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Influence of the concentration of carbon nanotubes on electrical conductivity of magnetically aligned MWCNT–polypyrrole composites

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Abstract. The goal of this work is to study the effect of high magnetic pulses on electrical property of carbon nanotube–polypyrrole (CNT–PPy) composites with different CNT concentrations. CNT–PPy composites are produced in fractions of 1, 5 and 9 wt%. During the polymerization process, the CNTs are homogeneously dispersed throughout the polymer matrix in an ultrasonic bath. Nanocomposite rods are prepared. After exposure to 30 magnetic pulses, the resistivity of the rods is measured. The surface conductivity of thin tablets of composites is studied by 4-probe technique. The magnitude of the pulsed magnetic field is 10 Tesla with time duration of 1.5 ms. The results show that after applying 30 magnetic pulses, the electrical resistivity of the composites decreases depending on the concentration of CNTs in the composites. The orientation of CNTs is probed by atomic force microscopy (AFM) technique. AFM images approved alignment of CNT–polymer fibres in the magnetic field. We found that the enhancement in the electrical properties of CNT–PPy composites is due to rearrangement and alignment of CNTs in a high magnetic field. The stability of nano-composites is studied by Fourier transform infrared spectroscopy.

Keywords. Pulsed magnetic field; CNT alignment; polypyrrole; AFM; RLC circuit.

1. Introduction

Pulsed magnetic facilities are established to prepare high magnetic fields up to 100 Tesla and pulse lengths up to 10 ms by resistor-inductor-capacitor (RLC) discharge systems [1,2]. CNTs have attracted great interest owing to their unique structure and their electronic, physical and thermal properties; such as high electrical conductivity, high thermal conductivity, high elastic modulus and high tensile strength. As a result, CNTs have been widely focussed as potential additives and reinforcing materials for advanced composites [3–5]. Studies on the effect of electric and magnetic fields on CNTs are carried out [6].

Recently, several studies on the alignment of CNTs under the influence of a magnetic field have been reported [7–14]. Because of low susceptibility of CNTs, the alignment occurs only in high magnitude magnetic fields [13,15]. The dispersion and alignment of CNTs in a polymer matrix have been focussed in some studies [8,16,17]. It is believed that the alignment of CNTs in a polymer matrix occurs due to the cooperative effect of the magnetic torque, directly exerted on the nanotubes by the magnetic field, and the dragging forces exerted on the nanotubes by the polymer chains [15,18]. Alignment of CNTs in a magnetic field depends on the magnetic properties of CNTs. Studies on the aligned multiwall carbon nanotubes show anisotropic behaviour for CNTs ($|\chi_{\parallel}| < |\chi_{\perp}|$) [16,19]. Lu [20] predicted that SWNTs have an anisotropic magnetic susceptibility and the lowest energy orientation for both metallic and semiconducting nanotubes and would be parallel to an impressed magnetic field [20].

In preparation of CNT-dispersed composites, the alignment of CNTs and the stable dispersion of CNTs are important factors in obtaining superior properties for potential applications. However, this is not always guaranteed because CNTs have high aspect ratios and are easily aggregated and form bundles due to the very strong van der Waals interaction between them [8,21]. The influence of shape and size of CNTs on their alignment in a magnetic field is reported [8]. When a magnetic field is applied, a CNT can rotate to an angle that minimizes the system energy [22]. The anisotropic susceptibility of CNTs is responsible for their alignment in the magnetic field [12–14,16,19,23,24].

In this work, multiwall carbon nanotube–polypyrrole (MWCNT–PPy) composites are prepared with different CNT weight fractions and the samples are exposed to pulsed magnetic fields. The electrical bulk resistivity and surface conductance of samples are studied by I–V measurements and 4-probe technique. Atomic force microscopy (AFM) techniques are used to observe the alignment and orientation of CNTs in pulsed magnetic field. Fourier transform infrared

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(FTIR) spectroscopy technique is used to observe any possible variations in the polymer structure under the influence of a high magnetic field. In this work, an RLC discharge circuit is designed to generate a pulsed magnetic field of 10 Tesla with duration of 1.5 ms.

The purpose of this work is (1) to investigate the influence of CNT concentration on the electrical property of CNT nano-composites after exposure to a pulsed magnetic field and (2) to study the morphology of the magnetized CNT–PPy microstructure.

2. Experimental

2.1 *Generation of pulsed magnetic field in RLC circuit*

Figure 1a shows an RLC discharge system for fabrication of a pulsed magnetic field. (A detailed design procedure of a magnetic coil is described elsewhere). The capacitor is charged with a direct current (DC) high voltage. The energy stored in the capacitor bank is discharged on a coil by activating a switching system. The coil is a multi-turn copper wire winding which is used as the self-inductance of the RLC circuit. The resulting current, which passes through the coil, produces a pulsed magnetic field inside the coil. The coil is designed to yield a maximum field in the critically-damped mode. Electrical, mechanical and thermal constraints are applied in the design process. The detailed design procedure of magnetic coil and pulsed magnetic fields apparatus are described elsewhere [25]. Figure 1b shows the cross-section of the magnetic coil with a minor mechanical reinforcement. The coil is supported by two teflon flanges to limit the axial and radial expansions of two ends and it is designed to work at room temperature. The magnetic field produced inside the coil is proportional to the coil current. It is also a function of some other parameters like number of coil layers, wire diameter, initial voltage of the capacitor and resistance and capacitance of the circuit. Equation (1) presents the maximum magnetic field at the centre of the coil:

$$B_{\max} = \frac{1}{e}\mu_0\sqrt{\frac{C}{L}}V_0\left(\sum\nolimits_k \frac{N_k}{\sqrt{(l^2+4R_k^2)}}\right). \qquad (1)$$

while $I_{\max} = \frac{V_0}{e}\sqrt{\frac{C}{L}}$ is the maximum current in the critically-damped mode of RLC circuit, μ_0 the permeability of the free space (1.26×10^{-6} Tm A^{-1}), C the capacitance of the bank, L the coil inductance, V_0 the initial voltage on capacitance, N_k the number of windings on the layer k, l the coil length and R_k the radial position of the layer k.

An approximation of the maximum field ($B_{\max}$) at the centre of a solenoid is presented in ref. [26] as well. The maximum magnitude of the magnetic pulse occurs at $t = \tau = \sqrt{LC}$ and the pulse duration is calculated by $\Delta t = 6.3\tau$.

In our experiment, the pulse duration is 1.5 ms and the maximum flux density is 10 Tesla. The coil length is 0.1 m, the coil bore size is 5 mm, the capacitor bank is 2000 μF, the initial voltage is 700 V, the external resistance is 0.2 Ω, the wire diameter is 1.9 mm and the coil has 8 layers. Figure 2 shows the diagram of the magnetic flux density *vs.* time.

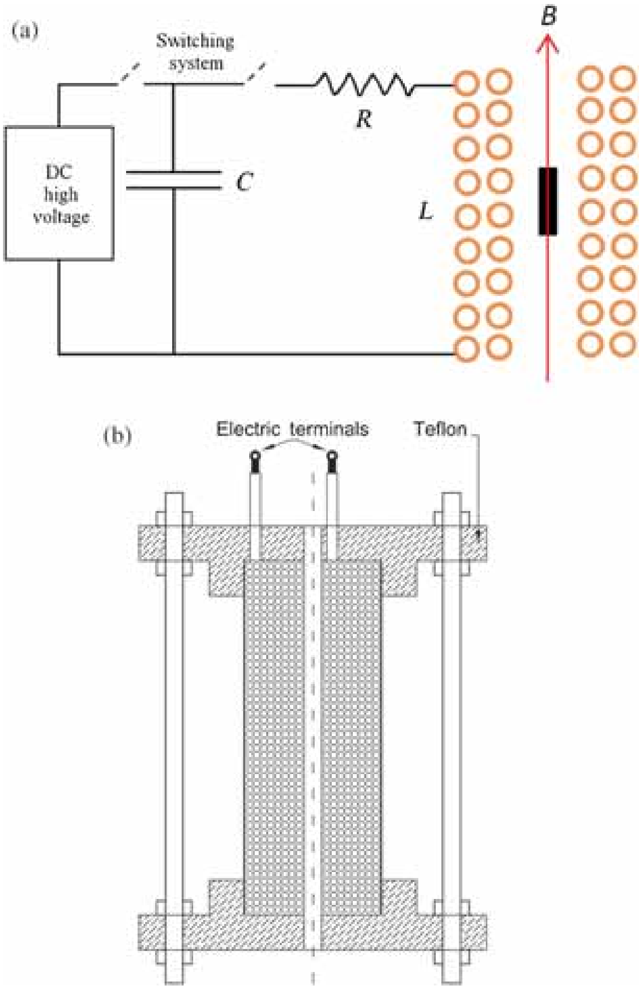

Figure 1. (**a**) Schematic view of an RLC-discharge circuit for fabrication of a high-pulsed magnetic field. (**b**) Cross-section of the 22 magnetic coil. A multi-turn coil is the self-inductance of the circuit; the wire diameter is 1.9 mm and the coil has 8 layers. The coil is supported by two teflon flanges to limit the axial and radial expansion of two ends. The system is designed to work at room temperature.

2.2 *Preparation of CNT–PPy composite*

Multiwall carbon nanotubes (purity 99 wt%, diameter = 7–15 nm, length = 0.5–200 μm) are used as received from Sigma-Aldrich (St. Louis, MO, USA). Pyrrole (Merck, India) is distilled under reduced pressure prior to use. Reagent grade ammonium persulfate (APS) (Merck, India) is used without further purification. P-Toluene sulfonic acid (PTSA) (Merck, India) is used as received. Deionized water is used for the synthesis and washing purposes.

Composites of CNT–PPy are prepared at three different weight fractions; 1, 5 and 9 wt%. First 10, 50 and 100 mg of CNT are selected and each one is dispersed in 35 cc distilled

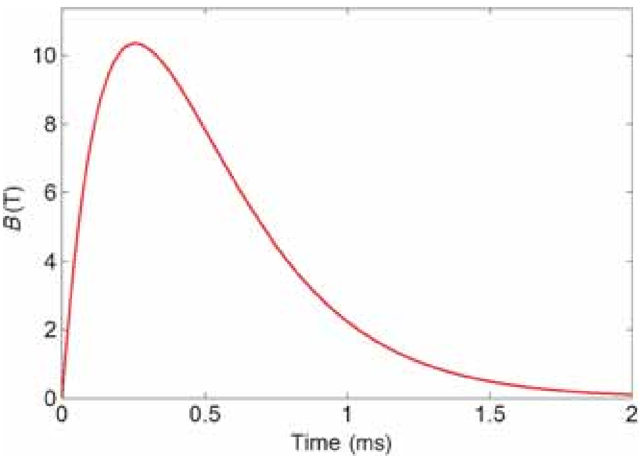

Figure 2. Magnetic flux density *vs.* time for a 8-layer coil; the maximum magnetic field ($B_{\max}$) is 10 Tesla and the pulse duration (T) is 1.5 ms.

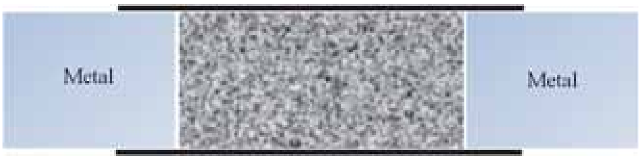

Figure 3. Rod-shaped composites are enclosed between two metal contacts to measure their bulk resistivity. Silver paste is used to make ohmic contacts to the composite.

water separately and put in an ultrasonic vibrator for 15 min. 29.8 mmol p-TSA is added to each solution and is vibrated for another 15 min. Then, 1 cc pyrrole is completely solved in the solution and 14.9 mmol APS, dissolved in 10 cc sulfuric acid (1 M), is added to start the polymerization process. The reaction is continued at 1–3°C. Finally, the products are filtered and dried in an oven.

Rods of CNT–PPy are prepared by compressing fine powder of the obtained materials in a cylinder cast at $5\ \times 10^7$ Pa pressure. The rods are 2 mm in diameter and 5 mm in length. Thin tablets of CNT–PPy composites with typical thickness of 0.3 mm are provided by a 1 ton press. The maximum width of the tablets is taken as less than 5 mm to fit the bore size of the magnetic coils.

2.3 *Applying magnetic pulses to PPy–CNT composite*

Magnetic pulses of 10 Tesla with duration of 1.5 ms are applied to CNT–PPy composites to study the effect of high magnetic field on the alignment of CNTs (details of designing a pulsed-magnetic field apparatus is described elsewhere).

Electrical bulk resistivity of the rod-shaped samples is measured to study the magnetic arrangement of CNTs embedded in polymer matrix. *I*–*V* characteristic and the volume resistivity of the samples are measured by Lutron DW6090 power analyzer. The electrical contacts are made using silver paste (figure 3).

Surface electrical property of the composites is studied by 4-probe technique. SPM model DME 9550 is used to investigate the microscopic effect of high magnetic field on CNT-composites in AFM mode. The AFM probe has a fine tip with a radius below 10 nm. FTIR Perkin-Elmer 800 spectroscopy is used to control the polymer stability in the high magnetic field. 4-Probe instrument is designed on the basis of the constant current measurement method. And platinum-coated needles are used as electrodes for this instrument. All the measurements are conducted at room temperature. The repeatability of the experiments is determined by observing the behaviour of several composite samples for each measurement.

3. Results and discussion

In this work, we study the alignment of multi-walled CNTs in CNT–PPy composites in high intensity pulsed-magnetic fields. The composites are prepared at three different CNT concentrations. It is known that in the presence of a magnetic field, a particle with an anisotropic magnetic susceptibility can rotate to an angle that minimizes the system energy [22]. However, good dispersion is an essential factor in the alignment of CNTs. Recently, several works on aligned CNTs in a polymer matrix have been reported and the electrical, mechanical andthermal behaviours of the composites are studied [7–10,17]. Kimura *et al* [16] were first to use a high magnetic field to align MWCNTs in a polyester matrix. Different simulations and experiments confirm the alignment of CNTs along the applied magnetic field [12,14,24]. However, due to the low susceptibility of CNTs, the alignment occurs only in high magnitude magnetic fields [27].

3.1 *Anisotropic CNT in magnetic field*

Alignment of CNTs in a magnetic field depends on their magnetic properties, especially when the differences in the susceptibility of CNT body is considered [7–11,13,19,27]. Studies on aligned multiwall nanotubes show anisotropic behaviour of CNTs [16,19]. In the absence of an external field, CNTs are randomly distributed in the polymer structure. However, when placed in a perturbing field CNTs are claimed to be aligned parallel to the field lines due to their anisotropic properties [11]. Lu [20] predicted that SWNTs should have an anisotropic magnetic susceptibility and both metallic and semiconducting nanotubes would be parallel to the applied magnetic field. The magnetic torque exerted on nanotubes is proportional to the value of magnetic anisotropy $(\chi_{\perp-}\chi_{\parallel})$ [11]. On the other hand, a CNT is known to have a large diamagnetic property perpendicular to its long axis. According to Kimura *et al* [16], the perpendicular diamagnetic susceptibility of a CNT is at least 3 times greater than its parallel susceptibility $(|\chi_{\perp}| \geq 3|\chi_{\parallel}|)$. Thus in a high magnetic field, CNTs are normally expected to be aligned parallel to the field direction [12,13,16,19,24].

The precise formula for magnetic equivalence of a CNT, as an anisotropic magnetic dipole, is studied elsewhere.

3.2 *Electrical property of CNT–PPy composite after exposure to pulsed-magnetic field*

Electrical characteristics of the rod-shaped samples are measured after they are exposed to 30 magnetic pulses with a flux density of 10 Tesla and time duration of 1.5 ms (The effect of magnetic pulse iteration on CNT–PPy is discussed elsewhere). Since the dispersion and alignment of CNTs in the polymer matrix significantly affect the electrical property of CNT-filled composites, it is difficult to compare the obtained electrical conductivity of the samples with the results of other published studies. Moreover, the CNT concentration levels vary widely in different reported experiments, ranging from <0.01 wt% to >10 wt% [10].

In this work, the ratio of R(30)/R(0) is calculated for the rod samples, as a criterion for observing the variations in resistance of the rods after and before exposure to the pulsed-magnetic field. R(30) is the resistance of the rod after exposure to 30 magnetic pulses and R(0) is the initial resistance of the rod. Figure 4 shows the diagram of the electrical resistance *vs.* CNT concentration level for the rod samples after exposure to 30 magnetic pulses. The decrease in the electrical resistance of the composites is an evidence for the alignment of CNTs in the magnetic field. This is consistent with the previous findings [10,17,18,22,23]. According to figure 4, a composite with CNT concentration of 5 wt% shows the highest decrease in the resistance compared to the composites with other CNT concentration levels.

Figure 4 shows that the influence of the applied magnetic field on the resistance of the composites. At lower concentrations the resistance of the composites decreases as the CNT concentration increases. This is the evidence of CNT alignment under a high magnetic field. However, at higher concentrations (9 wt%), we see that the influence of the magnetic field on the resistance of the composite decreases. In

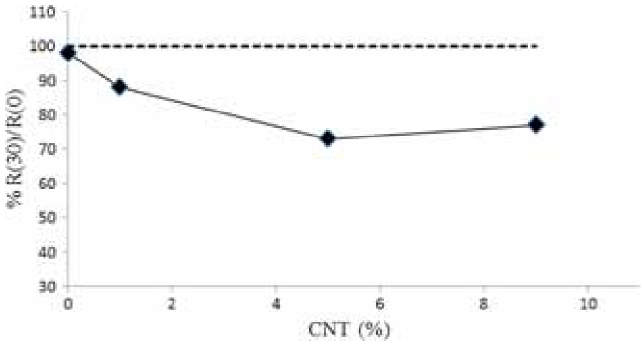

Figure 4. Variation in composite resistance *vs.* CNT concentration level after exposure to 30 magnetic pulses.

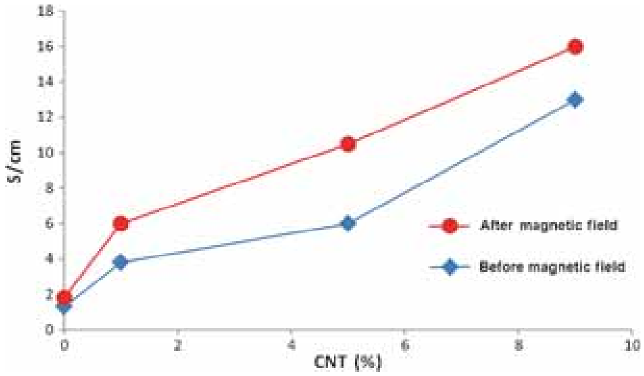

Figure 5. Four-probe conductivity measurements of CNT composites after and before exposure to 30 magnetic pulses. The fraction of CNTs vary from 1 to 9 wt%. At CNT concentration of 5 wt% the magnetic field has the maximum impact on the conductivity of the sample.

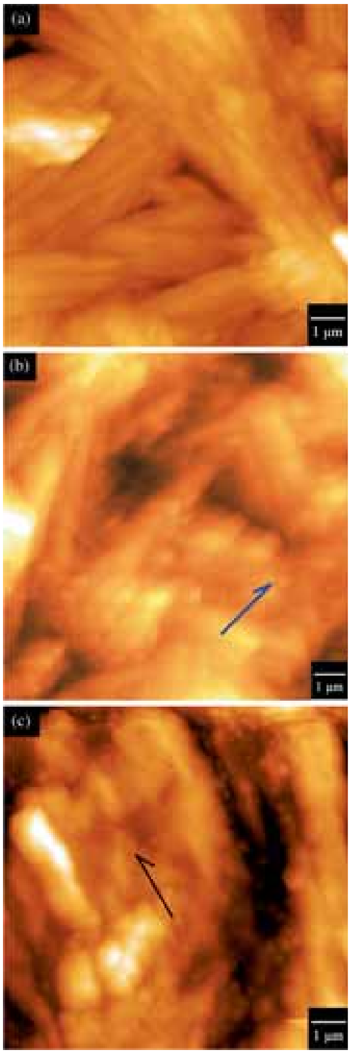

Figure 6. AFM micrograph of CNT–PPy composites with different CNT concentrations after exposure to a pulsed-magnetic field of 10 Tesla; (**a**) CNT concentration level of 1 wt%, (**b**) CNT concentration level of 5 wt% and (**c**) CNT concentration level of 9 wt%. At 1 wt% concentration level, the alignment is insignificant. At 5 and 9 wt% concentration levels, the composite fibres are aligned under influence of the magnetic field. The arrows show the direction of alignment.

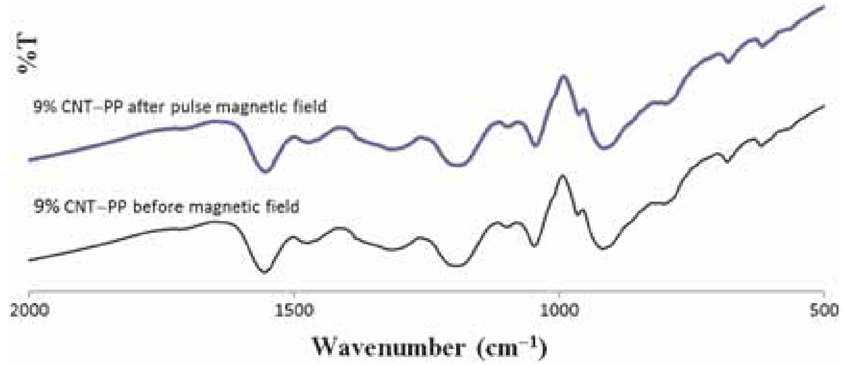

Figure 7. FTIR spectra of 9 wt% CNT–PPy composite; above: after exposure to 30 magnetic pulses of 10 Tesla and below: before exposure to the pulsed-magnetic field. The polymer structure remains intact after exposure to high magnetic field.

practice, at higher concentrations the CNTs are more prone to aggregate and tend to form bundles rather than being homogeneously dispersed in a polymer matrix [8,22,23]. We presume that at higher concentrations the CNTs embedded in the polymer matrix have less percolation chance due to a higher probability of agglomeration. This can be regarded as the adverse effect of high CNT concentrations. Figure 5 illustrates the 4-probe conductivity measurements of CNT–PPy thin tablets after and before exposure to 30 magnetic pulses. At lower concentrations, by applying the magnetic field, the conductance of the composites increases as the CNT concentration increases. The enhancement in the surface electrical conductivity of the tablets is a sign of CNT alignment. Again as discussed in figure 4 in a composite with 9 wt% concentration the field influence on the conductivity of the tablets reduces. This is due to the entanglement of the CNTs.

3.3 *Alignment of CNTs in polymer matrix after exposure to pulsed-magnetic field*

The morphology of CNT–PPy tablets are studied by AFM technique. The aim is to observe the magnetic orientation of CNTs embedded in the polypyrrole matrix. Figure 6 shows AFM micrograph of CNT–PPy composites with 1, 5 and 9 wt% CNT concentration levels after exposure to 10 Tesla pulsed-magnetic field. As figure 6a shows that at low concentration of CNT, the magnetic alignment is insignificant. While according to figure 6b and c, at higher concentrations (5 and 9 wt%) the CNT-embedded polypyrrole fibres are stretched and aligned along the magnetic field direction. This is consistent with the previous findings [15,20]. It should be considered that at higher magnetic fields ($B > 15$ Tesla) an orientation and alignment are observed in polymer matrix as well as the magnetizable impurities such as CNTs. Since the enhancements in the conductance of magnetized nanocomposites are evaluated for three different fractions of CNTs, the magnetic alignment and rearrangement of CNTs is taken the most probable factor to modify the electrical properties of magnetized nano-composites. As a matter of fact, any unwanted alteration in polymer structure is common for all three CNT composites, which we exposed to high magnetic fields. And this enables us to trace the mere influence of CNT presence in the magnetized composites.

3.4 *Fourier transform infrared spectroscopy*

FTIR spectrum is used to study the structure of polypyrrole matrix after exposure to pulsed-magnetic field. Figure 7 shows FTIR spectra of CNT–PPy composite after exposure to 30 magnetic pulses of 10 Tesla. The absorption peaks are equal before and after exposure to the magnetic field. This means that the polymer structure remains intact throughout the experiments. This is consistent with the previous experiments with high magnetic fields of below 15 Tesla [7,23].

Poor dispersion and uncontrolled alignment of CNT particles in the polymer texture adversely affects the desired properties of CNT composites. Recently, high magnetic fields and high gradient magnetic fields are regarded as useful methods in treatment of nano-composites and manipulation of carbon nanotubes embedded in the composites [28]. In this work, analysing the magnetic treatment of composites with different CNT fractions proves the impact of magnetic fields on alignment of CNTs. The present research is regarded as a high magnetic field treatment method for nano-composites.

Further experiments should be conducted in order to study the alignment of different types of CNTs (para/dia/ferromagnetic CNTs) in high magnetic fields.

4. Conclusion

We produced a 10-Tesla pulsed-magnetic field by an RLC discharge system in the critically-damped mode. Then, we prepared CNT–PPy composites with different CNT concentration levels (1, 5 and 9 wt%). The influence of high magnetic field on the electrical conductivity of the samples is studied by 4-probe technique. We found that magnetic alignment of CNTs, which occurs in the polymer matrix, enhances the electrical properties of the composites. The study shows that this enhancement depends on the concentration level of CNTs in the composite. However, we observed that in highly concentrated composite samples (9 wt%), due to the aggregation of CNTs, the magnetic field influence on the electrical properties of the samples decreases. The microstructural morphology of nanocomposites is studied by scanning probe microscopy technique. AFM images illustrate the alignment of CNTs with different concentration levels in the polymer matrix after exposure to the magnetic field. It is found that the aligning effect of pulsed-magnetic field is higher in CNT-composites with 5 and 9 wt% concentration levels. The stability of nano-composites is studied by FTIR spectroscopy. This work may have a good contribution to the magnetic treatment of nano-composites.

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