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Influence of three-hydroxy-2-naphthoic acid functionalized SWCNTs on the electrical and mechanical properties of poly (vinyl chloride)

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Two main groups of samples were prepared. The first one was poly (vinyl chloride) (PVC) loaded with different concentrations of as received single walled carbon nanotubes (SWCNTs), while the second was PVC loaded with different concentrations of single walled carbon nanotubes functionalized with three-hydroxy-2-naphthoic acid (□-HNA) at a concentration of 0.04wt%. The dc electrical conductivity and its temperature dependence of theses samples were investigated. Also, the tensile, rheological as well as the dynamical mechanical properties of all samples were studied. Functionalization of SWCNTs with □-HNA was found to enhance the dc electrical conductivity, elastic modulus, tensile strength, complex viscosity, storage modulus and the glass transition temperature. The dc electrical conductivity had a percolation behavior with a percolation threshold concentration of 0.35 and 0.22wt% of un-functionalized and functionalized CNTs, respectively. The enhancement of the electrical and mechanical parameters with functionalized SWCNTs indicated well dispersion of CNTs due to formation of side functional groups on their sides.

Keywords: CNTs, Electrical Conductivity, Stress-Strain, Elastic moduli, Glass Transition

1. INTRODUCTION

From the academic and industrial points of view, single walled carbon nanotubes (SWCNTs) have been the research focus and considered the most popular nanomaterials after C_{60} because of their unique and remarkable electrical, thermal optical and mechanical properties [1 – 5]. Carbon nanotubes (CNTs) tend to agglomerate in bundles and their Direct covalent chemical functionalization was done for purified SWCNTs during a fluorination reaction and C–F bonds were found [9, 10]. Strong acids like H_2SO_4 and HNO_3 or mixture of them create defect sites on CNTs sidewalls and ends which act as covalent functionalization [11]. Defects can be also created with ozone [12, 13], reactive plasma [14, 15] and strong oxidants [16].

Three-Hydroxy-2-Napthoic acid (β-HNA) was used as an external agent to induce the dispersion of MWCNTs in polystyrene [17]. It was found that β-HNA molecules were adsorbed onto the surface of MWCNTs due to inherent hydrophobic/hydrophilic sites with two polar groups: the carboxylic –COOH and the hydroxyl –OH, and create partial electrostatic charges [17 – 20].

The present work aims to study the effect of β-HNA and functionalized SWCNTs with β-HNA on the electric and mechanical properties of polyvinyl chloride (PVC). The dc electrical properties of PVC loaded with as prepared SWCNTs and β-HNA functionalized SWCNTs will be studied. The tensile mechanical properties namely; stress-strain behavior of such composites will be investigated. Rheological and dynamic mechanical thermal analysis tests of the prepared samples will be also done.

1. *Materials and samples preparation*

Polyvinyle chloride (PVC) used in this work was supplied from Sabic Company (Saudi Arabia). It was in the powder form (powder fraction of 90–120 μm, average size of 100 μm, density $\rho = 1.37$ g/cm^3) was used as a polymeric matrix for preparation of composites. Single walled carbon nanotubes SWCNTs, (Aldrich 704113) with outer diameter of 0.7–1.3 nm and average length of 800 nm was purchased. Three-Hydroxy-2-Naphthoic acid β-HNA, 98% in glass bottle was also purchased from Aldrich (H46007). In this work, two groups of samples were prepared. The first group consist of PVC-β-HNA functionalized SWCNTs. In this group, a fixed amount of β-HNA (0.04 wt%) was dissolved in THF solvent and stirred for 24 h. The desired amount of SWCNTs (0.0, 0.5, 1.0, 1.5 and 2.0 wt%) was dissolved in the THF- β-HNA solution and ultra-sonicated for 30 min followed by magnetic stirring for further 24 h. This sonicated SWCNTs solution was added to previously dissolved PVC in THF, and then sonicated again for 30 min, and stirred for 24 h. Solutions were cast in horizontal petri dishes and dried under ambient conditions to get functionalized SWCNTs loaded PVC films. The second group consist of PVC loaded with different concentrations of as received SWCNTs (0.0, 0.5, 1.0, 1.5 and 2.0 wt%) and prepared as described in a previous work [21].

2. *Experimental Tests*

The DC electrical specific conductivity σ_{dc} was measured using a two-electrode method. Sample was painted from both sides with a high-quality silver paste and placed between two brass electrodes to ensure a perfect composite-electrode contact. The values of σ_{dc} was calculated using the equation $\sigma_{dc} = Is/VA$, where I is the electrical current measured experimentally using a digital electrometer model 6517 type Keithley, 5 kV DC power supply, coaxial cable, metal shielding, and a common ground loop, V is the applied voltage, s and A are the sample thickness and area, respectively.

The tensile tests were carried out on dumbbell-shaped specimens. The measurements were done at 25 ^{o}C on a Dynamic Mechanical Analyzer DMA Q800 (TA Instruments LLC, Delaware, USA) instrument with film clamps at a force rate of 1.5 N/min.

The mentioned DMA Q800 instrument was used through the rheological and dynamic mechanical studies. For these tests a film-clamp was used in dry mode. A slow heating rate of 1 deg/min was employed throughout to ensure that the sample was in thermal equilibrium with the instrument. The oscillating frequency was changed from 0.1 to 200 Hz.

Rheological tests experiments were performed with the film under tension while the frequency is changed. A static pre-load force (0.01 N) was applied to the sample prior the dynamic oscillating force to prevent film buckling [22].

During measurement, the instrument was programed to maintain the static load at 125% of the force required to oscillate the sample. It is important that the film remained in its linear viscoelastic region during measurement (to ensure that the properties observed were independent of the deformation applied and truly reflected molecular motions), and so experiments were recorded maintaining constant strain. Generally, for thin polymer films, linear viscoelastic behavior can be assured with a strain less than 0.1%, and so this limit was used [22]. All experiments were carried out many times to ensure the reproducibility of results.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the dc electrical conductivity of PVC loaded with different concentrations of functionalized and un-functionalized SWCNTs at room temperature. Functionalization of SWCNTs increases the dc electrical conductivity for all SWCNTs contents from about two to three orders of magnitudes. At low loading of CNTs in PVC, the conductivity of the composite is essentially equal that of the polymer. As the loading increased, a critical loading or percolation threshold is reached where the conductivity starts to increase rapidly as a function of filler loading as shown in Figure 1. When the distance between nanotubes becomes sufficiently small for electrons to tunnel through the polymer or for many physical contacts between nanotubes are formed. The electrical response of the composites is then described by percolation theory, Eq. 1, and the CNTs concentration that marks this insulator-conductor transition is referred to as the percolation threshold concentration (w_c) [23]:

$$\sigma_{dc} = C[w - w_c]^p \tag{1}$$

where σ_{dc} is the composite conductivity, w the weight ratio of SWCNTs in the composites, C is a constant, and p is a critical exponent. The calculated values of w_c using Eq. 1 are 0.35 and 0.22 wt% of un-functionalized and functionalized CNTs, respectively.

Figures 2 and 3 show the temperature dependence of the dc electrical conductivity of PVC loaded with different concentrations of un-functionalized and functionalized SWCNTs, respectively. The electrical conductivity at 303 K is found to increase with the addition of either Un-functionalized or functionalized SWCNTs with greater values of the later as discussed before. As the temperature increases, the whole samples except those containing 1.5 and 2.0wt% of functionalized CNTs, have activated behavior. In this range of temperature, charge carriers are activated and jump the barriers between filler aggregates. This appears as an increase in conductivity with increasing temperature. This behavior is found to obey the well-known Arrhenius relation:

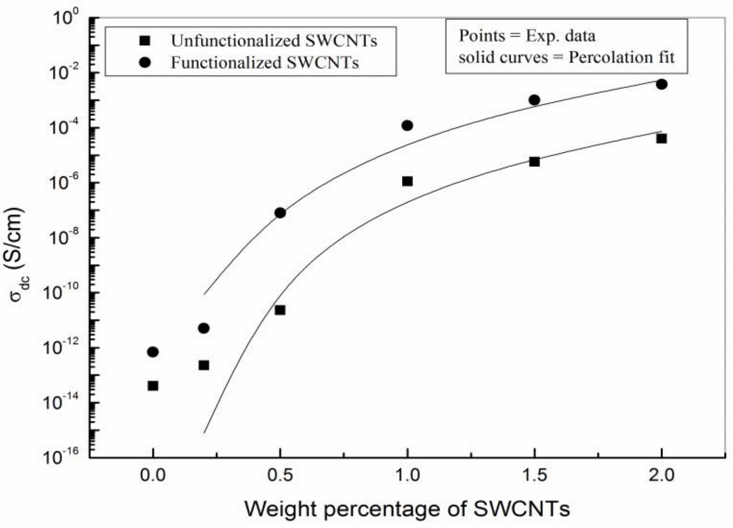

Figure 1 The dependence of the dc electrical conductivity of polyvinyl chloride on the weight ratio of functionalized and un-functionalized SWCNTs.

$$\sigma_{dc} = \sigma_{dco}\, exp\left(\frac{E_g}{k(T-T_o)}\right) \quad (2)$$

where σ_{dco} is the electrical conductivity at temperature T_o, σ_{dc} is the electrical conductivity at temperature T, k is Boltzmann constant and E_g is the activation energy with values 0.058, 0.042, 0.037, 0.008, 0.006 and 0.003 eV for all un-functionalized CNTs samples and 0.061, 0.052, 0.037and 0.005eV for 0.0, 0.2, 0.5 and 1.0 wt% functionalized CNTs, respectively. At high concentrations of either SWCNTs, E_g decreases because of barrier height limitation between conducting sites in the polymer matrix. Functionalization of CNTs decreases E_g faster and the concentrations 1.5 and 2.0 wt% of functionalized CNTs converts the conductivity-temperature behavior into descending one and the activated behavior disappears because of the attached configuration of CNTs. The advantage of functionalized CNTs over un-fictionalized ones is that, the behavior of σ_{dco}– 1000/T curves at concentrations 1.5 and 2.0 wt% of CNTs is approximately temperature independent. Thus, it can be better employed for electronic and microwave devices working at different temperatures.

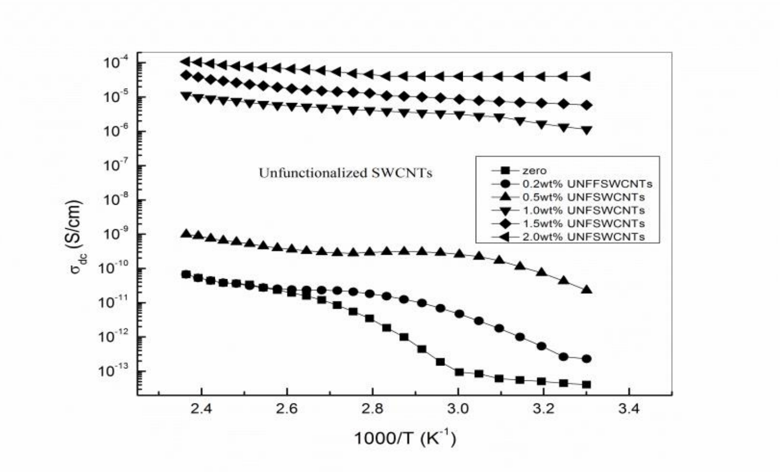

Figure 2 Temperature dependence of the dc electrical conductivity of polyvinyl chloride loaded with different weight ratios of un-functionalized SWCNTs.

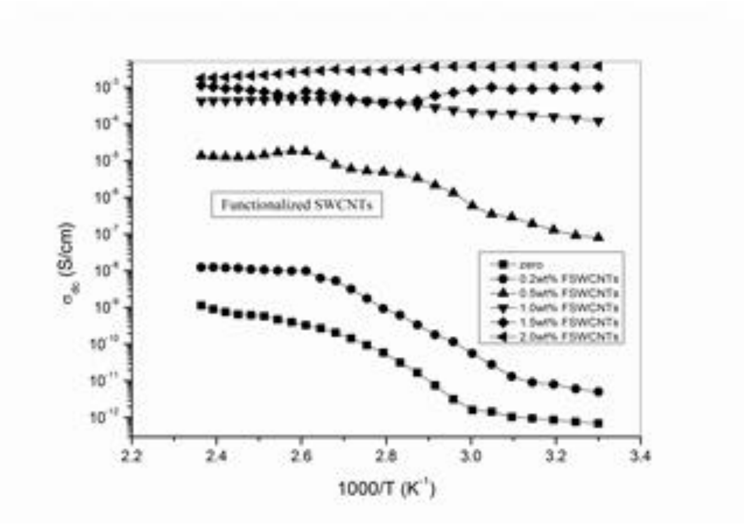

Figure 3 Temperature dependence of the dc electrical conductivity of polyvinyl chloride loaded with different weight ratios of functionalized SWCNTs.

The tensile, rheological and dynamic mechanical properties of PVC loaded with different concentrations of as received SWCNTs are studied in a previous work [21]. Fig. 4 illustrates the stress strain curves for PVC loaded with 0.2, 0.5, 1.0, 1.5 and 2.0 wt% of SWCNTs functionalized with β-HNA at 25 ^{o}C. As a result of the high strain at break of PVC loaded with 0.04 wt% of β-HNA, it is illustrated in the inset of Fig. 4 in order to see the rest of samples easily. The addition of functionalized SWCNTs with β-HNA up to 2.0 wt%, increases the length and the slope of the proportional region which reflects the Hookean behavior of these composites. This linear region is used to calculate the elastic modulus, E, of all composites.

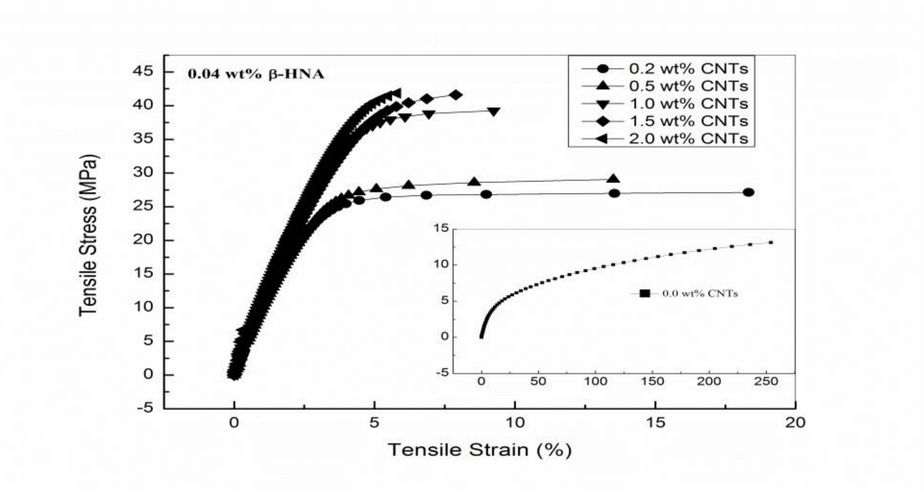

Figure 4 Tensile stress-strain curves of polyvinyl chloride loaded with different weight ratios of functionalized SWCNTs.

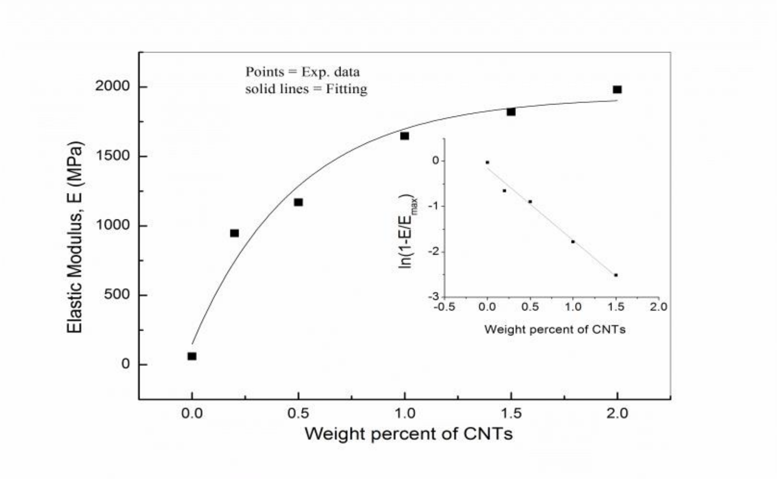

Figure 5 Dependence of the elastic modulus of polyvinyl chloride on the weight ratios of functionalized SWCNTs.

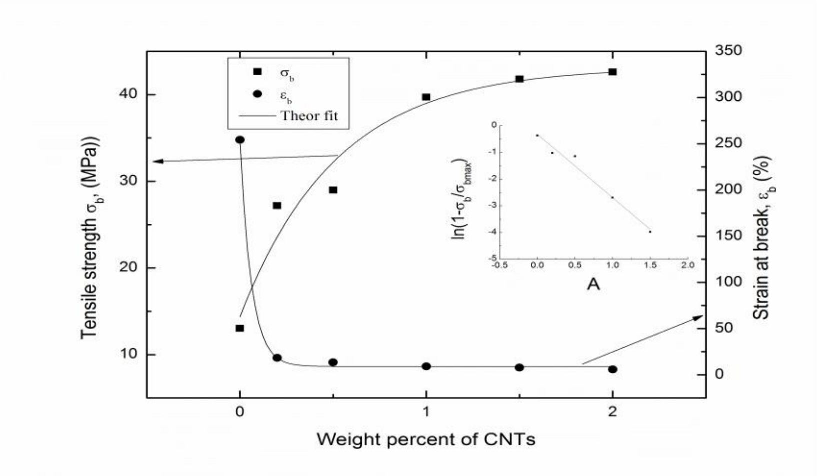

Figure 6 Dependence of the ultimate strength and strain at break of polyvinyl chloride on the weight ratios of functionalized SWCNTs

Figure 5 plots a relation between the calculated values of the elastic modulus and the weight percent of functionalized SWCNTs. The elastic modulus is found to increase with SWCNTs content according to the Equation:

$$E = E_{max}\,(1 - e^{-bw}) \tag{3}$$

where E_{max} is the maximum value of the elastic modulus at w = 2.0 wt%. The value of the constant b is equal to – 1.59 and calculated from the slope of a linear plot between $ln\left(1 - \frac{E}{E_{max}}\right)$ and w which shown as inset of Fig. 5. The functional groups formed on CNTs surfaces enhance the re-coiling and re-entangling of polymer chains, which results as an increase in the elastic modulus. As most of polymer chains are coiled and entangled, the elastic modulus reaches a saturation maximum value.

Figure 6 presents the dependence of both the ultimate tensile strength σ_b, and the elongation at break ε_b, on the weight percent content of functionalized SWCNTs. The tensile strength is also, found to obey Equation 3 with replacing E by σ_b and the constant b (= – 2.30) equals the slope of the linear relation between $ln\left(1 - \frac{\sigma_b}{\sigma_{bmax}}\right)$ and w presented as inset of Fig. 6. On the other hand, the strain at break decreases in an opposite behavior of both E and σ_b. This is due to the increase in the stiffness of the composites, which resulted from the increase of interfacial bonding between CNTs surfaces and polymer chains via β-HNA.

The complex viscosity, |η*| of PVC loaded with different weight ratios of β-HNA functionalized SWCNTs are shown in Figure 7. All samples exhibit shear thinning effect and show straight line dependence of the complex viscosity on frequency. Addition of 0.04 wt% of β-HNA-functionalized SWCNTs to PVC increases the complex viscosity for the whole range of studied frequencies as shown in Fig. 7. The effect of CNTs is most pronounced at low frequencies and the relative effect diminishes with increasing frequency due to shear thinning. This is in accordance with theoretical expectations and experimental observations for fiber reinforced composites [24 – 26].

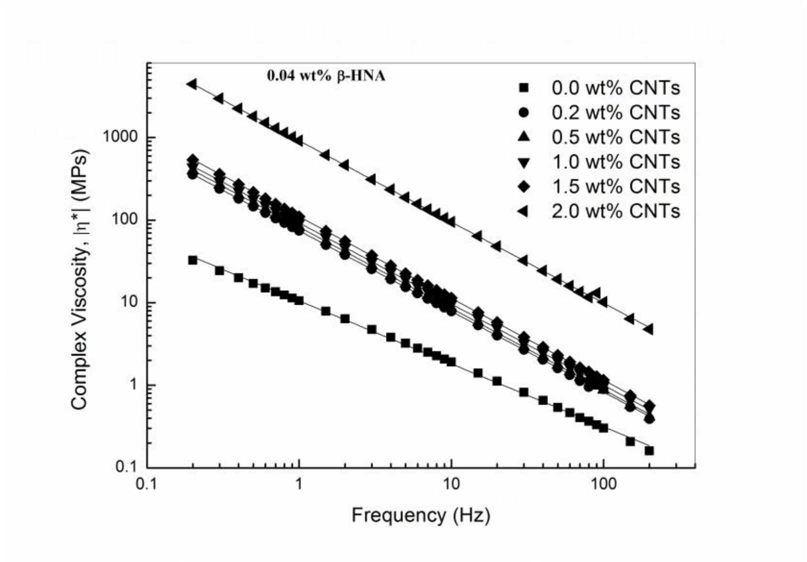

Figure 7 Frequency dependence of the complex viscosity of polyvinyl chloride loaded with different weight ratios of functionalized SWCNTs.

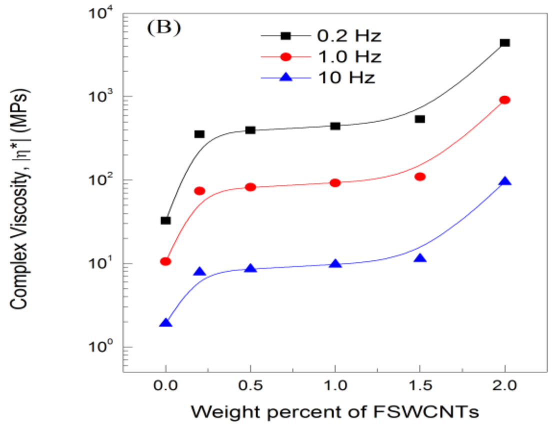

Figure 8 Dependence of the complex of polyvinyl chloride on the weight ratios of functionalized SWCNTs

Figure 8 shows the complex viscosity versus CNTs contents. There is an initial steep slope between concentrations of 0.0 and 0.2wt% of CNTs followed by a small rise in viscosity up to 1.5 wt% and the viscosity begins to increase again up to 2.0 wt% of CNTs. The change in viscosity is more pronounced at low frequencies. The increase in physical interactions between the PVC and CNTs which possess high aspect ratio and large surface area may be the reason behind this increase in η^* with increasing CNTs content.

The change in complex viscosity with CNTs is primarily caused by dramatic change in the storage modulus $G^{/}$, as seen in Fig. 9. The storage modulus increases with frequency as functionalized CNTs content increased; however, the rate of increase becomes less. The relaxation behavior of the typical filled-polymer composite systems showed a similar rheological response [27, 28]. It is known that the polymer chains are fully relaxed and exhibit characteristic homopolymer-like terminal flow behavior. This results in the flow curves of polymers are expressed by the power law $G^{/}(\omega)\alpha\omega^2$ [28 – 31], with ω is the angular frequency. Previous works [28, 31], reported that the slopes of $E^{/}(\omega)$ for polymer/layered silicate and polymer/Al_2O_3 nanopowder nanocomposite were much smaller than 2. In turn, these values are expected for linear homodispersed polymer melts. They suggested that large deviations in the presence of small quantities of fillers might be due to the formation of a network structure in the molten state.

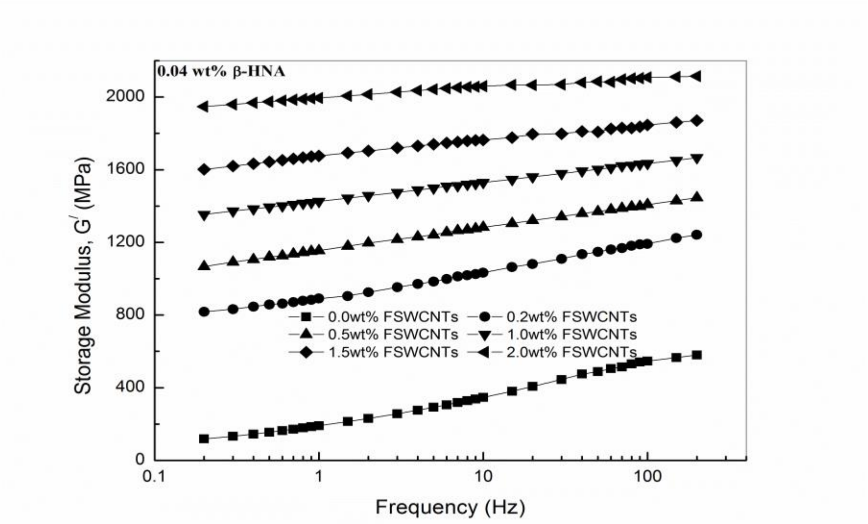

Figure 9 Frequency dependence of the storage modulus of polyvinyl chloride loaded with different weight ratios of functionalized SWCNTs.

Literature reported interconnected structures of anisometric fillers result in an apparently yield stress which is visible in dynamic measurements by plateau of the storage modulus versus frequency at low frequencies [32]. As the nanotube content increases in this composite system, nanotube-nanotube interactions being to dominate and lead to percolation and the formation of an interconnected structure of nanotubes. The slopes of the modulus curves, shown in Fig. 9, decrease with increasing CNTs and less dependence of the modulus on the driving frequency is found at 2.0 wt% CNTs. Therefore, an interconnected structure is assumed to form. The dependence of the storage modulus on the amount of CNTs content is shown in Fig.10, which improves percolation behavior. At high concentrations of nanotubes and above a certain critical composition regarded as rheological percolation composition, connectivity of nanotubes is more pronounced.

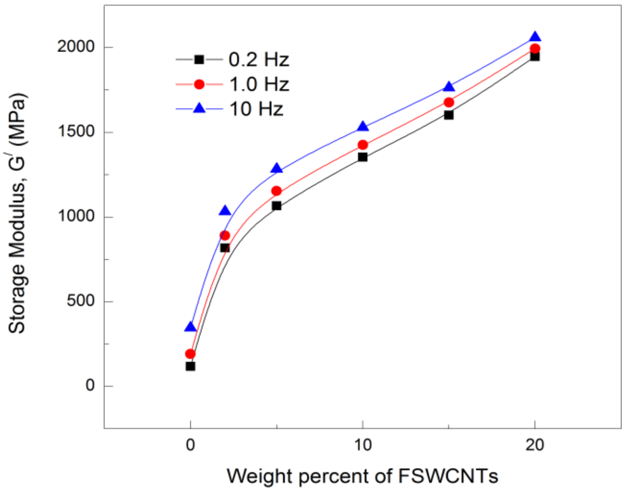

Figure 10 Dependence of the storage modulus of polyvinyl chloride on the weight ratios of functionalized SWCNTs

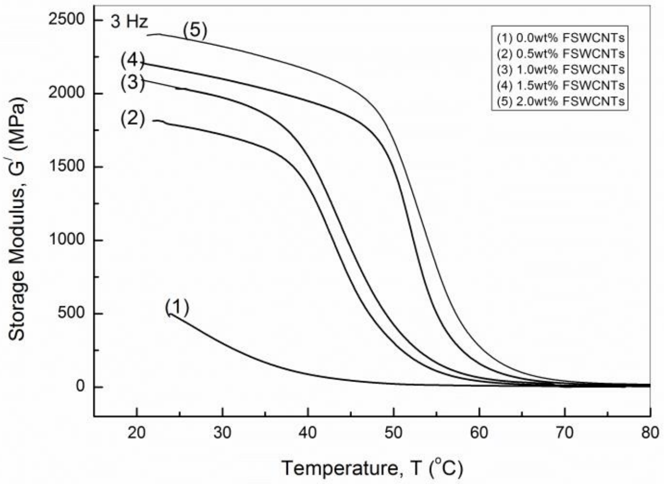

Figure 11 Temperature dependence of the storage modulus of polyvinyl chloride loaded with different weight ratios of functionalized SWCNTs.

Figure 11 plots the storage modulus $G^{/}$ and the loss factor $\tan\delta$, of PVC loaded with different weight ratios of β-HNA-functionalized SWCNTs, obtained by DMA measurement, as a function of temperature at a constant frequency of 3 Hz. The loss factor is very sensitive to the structural transformation of the materials, and can be calculated from the ratio of the loss modulus to the storage modulus ($G^{//}/G^{/}$). At room temperature and at a constant frequency of 3 Hz, the storage modulus increases as the amount of CNTs as discussed before, while, it falls down as the transition temperature reached. This behavior can be attributed to the increase in the molecular mobility of the polymer chains above T_g. The drop in the modulus in the glass transition region becomes higher and goes to higher temperatures with increasing CNTs content (Fig. 12). This indicates a polymer reinforcement processes by CNTs Figure 12 presents the change in the loss factor with temperature for PVC loaded with different concentrations of functionalized CNTs at an oscillating driving frequency of 3 Hz. The damping properties of the material give the balance between the elastic phase and viscous phase in a polymeric structure. In composites, damping is influenced by the incorporation of CNTs. It is observed that as temperature increases, damping goes through a maximum in transition region and then decreases in the rubbery region. Below T_g, damping is low because, in that region, chain segments are in the frozen state. Hence, the deformations are primarily elastic and the molecular slips resulting in the viscous flow are low. Also, in the rubbery region, the molecular segments are quite free to move and hence the damping is low and thus there is no resistance to flow [33].

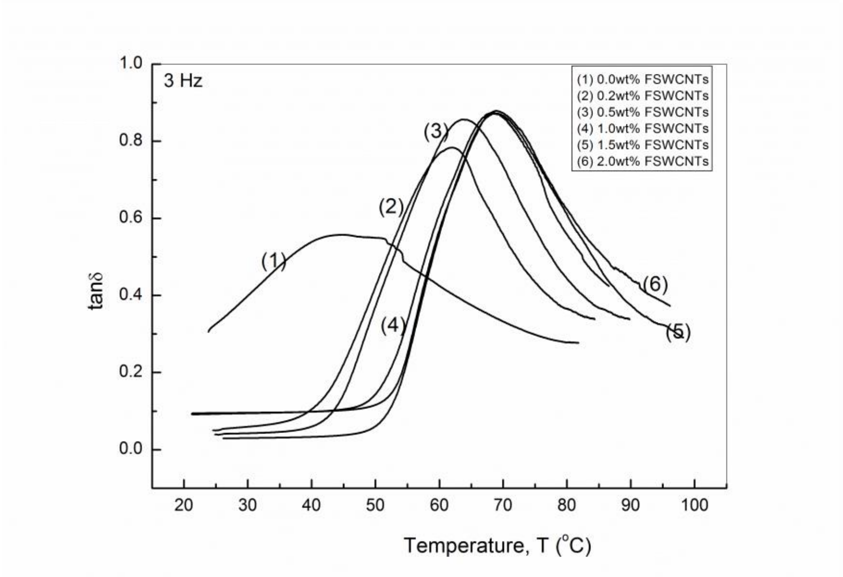

Figure 12 Temperature dependence of tan□ of polyvinyl chloride loaded with different weight ratios of functionalized SWCNTs.

The glass transition temperature T_g, of a polymer is usually taken from the peak position of loss modulus or tanδ versus temperature curves. Peaks of tanδ are typically found at somewhat temperatures depending on the intensity and/or width of the transition. Figure 12 presents the change of tanδ versus temperature for all studied samples at a frequency of 3 Hz. The addition of β-HNA- functionalized SWCNTs to PVC shifts the tanδ peak toward higher temperatures, indicating a reinforcement process caused by CNTs. The addition of β-HNA- functionalized SWCNTs to PVC increases the T_g values from 44.2 ^{o}C to 68.9 ^{o}C at 2.0 wt% of SWCNTs. Interfacial interactions between CNTs and polymer chains may be the reason behind the increase in T_g. It is noticed that, sample without CNTs has a low T_g value (44.2 ^{o}C) down the normal because of the presence of β-HNA, which act as a softener for PVC or the interaction of carboxyl (–COOH) and hydroxyl (–OH) groups directly with PVC chains.

Finally, because of the presence of β-HNA, the side walls of SWCNTs are covered with functional moieties like carboxyl (–COOH) and hydroxyl (–OH) groups [34] resulting in an enhanced dispersion and consequently, enhancement of the electrical conductivity, elastic modulus, storage modulus and glass transition temperature.

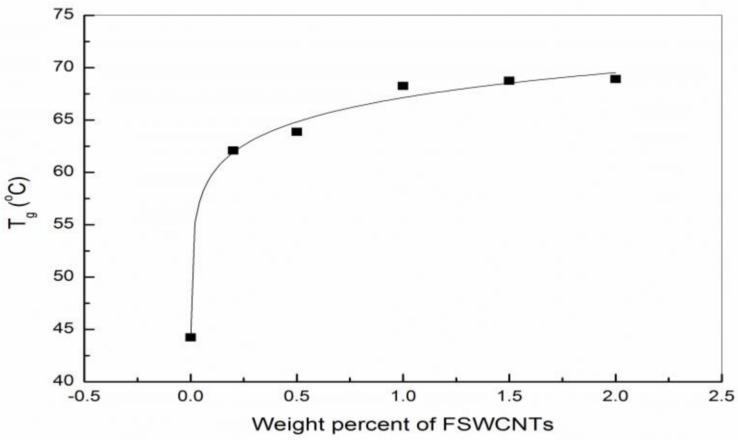

Figure 13 Dependence of the glass transition temperature of polyvinyl chloride on the weight ratios of functionalized SWCNTs

4. CONCLUSIONS

Functionalization of single walled carbon nanotubes with β-HNA forms functional moieties like carboxyl (–COOH) and hydroxyl (–OH) groups on its side walls surfaces. This appears in lowering the electrical percolation threshold concentration from 0.35wt% for unfunctionalized CNTs to 0.22wt% for functionalized ones. These groups enhance the dispersion of CNTs in the polymer matrix, which appear as an enhancement of the electrical and mechanical properties. In addition, functionalization of CNTs increases the glass transition from 44.2 °C to 68.9 °C at 2.0 wt% of SWCNTs.

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