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Strain sensing in polymer/carbon nanotube composites by electrical resistance measurement

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ABSTRACT

In this work multiwall carbon nanotubes (MWCNTs) dispersed in a polymer matrix have been used for strain sensing of the resulting nanocomposite under tensile loading. This was achieved by measuring the relative electrical resistance change ($\Delta R/R_0$) in conductive polyvinylidenefluoride (PVDF)/MWCNTs nanocomposites prepared by melt-mixing with varying filler content from 0.5 wt.% to 8 wt.%. Two main parameters were systematically studied. The PVDF/MWCNTs mixing procedure that results in a successful MWCNTs dispersion, and the effect of MWCNTs content on material's sensing behaviour. The samples were subjected to tensile loading and the longitudinal strain was monitored together with the longitudinal electrical resistance. The results showed that MWCNTs dispersed in insulating PVDF matrix have the potential to be used as a sensitive network to monitor the strain levels in polymer/carbon nanotube nanocomposites as the deformation level of each sample was being reflected by the resistance changes.

1. Introduction

It is well established that the introduction of inorganic fillers into a polymer matrix can lead to the development of composites with enhanced properties as well as the introduction of new ones. In the case of composites used for the fabrication of structural parts in engineering applications the main goal is the improvement of mechanical performance by keeping at the same time the good processability properties of the polymer matrix. Fillers such as carbon fibers, carbon black and more recently carbon nanotubes (CNTs) and graphene, have been extensively studied for the improvement of the mechanical properties when incorporated in polymer composites. A common characteristic of the above fillers is their intrinsic conductivity which makes them multifunctional and suitable for a wide variety of applications such as their usage as sensors for strain sensing for structural health monitoring [1]. The main concept is using the structural material itself as the sensor. This concept is also referred to as self-sensing and has the advantages of being low-cost, it can be applied to a large volume of the structural material and there is an absence of mechanical property loss [2]. The concept is based on the monitoring of the changes in electrical conductivity in order to detect the onset, nature and evolution of dangerous deformation levels in advanced polymer-based composites.

The enhancement of mechanical and electrical properties of composites incorporating both single- and multi-walled carbon nanotube based on the excellent electrical and mechanical properties of this allotropic form of carbon is well established [3]. Furthermore CNTs appear to be promising candidates for using in sensor applications (gas sensors [4], strain sensors [5], etc). When incorporated in a polymer matrix, above a critical concentration, a network is formed making the nanocomposite electrically conductive. The overall conductivity is influenced by the filler volume fraction, the connectivity and topology of the network (the nanotube dispersion state, the nanotube orientation state) as well as by the polymer-filler interaction [6,7]. All the above parameters are also closely related to the sensing characteristics when used in sensor applications.

Strain sensing of polymer/CNTs nanocomposites is based on the electrical resistance changes induced by matrix deformation and failure during loading [8–10]. Focusing on the alternation of the conductive network formed by the nanotubes the piezoresistivity of conductive carbon nanotube composites is attributed to the following reasons [11]: (a) destruction of the conductive networks formed by CNTs, due to the loss of contact between adjacent CNTs (b) alteration of tunnelling resistance change in neighbouring CNTs

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due to variation of the distance between them and (c) changes in piezoresistivity of CNTs themselves due to their deformation. Among the previous, the first two factors are believed to be far more influential on the reported changes in electric resistance upon mechanical deformation [12].

Polyvinylidene fluoride (PVDF) is an engineering thermoplastic used in many applications due to its easy of processability, the combination of flexibility, low weight, low thermal conductivity, high chemical corrosion resistance, and heat resistance [13]. Additionally, PVDF in some of its polymorphic forms have relatively large piezoelectric response, which can be exploited in electronic applications [14]. Ferroelectric properties are devoted to the polar crystal structure (β, γ, δ, ε), where all the dipoles associated with individual molecules are parallel, resulting in a non-zero dipole moment of the crystal. The most desirable form regarding the polarization and its piezoelectric, pyroelectric and ferroelectric properties is the β-phase [15]. The fifth known crystal form α is non-polar, where the molecular dipoles are anti-parallel and there is no net dipole [16]. When PVDF is slowly cooled from the melt or cast from the solution, formation of α-crystals are favored over the β-phase, so with common preparation conditions non-polar polymer is achieved [17]. Another way to prepare piezoelectric material is to fill PVDF matrix with various conductive fillers as carbon nanotubes. This type of composite has been recently exploited for strain sensor applications [18]. For the incorporation of CNTs the casting from solution [19] or melt mixing can be used [20]. For the incorporation of nanofillers in this work the method of melt mixing has been used as it is proven to be an efficient and easy method for dispersing CNTs in thermoplastic matrices, additionally it is the most suitable method from an industrial application point of view [21,22].

In international bibliography, a lot of study on such nanocomposites under mechanical loading has been done concerning electrical measurements such as resistivity or capacitance to examine their potential use in deformation or pressure sensors. This work focuses on the impact of the filler content on the electrical properties of PVDF/MWCNTs nanocomposites which will be later used for strain sensing. The study of percolation aspects and the relation to mechanical parameters is of great importance for the fundamental understanding of the sensing mechanisms as well as for practical applications. In this work, nanocomposites with various filler content ranging from 0.5 to 8 wt.% have been prepared for the investigation of the sensing behaviour in relation to MWCNTs content. As the performance concerning electrical and sensing properties strongly depend on the dispersion state of the inorganic filler, the morphology of the prepared composites was studied by electron microscopy. A non-contact experimental method, based on a laser extensometer was employed for detailed strain measurement. The gauge length of each sample, used for strain sensing under mechanical deformation, was divided into different zones and the electrical response as well as the strain of each zone was simultaneously recorded in situ and in real time. The above method allowed illuminating the differences in strain in the different zones due to the inhomogeneous strain distribution along the sample's length and its relation to the corresponding electrical changes. This allowed to examine the behaviour near the point where fracture took place (fracture zone) and away from it. During the tensile experiment each sample broke at different point within the gauge length. The zone where fracture took place is the fracture zone that is being mentioned in this paper.

2. Experimental

2.1. Materials, preparation of the samples

The PVDF (SOLEF®1010, Solvay Solexis S.A., Belgium) as insulating matrix was supplied in the form of pellets. The MWCNTs (Nanocyl®7000, Belgium; purity of 90%, outer diameter of 9.5 nm and length 1.5 μm) were used as received. Preliminary tests were conducted in order to find the optimal mixing conditions for the preparation of the composites as the viscosity is influenced by filler concentration and especially when nanofillers are used. The results showed that a mixing temperature of 190 °C appeared to be low for processing composites with high MWCNTs loading. Finally, the composites were prepared by melt mixing in a microcompounder DSM Xplore TM 15 (the Netherlands) using the following parameters: 50 rpm and a temperature of 220 °C for 15 min mixing. The above conditions were sufficient for processing the composites even when using 20 wt.% of MWCNTs, although the viscosity becomes higher. However for the present study the highest filler content used was 8 wt.%. Then, slabs were formed by compression molding of the mixed composites using a laboratory hydraulic press at 2.4 MPa and 190 °C for 6 min as follows: first 2 min without pressure, then two minutes with a pressure of a few Pascal and the two last minutes with a pressure of 2.4 MPa. Finally, dog-bone shaped sample were cut.

On these samples four gold stripe electrodes were sputtered perpendicular to the loading direction using a sputter coater EMS 550 (Electron Microscopy Sciences), as shown in Fig. 1(a). Copper cables were glued on these stripes using conductive glue. Thus, each sample was separated into three zones. Each sample's neck was 3 cm long, 4 mm wide and 0.65 mm thick. Gold stripes were 4 mm long, like the latitude of the neck, 2 mm wide and 60 nm thick. The distance between two successive stripes was 7 mm.

Finally, samples of pure matrix without any inclusion were manufactured. These samples were subjected to tension under the same conditions as PVDF/MWCNTs samples and the corresponding results were employed as a reference, regarding the tensile experimental data.

2.2. Methods

Scanning electron microscopy (SEM) was used for direct observation of the MWCNTs distribution in the PVDF matrix. For SEM, slabs were cryo-fractured after freezing in liquid nitrogen and the gold-sputtered fracture surface was analyzed using an EVO® 40 Series microscope (Carl Zeiss, Germany). The cryo-fracture method is preferred to cutting or slicing for SEM study of composite samples. Polymeric matrices are much softer compared to fillers of inorganic particles or CNTs, and during cutting of such nanocomposite at room temperature fillers like CNTs can be removed from matrix by the knife, which can influence the image of the filler dispersion in the matrix. At low temperature almost all polymers, including PVDF, are brittle and cryo-fracture allows the study of matrix-filler interaction (wetting, de-wetting, etc.).

Infra-red spectra (FTIR) of pure PVDF and PVDF/MWCNTs nanocomposite films were acquired with NICOLETE 8700 (Thermo Scientific, Madison USA) in Micro-ATR mode, with resolution 4 cm^{-1}, 320 scans, in the range between 4000 and 650 cm^{-1}. Three different positions on the films were investigated by FTIR. The analysis using FTIR and SEM was performed on a few but specially selected samples only.

The samples were subjected to tensile loading until fracture using an Instron 1121 tensile machine. For each filler rate, at least three samples were measured. During each experiment, the tensile stress, the longitudinal strain and the electrical resistance as a function of time were being measured simultaneously. The strain was being measured in each of these three zones individually by a laser extensometer, which permits a non-contact measurement with very high accuracy. The crosshead speed was 0.6 mm/min. A scheme of the experimental set up is shown in Fig. 1(b).

For the electrical measurements a fixed direct current (DC) was applied to the two outer contacts using a Keithley Current Source