-sized CF	4033	7.22	4033	7.22
unsized CF	4175	5.66	4175	5.66
treatment	**30s**		**120s**	
EP-sized CF + CO_2-plasma	3582	6.42	2753	4.62
EP-sized CF + O_2-plasma	4234	2.07	3079	4.64
unsized CF + CO_2-plasma	3948	4.74	3949	5.38
unsized CF + O_2-plasma	3814	4.58	3982	5.37

3.4. Fiber-matrix adhesion

The SFPO is a very sensitive method related to changes due to fiber surface modification. For the EP-sized CF the results of SFPO (Table 3) mirror the results that have been received by testing the wetting behavior and the filament tensile strength. It was shown that the EP-sizing is removed during plasma-modification. Since the EP-sizing is not appropriate for fiber-matrix interaction because of its chemical and physical properties, the lowest adhesion strength is measured for EP-sized CF. The removal of the sizing exposes the unsized carbon surface that enables an improved interaction with the MAH-g-PP matrix due to the functional groups on the surface as was determined by XPS. However, also the shear strength of the unsized CF is on the level of EP-sized CF after removing of the sizing. After treatment in CO_2- and O_2-plasma over 30 s no increase of the shear strength was detected, though a longer treatment time of 60s leads to enhanced pull-out force and the highest shear strength in this work. Based on the XPS data after 30 s plasma treatment time it can be assumed that after 60 s the amount of HO-C=O-/⁻O-C=O-groups might have increased and therefore causes improved fiber-matrix interaction.

Table 3. Apparent shear strength and pull-out work for EP-sized and unsized CF embedded in PP matrix before and after plasma treatment.

sample	treatment	t_{app} [MPa]	SD [MPa]
EP-sized CF	none	19.6	9.5
	CO_2, 30 s	25.4	9.7
	O_2, 30 s	27.8	5.6
unsized CF	none	26.5	5.4
	CO_2, 30 s	22.2	4.7
	O_2, 30 s	27.5	9.3
	O_2, 60 s	30.5	5.5

4. Conclusion

Based on this data it can be concluded that primarily the O_2-plasma modification of CF surfaces reveals potential for the application of functional groups on the carbon surface and therefore an improved fiber-matrix adhesion. However, a crucial change of the carbon fiber surface properties due to the carefully chosen parameters for plasma treatment used in this study is not achieved yet. The nearly constant mechanical properties of the unsized CF imply the possibility of using wider limits for process parameters that come closer to the requirements for a continuously plasma modification concept (short treatment times at high energies).

References

[1]   Soutis C 2005 Fiber reinforced composites in aircraft construction *Prog Aerospace Sci* **41** 143–51
[2]   Paiva J M F, Santos A D N and Rezende M C 2009 Mechanical and morphological characterizations of carbon fiber fabric reinforced epoxy composites used in aeronautical field *Mater Res*, **12 (3)** 367–74
[3]   Edie D D and McHugh J J 1999 High performance carbon fibers *Carbon materials for advanced technologies* ed T D Burchell (Pergamon) chapter 4 119–38.
[4]   Sharma M, Gao S L, Mäder E, Sharma H, Wei L Y and Bijwe J 2014 Carbon fiber surfaces and composite interphases *Compos Sci* **102** 35-50
[5]   Kamath Y K, Dansizer C J and Weigmann H D 1984 Surface wettability of human hair. I. effect of deposition of polymers and surfactants *J Appl Polym Sci* **29** 1011-26
[6]   Mäder E, Grundke K, Jacobasch H J and Wachinger G 1994 Surface, interphase and composite property relations in fibre-reinforced polymers *Compos* **25 (7)** 739-44
[7]   Fu S Y, Lauke B, Mäder E, Yue C Y and Hu X 2000 Tensile properties of short-glass-fiber-and short-carbon-fiber-reinforced polypropylene composites *Composites Part A* **31 (10)** 1117-25
[8]   Dilsiz N and Wightman J P 2000 Effect of acid-base properties of unsized and sized carbon fibers on fiber/epoxy matrix adhesion *Colloids and Surf* A **164** (2000) 325-36
[9]   Tiwari S, Sharma M, Panier S, Mutel B, Mitschang P and Bijwe J 2011 Influence of cold remote oxygen plasma treatment on carbon fabric and its composites with specialty polymers *J Mater Sci* **46** 964-74
[10] Huson M.G, Church J S, Kafi A A, Woodhead A L, Khoo J, Kiran M S R N and Fox B L 2014 Heterogenity of carbon fibre *Carbon* **68** 240-49
[11] Moulder J F, Stickle W F, Sobol P E and Bomben K D 1992 *Handbook of X-ray photoelectron spectroscopy* ed Chastain J (Perkin-Elmer Corporation) Physical Electronics Division
[12] Scheffler C, Förster T, Mäder E, Heinrich G, Hempel S and Mechtcherine V 2009 Aging of alkali-resistant glass and basalt fibers in alkaline solutions: Evaluation of the failure stress by Weibull distribution function *J Non-Cryst Solids* **355 (52)** 2588-95

[13]   Bogoeva-Gaceva G, Mäder E, Häussler L and Dekanski A 1997 Characterization of the surface and interphase of plasma-treated HM carbon fibres *Compos Part A* **28 (5)** 445-52

[14]   Tiwari S, Sharma M, Panier S, Mutel B, Mitschang P and Bijwe J 2011 Influence of cold remote nitrogen oxygen plasma treatment on carbon fabric and its composites with specialty polymers *J Mater Sci* **46 (4)** 964-74

[15]   Han S H, Oh H J and Kim S S 2014 Evaluation of fiber surface treatment on the interfacial behavior of carbon fiber-reinforced polypropylene composites *Compos Part B* **60** 98-105

[16]   Farrow G J and Jones C 1994 The effect of low power nitrogen plasma treatment of carbon fibres on the interfacial shear strength of carbon fibre/epoxy composites *J Adhes* **45 (1-4)** 29-42

[17]   Yuan L Y, Shyu S S and Lai J Y 1991 Plasma surface treatments on carbon fibers. II. Mechanical property and interfacial shear strength *J Appl Polym Sci* **42 (9)** 2525-34

[18]   Park S J, Chang Y H, Moon C W, Suh D H, Im S S and Kim Y C 2010 A study of atmospheric plasma treatment on surface energetics of carbon fibers *Bull Korean Chem Soc* **31 (2)** 335-38

[19]   Li J 2009 The research on the interfacial compatibility of polypropylene composite filled with surface treated carbon fiber *Appl Surf Sci* **255 (20)** 8682-84

[20]   Bismarck A, Kumru M E and Springer J 1999 Influence of oxygen plasma treatment of PAN-based carbon fibers on their electrokinetic and wetting properties *J Colloid Interface Sci* **210 (1)** 60-72

[21]   Allred R E and Schimpf W C 1994 CO_2 plasma modification of high-modulus carbon fibers and their adhesion to epoxy resins *J Adhes Sci Technol* **8 (4)** 383-94

[22]   Jang J and Yang H 2000 The effect of surface treatment on the performance improvement of carbon fiber/polybenzoxazine composites *J Mater Sci* **35 (9)** 2297-2303

[23]   Tsutsumi K, Ban K, Shibata K, Okazaki S and Kogoma M 1996 Wettability and adhesion characteristics of plasma-treated carbon fibers *J Adhes* **57 (1-4)** 45-53

[24]   Ho K K, Lamoriniere S, Kalinka G, Schulz E and Bismarck A 2007 Interfacial behavior between atmospheric-plasma-fluorinated carbon fibers and poly (vinylidene fluoride) *J Colloid Interface Sci* **313(2)** 476-484

[25]   Xie J, Xin D, Cao H, Wang C, Zhao Y, Yao L and Qiu Y 2011 Improving carbon fiber adhesion to polyimide with atmospheric pressure plasma treatment *Surf Coat Technol* **206 (2)** 191-201

[26]   Erden S, Ho K K, Lamoriniere S, Lee A F, Yildiz H and Bismarck A 2010 Continuous atmospheric plasma oxidation of carbon fibres: influence on the fibre surface and bulk properties and adhesion to polyamide 12 *Plasma Chem Plasma Process* **30 (4)** 471-87