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Carbon 42 (2004) 5–9
CARBON
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Production and characterisation of vapour grown carbon fiber/polypropylene composites

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Received 19 July 2003; accepted 15 September 2003

Abstract

Polymeric composites are widely used in the aircraft and automotive industries. Their high strength-to-weight ratio makes significant weight reduction possible. Beside this advantage, the polymer materials also offer a good corrosion resistance but the mechanical and electrical properties are not satisfactory. In order to increase these properties, vapour grown carbon fibers (VGCF) with high strength and metal-like electrical conductivity can be embedded in the polymeric matrix. To ensure a good adhesion between the fibers and the polymer matrix a functionalization of the chemically inert surface of the fibers is necessary.

In the present research work oxygen-containing functional groups were introduced on the fiber surface through cold plasma treatment. Measurements of the fiber surface energy after plasma functionalization showed an enhancement of at least 50% of the initial value. The VGCF/PP composites with different amounts of VGCF were made through extrusion and injection molding. The results show that the degree of fiber surface functionalization and the fiber distribution and orientation in the polypropylene (PP) matrix may strongly influence the mechanical properties of the composite.

Keywords: A. Carbon fibres; A. Carbon composites; B. Surface treatment

1. Introduction

Vapour grown carbon fibers are a relatively new type of carbon fiber which are produced from the pyrolysis of a hydrocarbon gas, such as benzene and methane, in the presence of hydrogen at temperatures around 950–1200 °C [1–6]. The fiber growth is initiated by ultra-fine transition metal catalyst particles, usually Fe, Co, Ni, deposited on a substrate (seeded catalyst method) or directly injected into the gas (floating catalyst method) [1]. Depending on the preparation conditions, VGCFs can be made with diameters between several tens of nanometers up to tens of microns and length from several microns up to many centimeters [4–6]. These fibers have been characterized in terms of the highly preferred orientation of their graphitic basal planes parallel to the fiber axis, with an annular ring texture in the cross section. This structure gives rise to excellent mechanical properties, very high electrical and thermal conductivity for a high graphitisation degree of the fibers [2,3]. Due to their physical properties and their potentially low cost of production this fibers are interesting for their possible applications, principally as reinforcement in composite materials [1,7]. Therefore, polymer matrix composites are the main application of carbon fibers.

For application of the VGCFs as reinforcement, fibers must possess a good functionalization of the outer surface (low contact angle and high surface energy). The modification of fibers surface can be made by gas treatments or liquid treatments [8]. Plasma treatment at room temperature and low pressure is an interesting and relatively new method between all gas treatments. Oxygen plasma represents an alternative to conventional oxidation treatments aimed at modifying the surface properties of carbon fibers and does not lead to substantial changes in fiber texture [9,10]. Measurements of the contact angle in different liquids, especially water,

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doi:10.1016/j.carbon.2003.09.012

indicated that plasma oxidation of activated carbon fibers increased its hydrophilicity, which suggests chemical addition of oxygen containing functional groups to the carbon fibers' outer graphite layers.

2. Experimental

In the present work the morphology of carbon fibers before and after the treatment by oxygen plasma as well as the composite interface between the reinforcement material (VGCNFs) and polymer matrix (PP) were characterized and the mechanical properties of the composites were measured.

Vapour grown carbon nano-fibers (VGCNFs) are *PYROGRAF III* from Applied Sciences, Inc. with diameters of 50–200 nm and length of 100–200 μm. The morphology of the VGCNFs was studied by SEM (scanning electron microscopy) XL 30 ESEM from Philips and TEM (transmitting electron microscopy) from Philips-CM 200. The graphitisation degree was measured using the X-ray diffractometer Philips X'pert. The fibers were treated in a plasma reactor from Plasma Finish model V 15-G, equipped with a HF-generator (high frequency generator) from Hüttinger model PFG 300 RF, working at a frequency of 13.56 MHz ± 0.05% and a power up to 300 W. The treatment time was between 3 and 50 min and the plasma power 50–180 W. The chamber pressure (100 Pa) and oxygen flow rate (100 ml/min) were kept constant during the plasma treatment. For each experiment, the same quantity of fibers (1 g) was introduced into the plasma chamber in which a rotary barrel was mounted in order to assure a homogeneous treatment of the material.

The nano-fibres were also functionalised in a self-constructed fluidized bed plasma reactor under radio frequency, 300 W power, 1.2 mbar pressure, Ar/O_2:35/35 scm^3/min. The time of exposure was up to few seconds.

The different degree of surface functionalization was measured by water contact angle measurements (gravimetric method) using an electronic balance DCAT 11 from DataPhysics Instruments. For all measurements the powder method (with the same bulk density) was used, where the liquid uptake was measured in time. For determination of the fibers surface energy (Wendt–Owens method), measurements of the contact angle in three different liquids of known surface tension (water, isopropanol and diiodmethane) were carried out. The increase of the fiber surface energy (especially the polar component), is a direct result of introducing polar functional groups onto fiber surface during the oxygen plasma treatment. The surface energy has two important components: the dispersive component (γ^d) and the polar component (γ^p). The latter is correlated with the amount of functional groups on the fibers surface [11]. The total amount of surface acidic functional groups, consisting of carboxylic, carbonylic and phenolic or hydroxylic groups, generated in oxygen plasma treatment were determined by NaOH-titration according to Boehm [12]. The nano-fibers were stirred for 48 h in 0.1 N NaOH under inert atmosphere and subsequently vacuum filtered. The obtained solution was back-titrated with HCl 0.1 N and using the value for the necessary titration volume, the total amount of oxygen acid containing functional groups was calculated.

A polypropylene powder (PP) from Sabic Polyolefine GmbH was used as matrix. Three types of composites were made: PP + 5% VGCNFs untreated and oxygen plasma treated in two different plasma reactors under different parameters. PP + VGCNFs were manually mixed before extrusion. Composites were manufactured in a co-rotating twin screw extrusion with a capacity of maximum 5 kg/h. After extrusion, the samples necessary for the measurement of the mechanical properties were manufactured by injection molding. The morphology of the obtained composites was characterized by SEM and the modification in the mechanical properties were determined by tensile test using an Instron testing machine.

3. Results and discussion

SEM micrographs of the untreated carbon nano-fibers studied in this work are presented in Fig. 1. This fibers are in the as-grown state, without any heat treatment which could be done in order to increase the graphitisation degree. It is well known that the VGCNFs have hollow cores and are in fact carbon nano-tubes. The nano-fibers are generally composed of concentric cylindrical graphene tubules, each with the structure of role-up sheet and have a smooth surface. This kind of morphology is very favorable when nano-fibers are applied as filler to improve electrical conductivity.

The wetting behavior of the plasma treated VGCNF is characterized by the values of the water contact angle

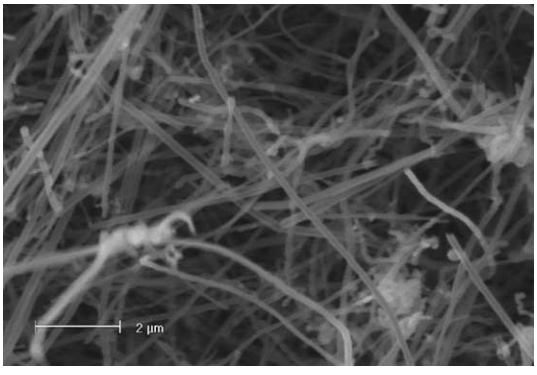

Fig. 1. SEM-micrograph of the VGCNFs-as grown.

Table 1
The water contact angles as a function of plasma parameters

Sample	Plasma treatment parameters	Contact angle (°)
1	Untreated	88 ± 0.1
2	100 ml/min O_2, 50 W, 50 min	64 ± 1.3
3	100 ml/min O_2, 80 W, 40 min	58 ± 1.8
4	100 ml/min O_2, 100 W, 20 min	65 ± 2.2
5	100 ml/min O_2, 120 W, 7.5 min	66 ± 2.5
6	100 ml/min O_2, 150 W, 6 min	66 ± 1.4
7	100 ml/min O_2, 180 W, 3 min	60 ± 1.8

of the fibers. After submission of the VGCNFs to a plasma treatment the carbon nano-fibers surface will became highly hydrophilic. Table 1 reports the contact angles in water on carbon nano-tubes after cold oxygen plasma treatment, as a function of the plasma parameters. The individual values of the water contact angle presented in Table 1 are the lowest values selected from a set of measurements made for plasma treated fibres at the same plasma power and for different treatment times. For example, a good functionalization (a lower contact angle) of the fibres treated at 50 W was achieved only for 50 min treatment time. A shorter period will lead to a lower or no fibre functionalisation. The value of the water contact angle decreased already after few minutes of plasma treatment. The main factors of plasma treatment are plasma power and treatment time. Depending on the adjustment of parameters, the depth of plasma etching effect could be well controlled. It is very important to correlate the treatment time with plasma power in order to functionalize the carbon fibers surface without any destruction of the bulk material (Fig. 2a compared with Fig. 2b). The outer surface of the fiber is slightly etched after 20 min plasma treatment (see arrows, Fig. 2a), and by increasing the plasma treatment time up to 40 min (under constant plasma power—100 W) it can be seen that the fibre outer surface was partially burned off (see arrows, Fig. 2b).

Similar degrees of functionalization of the nano-fibers can be reached at a chamber pressure of 100 Pa under different plasma parameters (samples 2, 3 and 4). Depending of the plasma power and treatment time, it can be observed that for the same value of the surface energy (Fig. 3) the ratio between the polar and the dispersive component has been modified. In order to obtain a higher value for the polar component of the surface energy, a lower plasma power and a longer treatment time is indicated (samples 2, 3 and 4). For the production of polymer composites, a larger quantity of plasma treated carbon nano-fibers is necessary. Therefore, in order to avoid an expensive functionalization process a reduction of treatment time has been made. By increasing the plasma power, the suitable treatment time will be shorter but the value for the polar component (the functionalization degree) will slowly decrease (samples 5, 6 and 7).

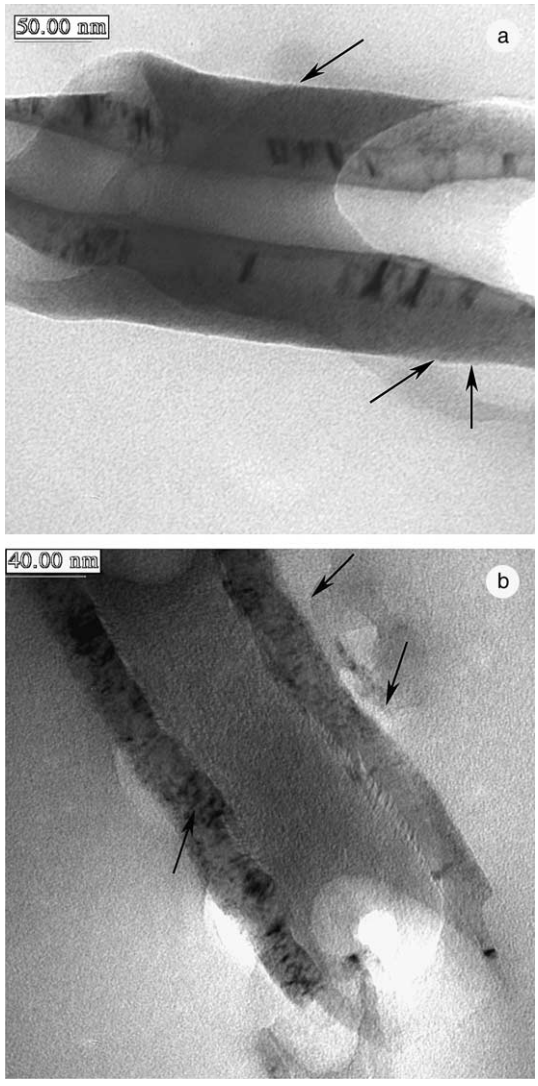

Fig. 2. TEM-images of the plasma treated nano-fibers for 20 min (a) and 40 min (b), at 100 W plasma power.

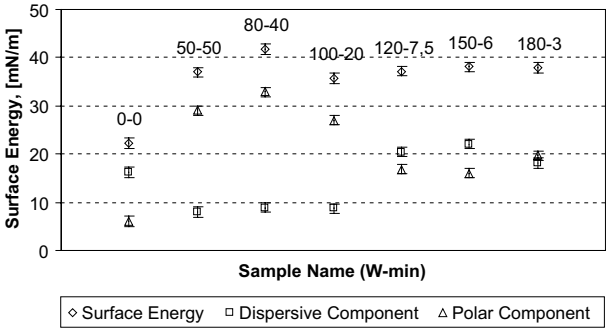

Fig. 3. Dependence of the surface energy components on the plasma parameters.

There is known that the polar component of the surface energy characterize the degree of functionalization of the fiber surface. A lower value of the polar component means a reduced number of oxygen

Table 2
Total amount of the NaOH-titrated acidic groups

Sample	mmol/g
1	0.2
2	1.1
3	1.8
4	0.9
5	0.5
6	0.4
7	0.5

containing functional groups created on the nano-tubes outer surface. The same conclusion is reflected in the values for the total amount of acidic functions calculated from the NaOH-titration (Table 2).

The first composite has as reinforcement untreated carbon nano-fibers. The morphology in the cross section (fracture of the dog-bone samples under liquid nitrogen) of the extrudated and injection-molded PP composite with 5 wt.% nano-fibres was studied by SEM (Fig. 4a). A weak adhesion between PP and carbon reinforcement can be seen (presence of fibres pullout). The mechanical properties of the composite especially tensile test was measured and the value of the PP composite with 5 wt.% is about identical with tensile strength of PP (Table 3).

The fibers used as reinforcement in the second composite with 5 wt.% were treated in the fluidized bed oxygen plasma reactor under the following conditions: power 300 W, treatment time up to few seconds under Ar:O_2 1:1. Before treatment, the nano-fibers were sieved in order to reach a relatively homogenous product regarding the dimensions of the fibers. The plasma parameters used for the treatment of the not sieved VGCNFs in rotating barrel reactor were as follow: 120 W, 7.5 min, 100 Pa, 100 ml/min O_2. The quantity of fibers treated in one charge was 10 g.

The value of the tensile strength of composite with fibers treated in fluidized bed plasma reactor increase only slightly with about 10% (Table 3) in comparison with composite with 5 wt.% untreated nano-fiber. A good functionalization of the fibers, therefore a good wettability of the fibers by the polymer matrix in the time production of the composite can be observed and was analyzed by SEM examination (micrograph, Fig. 4b).

A good adhesion between matrix and reinforcement was observed in both cases of composites containing plasma functionalized nano-fibers.

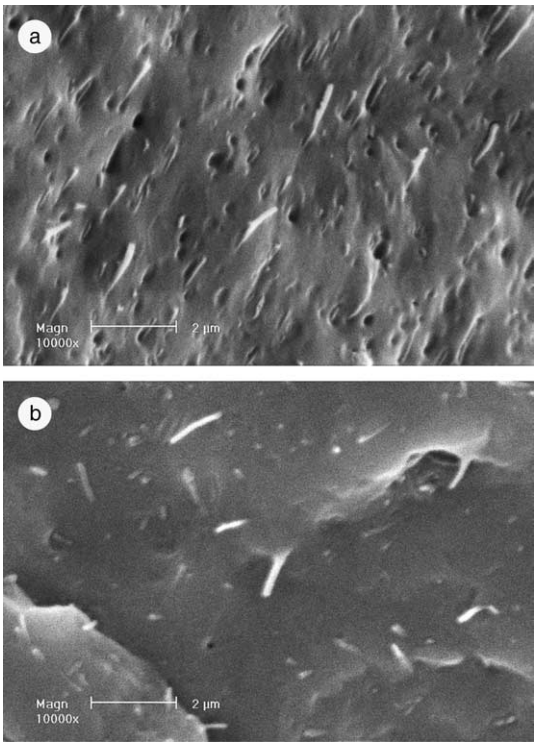

Fig. 4. SEM-micrographs of the PP/VGCNF composites with 5 wt.% untreated (a), and treated in rotating barrel reactor (b) fibers.

4. Conclusions

The adequacy of oxygen plasma treatment to improve the adhesion in carbon fiber/polypropylene composites has been demonstrated in the present work. VGCNFs were treated by RF oxygen plasma in a rotating barrel and fluidized bed plasma reactor at different plasma parameters. The oxygen plasma treatment increased the surface energy of the fibers and decreased its water contact angle leading to an improved wettability of the fibers by the PP-matrix. The introduction of oxygen containing functional groups is favorable to form strong chemical bonds between fiber reinforcements and polymer matrix of the composite. Beside the surface functionalization an additional etching process of the fibres surface took place. Moreover, the mechanical and electrical properties of the fibers remain almost unaltered after the fiber oxidation.

The mechanical properties of the PP/VGCNF composites are improved when plasma finctionalized carbon fibers are used. For the same quantity of plasma func-

Table 3
Tensile strength of PP and PP composite with 5 wt.% carbon

Sample	PP	PP + 5% untreated	PP + 5% treated in flying bed plasma reactor	PP + 5% treated in rotating barrel reactor
Tensile strength (MPa)	31.3	32.1	35	37.1
E-modulus (MPa)	804	1014	1000	1200

tionalized nano-fibres were used for the production of the PP-composites. It was also observed that reducing the fibres dimensions by sieving leads to lower values (only 10% improvement) of the tensile strength comparing with the unsieved plasma treated nano-fibres (16% improvement). E-modulus for the sieved nano-fibres was not modified but the nano-fibres/PP composites containing unsieved plasma treated fibres showed a higher value (18% improvement).

Acknowledgements

Financial support by the German Federal Ministry for Education and Research (contract number 13N7741) in gratefully acknowledged.

References

[1] Paredes JI, Matinez-Alonso A, Tascon JMD. Surface characterization of submicron vapor grown carbon fibers by scanning tunneling microscopy. Carbon 2001;39(10):1575–87.
[2] Endo M et al. Vapor-grown carbon fibers (VGCFs) Basic properties and their battery applications. Carbon 2001;39(9): 1287–97.
[3] Chung DDL. Comparison of submicron-diameter carbon filaments and conventional carbon fibers as fillers in composite materials. Carbon 2001;39(8):1119–25.
[4] Cheol Jim Lee, Jeunghee Park. Growth and structure of carbon nano-tubes produced by thermal chemical vapor deposition. Carbon 2001;39(12):1891–6.
[5] Maragoni R, Serp P, Feuer R, Kihn Y, Kalck P, Vahlas C. Carbon nano-tubes produced by substrate free metalorganic chemical vapor deposition of iron catalysts and ethylene. Carbon 2001;39(3):443–9.
[6] Ci L, Wie J, Wie B, Liang J, Xu C, Wu D. Carbon nano-fibers and single-walled carbon nano-tubes prepared by the folating catalyst method. Carbon 2001;39(3):329–35.
[7] Montes-Moran MA, Martinez-Alonso A, Tascon JMD, Paiva MC, Bernardo CA. Effects of plasma oxidation on the surface and interfacial properties of carbon fibers/polycarbonate composites. Carbon 2001;39(7):1057–68.
[8] Donnet JB. Carbon Fibers, second ed. New York: Dekker; 1990. p. 145–200.
[9] Boudou JP, Martinez-Alomzo A, Tascon JMD. Introduction of acidic groups at the surface of activated carbon by microwave-induced oxygen plasma at low pressure. Carbon 2000;38(7):1021–9.
[10] Cuesta A, Martinez-Alonzo A, Tascon JMD. Carbon reactivity in an oxygen plasma: a comparison with reactivity in molecular oxygen. Carbon 2001;39(8):1135–46.
[11] Donnet JB, Brendle M, Dhami TL, Bahl OP. Plasma treatment effect on the surface energy of carbon fibres. Carbon 1986;24(6): 757–70.
[12] Boehm HP. Funktionelle Gruppen an Festkörper-Oberflächen. Angewandte Chemie 1966;12:617–52.