Thin Solid Films 538 (2013) 7–15

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Low pressure plasmachemical processing of multi-walled carbon nanotubes for the production of polyurethane composite films with improved mechanical properties

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ARTICLE INFO

Available online 19 December 2012

Keywords:
Plasma functionalization
CCP
Carbon nanotubes
Polyurethane composites
XPS
FTIR
Depth sensing indentation

ABSTRACT

Multiwalled carbon nanotubes (CNTs) were modified in low pressure capacitively coupled discharges (13.56 and 27.12 MHz) in Ar/NH_3 and oxygen-containing gas mixtures. A direct functionalization by nitrogen groups was not possible but 1–3 percentage of carbon–oxygen bonds increased with the total oxygen content on the expenses of sp^2C almost independently on the plasma conditions. The plasma modified CNTs were used as fillers for polyurethane (PU) composites prepared by in situ polymerization. The composites were investigated by depth sensing indentation that revealed the existence of surface harder layer caused probably by different polymerization process in the bulk and at the surface that was in a contact with air. The significant improvement of the hardness and elastic modulus was observed when plasma-modified CNTs with high amount of oxygen were added to PU. It also improved the creep resistance of the PU, whereas the ability to recover from a deformation, i.e. anelastic recovery, did not change much.

1. Introduction

Polyurethane (PU) is a versatile polymer [1–3] that can be tailored to desired applications choosing carefully the reactants, their ratio and their synthesis procedure [4]. Different combinations of strength, ductility, biodegradability or hardness can be achieved with the proper formulation and preparation. Nevertheless, there are still some properties such as thermal stability, electrical and thermal conductivity, stiffness or stress recovery, which could be improved with the addition of carbon nanotubes (CNTs).

Polymer composites filled by CNTs are in the center of interest because they represent a class of materials with multifunctional applications. The idea behind preparation of these composites seems to copy engineered structure of polymers reinforced by carbon or glass microfibers, i.e. a soft matrix (polymer) encapsulating a stiffer, high aspect ratio, load-bearing filler. However, CNTs are entirely different from traditional fibers because their dimensions and mechanical flexibility are similar to the polymer chains used as composite matrices [5] and there are fundamental differences between the interaction behavior of the composite constituents in conventional composites and nanocomposites [6].

The CNTs have excellent mechanical and electrical properties over the microfibers. The tensile strength of multi-walled CNTs (MWCNTs) was reported at approximately 150 GPa by Lu et al. [7] and, even though recent measurements by nanostressing stage located within a scanning electron microscope showed that the tensile strength of outermost MWCNTs layer was 11–63 GPa [8], it is still higher than 6 GPa of the highest-strength carbon microfibers. The MWCNTs, having Young's modulus 0.8–1.3 TPa [7,9,10], are also stiffer than e. g. carbon fibers, which have Young's modulus of up to 750 GPa [11]. The most striking difference is, however, the combination of high flexibility and strength with high stiffness, a property that is absent in graphite fibers [10].

The MWCNTs exhibit the dominating metallic or semimetallic nature while small band gap was reported and attributed to presence of defects or an electric contact barrier [12]. Because of their very low energy dissipation, nanotubes carry tremendous current densities, higher than 100 MA/cm^2, which may be compared to current densities of tens of kA/cm^2 for superconducting wires [11]. The thermal conductivities of CNTs are highly anisotropic, diamond-like over the length of the tube and insulating in the transverse direction [13].

The above mentioned MWCNT properties initiated a high amount of research work on the applications of their polymer composites. It comprises nanocomposites prepared for improvement of the strength and durability [14], thermal stability [3,14], electromagnetic interference shielding [15,16], biochemical and sensoric applications [17] etc. However, the polymer composites filled with CNTs do not yet fulfill the expectations. The CNTs form aggregates that are difficult to disperse on the nanoscale level. Chemical inertness of the CNTs causes problems with their fixation to the polymer matrix. Covalent attachment of functional groups to CNTs is one of the critical steps for the

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http://dx.doi.org/10.1016/j.tsf.2012.11.126

application of CNTs in nanocomposites where it should ensure better dispersion of CNTs and increase binding ability to the matrix [5].

The application of CNTs in nanocomposites requires development of effective and environmentally friendly method for CNTs functionalization. In many applications, plasma processing of materials appears to be an advantageous alternative to conventional chemical methods. However, plasmachemical approaches used for these purposes are less studied and understood. The low pressure plasma processes were extensively investigated for the functionalization of various materials. About 400 papers on low pressure plasma functionalization or treatment of CNTs have been published during last 5 years but there are only few studies in which plasma modified CNTs (pmCNTs) were used as fillers in polymer composites. In this work the MWCNTs were modified in low pressure capacitively coupled discharges using two excitation frequencies and various gas mixtures. The plasma conditions were compared not only with respect to the incorporation of oxygen or nitrogen functional groups but also regarding the performance of pmCNTs as polyurethane filler that should improve composite mechanical properties.

2. Experimental details

2.1. Materials

The MWCNTs were purchased from the Nanocyl as Nanocyl-3100 and Nanocyl-3150 (research grade series). According to the datasheet provided by the supplier, the CNTs were prepared by catalytic chemical vapor deposition (CCVD) and purified to 95%,the rest being metal oxides. Their average diameter was 9.5 nm and the length 1.5 μm or below 1 μm for 3100/3101 and 315*X* (*X* = 1–3) grades, respectively. The TEM micrograph of Nanocyl-3150 is in Fig. 1. Commercially functionalized MWCNTs from Nanocyl, Nanocyl-3101 and Nanocyl-315X grades, were used for the reference purposes. Their expected functional groups are listed in Table 1.

The polyurethane was prepared by in situ polymerization from polyol (AXAPUR U100X), isocyanate (U7012) and solvent thinner (U6002) supplied by Colorlak a. s. The antistatic agent Atmer™ 163 (synthetic ethoxylated amine) was purchased from Croda Polymer Additives.

2.2. Plasma modification of CNTs

The Nanocyl-3100 and Nanocyl-3150 MWCNTs were modified in low pressure capacitively coupled plasma (CCP) discharges operating at two different frequencies, 13.56 or 27.12 MHz. The corresponding applied RF power was 15 and 45 W, respectively. The CCP reactor was a horizontally mounted glass tube, 8 cm in diameter, closed by two aluminum electrodes (Fig. 2). The perforated grounded electrode enabled gas feeding whereas perforated RF electrode was used to pump the reactor by a rotary pump. The distance between the grounded and RF electrodes was 18.5 cm. Different gas mixtures, summarized in Table 2, were tested at the total pressure of 100 and 180 Pa for 13.56 and 27.12 MHz, respectively. The flow rates of gases were regulated by electronic flow controllers Hastings, whereas flow rates of water and ethanol vapors were set by a needle valve. For each experimental run, the reactor was loaded with 50 mg of CNT powder distributed on the glass tube along the distance of 50 mm. The thickness of the powder layer in the reactor was below 1 mm. The treatment time ranged from 30 to 180 min. However, the process was interrupted at half of the treatment time in order to mix the CNTs and thereby obtain more homogeneous treatment.

Table 1
Overview of used Nanocyl research grade CNTs together with their XPS elemental analysis.

Grade number	Functionalization	Oxygen (%)	Nitrogen (%)
3100	Pristine	1.2–1.8	0
3150	Pristine	1.2–1.7	0
3101	COOH	6.3	0
3151	COOH	4.7	0
3152	OH	1.1	0
3153	NH_2	0.6	0.3

2.3. Preparation of PU and PU/CNTs composites

The preparation of PU/CNTs composites consisted of the following steps:

(i) polyol, solvent thinner, MWCNTs and antistatic agent were weighed out and stirred well manually,
(ii) the mixture was ultrasonicated for 60 min at temperature of 300 K together with glass beads added for better separation and mixing of CNTs,
(iii) isocyanate was stirred into the mixture,
(iv) the final mixture was sucked up with syringe and poured onto a glass substrate (100 × 100 mm) enclosed in a frame,
(v) homogeneously spread and carefully leveled liquid composite was dried in air at laboratory temperature of 300 K for 48 h.

Polyol, isocyanate and solvent thinner were used, according to the recipe of the producer, in the weight ratio of 7:2:1. The MWCNTs and the antistatic agent for improved dispersion of MWCNTs were added in the amount of 0.1 wt.% and 0.2 wt.% of final composite, respectively. Control samples of pure PU were prepared using the same procedure but omitting the MWCNTs and the antistatic agent.

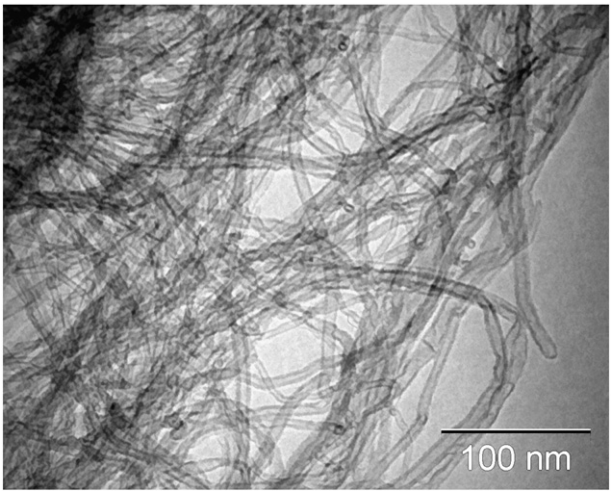

Fig. 1. TEM micrograph of Nanocyl-3150 MWCNTs.

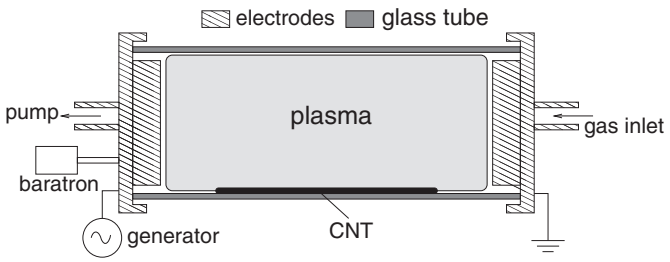

Fig. 2. Schematic drawing of capacitively coupled plasma (CCP) discharge used for modification of CNTs.