ELECTRICALLY CONDUCTIVE EPOXY/CNT COMPOSITES CONTAINING LOW CNT CONTENTS.

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Abstract
A few types of epoxy resins and MWCNT were used to study the electrical conductivity behavior and morphology of the epoxy/CNT composites. CNT were added to the hardener and sonicated. An extremely low percolation threshold of electrical resistivity, about 0.01wt. %, CNT content was found. Significant enhancement (~60%) of the inter-laminar shear strength (ILSS) was found for nanocomposite containing only 0.2 wt.% MWCNT. SEM studies have shown a high level of CNT dispersion in the form of conductive clouds of CNT in the matrix, where CNT were dispersed very uniformly. Thus, a good CNT dispersion in the epoxy matrices is accompanied by high conductivity levels at extremely low CNT contents and also by enhanced ILSS.

1 Introduction

Epoxy Resins are widely used in structural industry because of their intrinsic stiffness, heat resistance and possibility to combine it with fibers to decrease their brittleness and enhance their mechanical properties, especially interlaminar shear strength.

Carbon nanotubes (CNTs) are known by their high aspect ratio, nanometric diameter, excellent mechanical and electrical properties, and high thermal conductivity. Incorporation of carbon nanotubes into epoxy resins can lead to a new class of materials for applications such as aerospace [1]. To accomplish this potential, carbon nanotubes should be dispersed uniformly in the polymer matrix, with an efficient method that breaks the strong van der Waals interaction forces between the fibers and their tendency to agglomerate [2]. A low percolation threshold usually results in by homogeneous dispersion of CNT [3]. Dispersion of CNTs can be done using pristine CNT or functionalized CNT. Functionalization of CNT usually includes strong acidic oxidations followed by grafting of amines or carboxylic groups [4]. Gojny et al. examined the influence of functionalized CNT on the electrical percolation threshold and found that amino-functionalized CNT exhibited higher percolation threshold than untreated CNT [5]. Chemical functionalization of CNT may affect the crosslinking process [6]. Dispersion of pristine CNT can be done using surfactants, solvents, ultrasonication, and high shear mixing. Use of a solvent can also affect the curing reaction of the epoxy system and lead to a decrease of glass transition temperature (T_g) [7]. This dispersion method can be time consuming since the solvent must be entirely evaporated.

Therefore, dispersion techniques which do not use solvents are more desired. Three roll milling is a high shear mixing process which disperses CNT directly into the epoxy resin. Schulte et al achieved a percolation threshold of 0.025%wt MWCNT using three roll milling [8]. Sonication is another technique that uses ultrasonic waves to separate the agglomerated CNT [9]. The CNT disperse directly in the epoxy matrix [9], or solvent may be used. Recently, sonication is also used to disperse CNT into the hardener of the epoxy system. The hardener of epoxy curing process is usually an amine molecule. Amines have the ability of interfacially interact with CNT and thus achieve fine CNT dispersions [10, 11]. Gojny and Schulte dispersed multi wall carbon nanotubes in poly-etheramine hardener (Jeffamine T-403) via sonication and found a change in glass transition for non-functionalized CNT at high levels of CNT loadings [12]. Ivanov et al studied the dispersion of CNT in an amine hardener, or epoxy resin, using mechanical mixing combined with ultrasonic mixing. The percolation threshold has changed from 0.05%wt for the first dispersion in the epoxy to 0.08%wt of CNT dispersion in an amine hardener, with conductivity values of ~10^{-8} S/cm. No significant change was observed in the glass transition temperature with the addition of CNT by their method [13]. The change of glass transition temperature in the presence of CNTs was recently reviewed by A. Allaoui and N. El Bounia [7].
Enhancement of mechanical properties, e.g. interlaminar shear strength (ILSS), is another important aspect in dispersion of CNT in epoxy resins. Homogenous dispersions are important for achieving high values of ILSS. Chandrasekaran et al concluded that the manufacturing process may play a critical role in MWCNT distribution. When %0.5 MWCNT and control samples were manufactured using flow flooding chamber (FFC), ILSS has improved by 21.3% [14]. Bekyarova et al [4] used functionalized MWCNT and SWNT for selective deposition on carbon fiber surface by electrophoresis. The introduction of %0.25of MWNTs in the CF/epoxy composites resulted in an enhancement of the interlaminar shear strength of 27%. Fan et al dispersed oxidized 2%wt MWNT using acetone and an ultrasonic bath and achieved 33% increase in ILSS [15].

2 Experimental

Four types of epoxy resins and amine-type hardeners were used. Their characteristics are listed in Table 1.

##	Resin	Hardener	Blend ratio	T_g °C
1	DER332 *Dow, USA*	Jeffamine T-403, *Huntsman Adv. Mat., USA*	100:40	70
2	ER2037 *Crosslink Techn. Inc., USA*	CT2037 *Crosslink Techn. Inc., USA*	50:50	-2.5
3	Epon 828 *Miller-Stephenson Co, USA*	Jeffamine T-403 *Huntsman Adv. Mat., USA*	100:40	74
4	DGEBA type resin, *Huntsman Adv. Mat., USA*	Amine type hardener, *Huntsman Adv. Mat., USA*	100:35	145

Table 1. Epoxy resins and hardeners.

Pristine MWCNT Nanocyl 7000 (Nanocyl, Belgium) were used at different concentrations, ranging from 0.01 to 1.0wt.% . In some cases a dispersant (Dodecyl benzene sulfonic acid, DBSA) was added during CNT mixing with a hardener as 33% related to CNT weight. The procedure of epoxy/CNT nanocomposite preparation was performed as follows: MWCNT were added to the hardener, mixed shortly by hand followed by 5 min. US probe treatment (Vibra cell VCX 750, Sonics and Materials Inc., Newtown, CT). Then epoxy resin was added

to the hardener/CNT mixture and intensively mixed by hand. The mixture was degassed, poured to rectangular Teflon mold and cured to produce a sample of 25x15x3 mm^3.
A two-probe technique was applied for electrical measurements using a Keithley 175A Autoranging Multimeter and a Twin Transistor Power Supply (model TTPS-3), or using a Keithley 6514 Electrometer and a Keithley 240A High Voltage Supply, depending on the conductivity level of the samples. A dc voltage of 1 V was applied across the specimen thickness. The two surfaces of a specimen were coated with silver paint to eliminate contact resistance. Electrical resistivity was measured on three-four specimens for each composition and results averaged.
Morphology of the composites was studied using environmental SEM (FEI E-SEM Quanta 200) or HRSEM (Zeiss, Germany) by observing freeze-fractured or hot-fractured surfaces. The entire surface of each specimen (cross-section about 3x3 mm) was thoroughly inspected at a wide range of magnifications allowing to see different levesl of CNT dispersion, from presence or absence of CNT clusters (not-dispersed CNT) up to single CNT dispersed in the matrix. HRSEM was mostly used to study individual CNT and their appearance in the matrix.
Thermal gravimetric analysis (TGA) was carried out using a TA 2050 TGA analyzer. Samples of ~20 mg weight were heated under an air atmosphere, at a heating rate of 20°C/min., monitoring their weight loss as function of temperature.
Dynamic mechanical properties were measured by a dynamic mechanical thermal analysis system, DMTA Perkin Elmer Series 7, in the three-point bending mode (sample dimensions 15x3x1 mm^3). The system was operated at 1Hz. under nitrogen atmosphere, at a heating rate of 3°C/min.
Interlaminar shear stress (ILSS), which determines the short-beam shear strength of high-modulus fiber-reinforced composite materials, was measured according to ASTM D-2344. A specimen was a short beam machined from a curved or a flat laminate up to 6.00 mm thick. The beam was loaded in the three-point bending mode.

3 Results and discussion

Figure 1a shows percolation curves of studied epoxy nanocomposites.

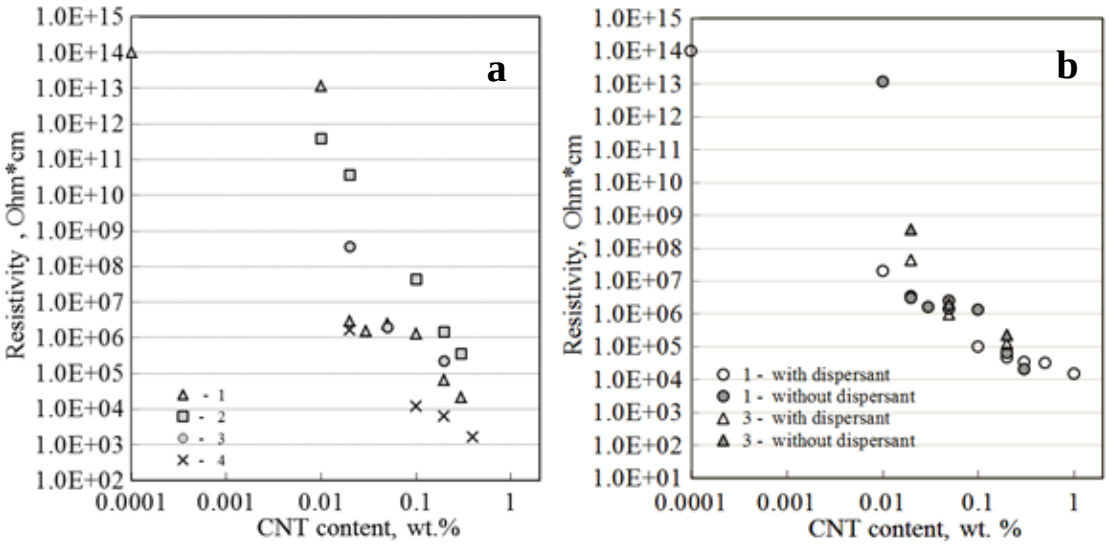

Figure 1. Specific resistivity vs. CNT concentration for (**a**) four studied epoxy systems and for (**b**) DER/Jeff(#1) and Epon828/Jeff (#3) systems with and without dispersant addition.

It should be pointed out that all composites became conductive at 0.1 wt. % CNT content. The lowest specific resistivity value indicates nanocomposite #4, characterized by a high T_g value while nanocomposite #2 characterized by lowest T_g value shows the highest resistivity level at all CNT concentrations studied. Three of the studied nanocomposites (#1, 3, 4) exhibit

percolation thresholds at very low CNT content - 0.02 wt. %. When a dispersant is added during mixing of CNT with the hardener it influences the resistivity only at very low CNT contents. Figure 1b depicts percolation curves for epoxy systems #1 and #3 cured with the same hardener, Jeffamine 403 prepared with and without dispersant. It is seen that the dispersant's presence does not change noticeably the resistivity level of the nanocomposites except those with the lowest CNT contents. A strong decrease of resistivity is found for epoxy system #1 containing 0.01 wt. % CNT thus showing an exceptionally low percolation threshold. Thus, high conductivity levels at relatively low CNT contents (resistivity about 10^3-10^6 ohm*cm in the range of 0.1-0.2 wt. %CNT) along with the low value of percolation threshold is a result of intensive CNT dispersion in the epoxy matrix accomplished by the described mixing procedure.

This finding has been confirmed by morphology observation, Figs. 2-4. The entire fractured surface of each specimen was thoroughly inspected aiming to detect the presence of agglomerated CNT (clusters) and to evaluate the quality of CNT dispersion. Fig.2 show SEM micrographs of freeze-fractured (a, b) and hot-fractured (c, d) surfaces of nanocoposite #2 containing 0.2 wt. % CNT at two magnifications. These pictures reveal a good level of CNT dispersion in the matrix such as nanotubes "clouds", and within the "clouds" the carbon nanotubes are uniformly dispersed. In a more dense "cloud", Figs. 4b or 4d, which is about 1.5 μm in cross-section, CNT appear as separate nanotubes located closer one to the other

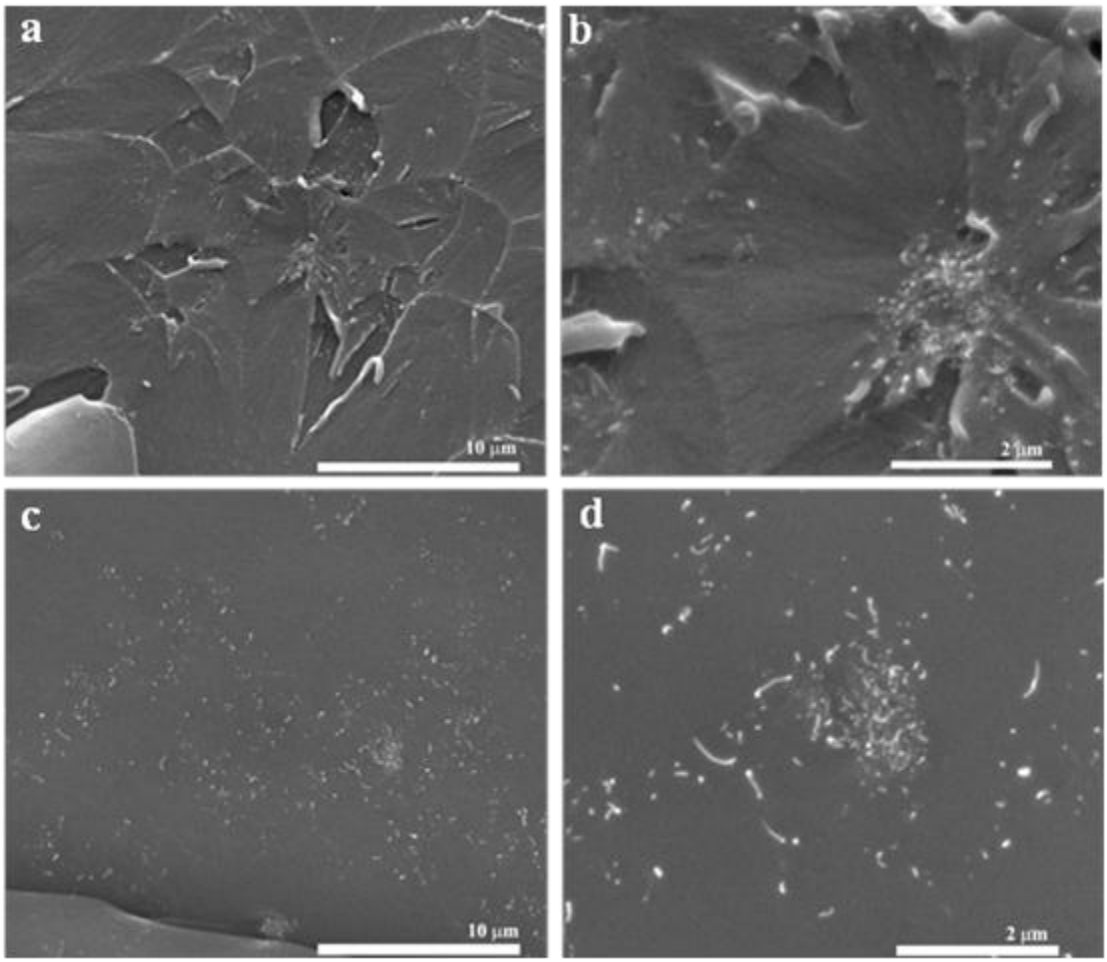

Figure 2. SEM micrographs of (a, b) freeze-fractured and (c, d) hot-fractured surfaces of epoxy resin #2 Epon/Jeffamine containing 0.2 wt. % MWCNT.

forming more contacts between nanotubes. Such a "cloud" could be considered as a diluted or very diluted cluster. In addition it is important to notice that a hot-fractured surface looks smoother and thus easy for clear CNT observation in the micrograph. Thus the rest of the micrographs are presented for hot-fractured nanocomposite surfaces. Figure 3 presents HRSEM micrographs of hot-fractured surface of epoxy system #4 containing 0.4 wt. % MWCNT at different magnifications. This sample is the most conductive among the studied nanocomposites and characterized by a resistivity level of $1.3x10^3$ ohm*cm.

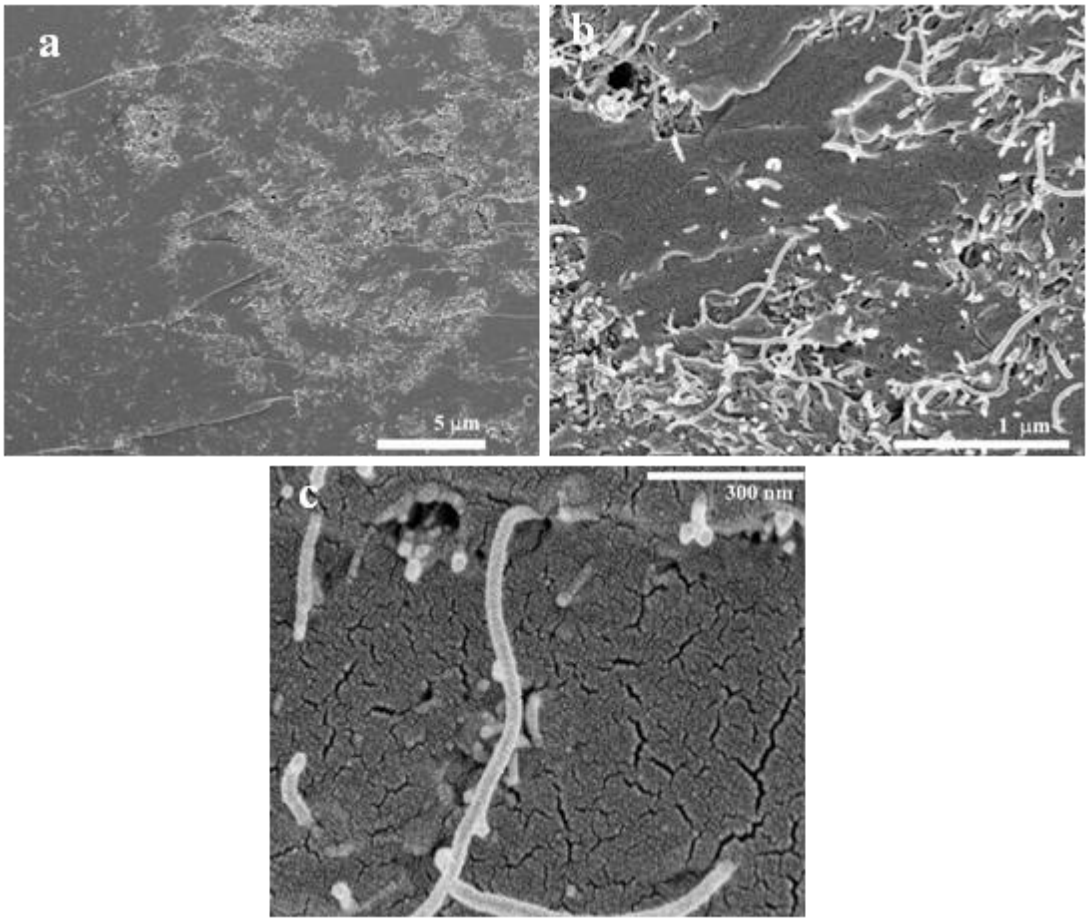

Figure 3. HRSEM micrographs of hot-fractured surface of epoxy system #4 containing 0.4 wt. % MWCN at different magnifications: bars are (a) - 5 μm, (b) - 1 μm, (c) - 300 nm.

One can see CNT dispersion as clouds and some separate nanotubes (Fig.3a). The clouds consist of small bundles of nanotubes while a lot of detached nanotubes are separately dispersed within the matrix too (Fig. 3c). Apparently this combination of separately dispersed nanotubes with CNT "clouds" (diluted clusters) is responsible for the high conductivity.
Figure 4 depicts SEM micrographs of nanocomposite #1 containing only 0.03 wt. % CNT. Despite the low CNT loading this nanocomposite is well-conductive, its resistivity is about $2x10^4$ ohm*cm. The presented micrographs reveal an extraordinary fine nanotubes dispersion within the matrix showing separate pairs of contacting nanotubes which form connectivity and the nanotube networks. The observed morphology supports the measured electrical conductivity of this nanocomposite. Therefore, the procedure of MWCNT mixing directly in the hardener using US treatment provides excellent CNT dispersion in the matrix as reflected by morphology and electrical properties. Our previous studies have shown that the presence of certain molecules significantly facilitate CNT dispersion within a liquid matrix due to a

strong affinity of nanotube to molecules, such as aniline [11]. In the present case the hardeners used are amines. High mechanical energy introduced by US treatment to the CNT dispersion combined with the affinity of CNT to the above-mentioned molecules are both responsible for the observed fine CNT dispersion, especially at the low nanotubes content.

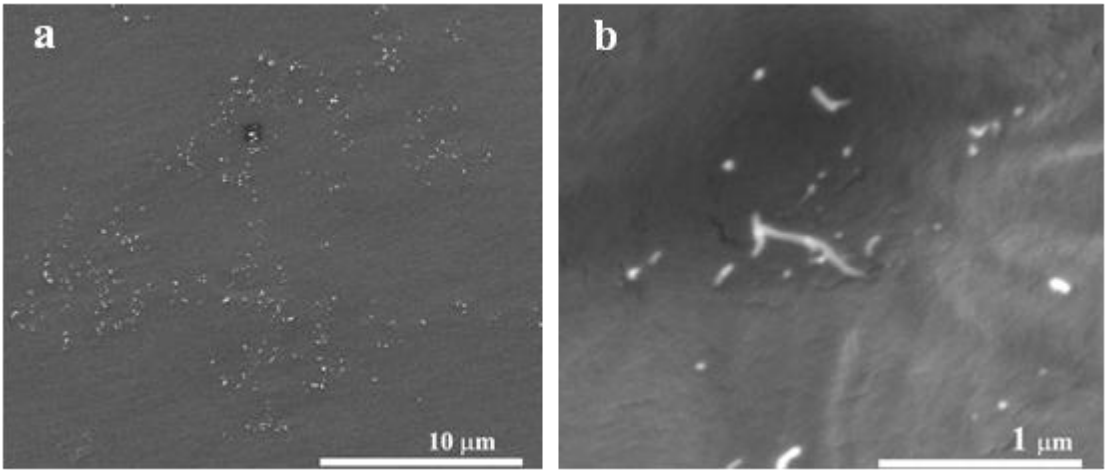

Figure 4: SEM micrographs of hot-fractured surface of epoxy system #1 containing 0.03 wt. % MWCNT at two magnifications.

Some results of thermal properties are presented in Figs. 5 and 6. Figure 5 depicts weight loss curves of nanocomposite #1 containing different CNT contents. At the low CNT concentrations studied no changes of nanocomposite's thermal stability were observed. Some samples containing 0.4 - 0.5 wt. % CNT tested by TGA (not presented here) also did not show marked changes in weight compared with neat epoxy system.

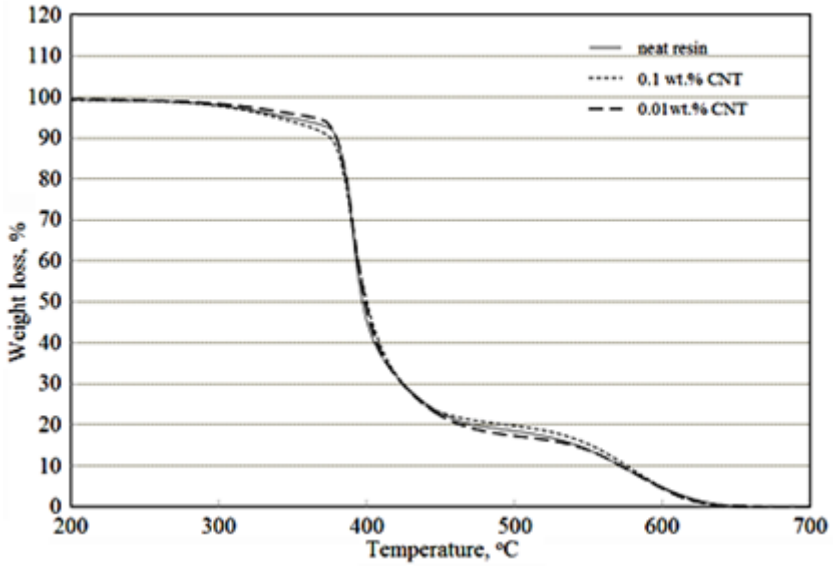

Figure 5. Weight loss vs. temperature by TGA of epoxy systems #1 [DER/Jeff].

Figure 6 present storage and loss modulus of nanocomposites #1 measured by DMTA test. The addition of CNT to the epoxy resin shows a marked increase of the storage modulus in the glassy region and in the rubbery region. A similar behavior was reported [8, 12] and it is attributed to an interaction of CNT with the epoxy. It should be noted that the nanocomposite with only 0.03 wt. % CNT shows the maximum modulus increase in the glassy region

whereas the epoxy systems with higher CNT contents (0.2 or 0.3 wt.%) reveal higher storage modulus in the rubbery region. The influence of CNT addition on loss modulus is less significant however in the glassy region its increase is clearly seen. No marked changes in peaks of loss modulus were observed thus indicating an absence of Tg changes in the studied range of CNT content. Such a Tg behavior was previously reported [7, 13].

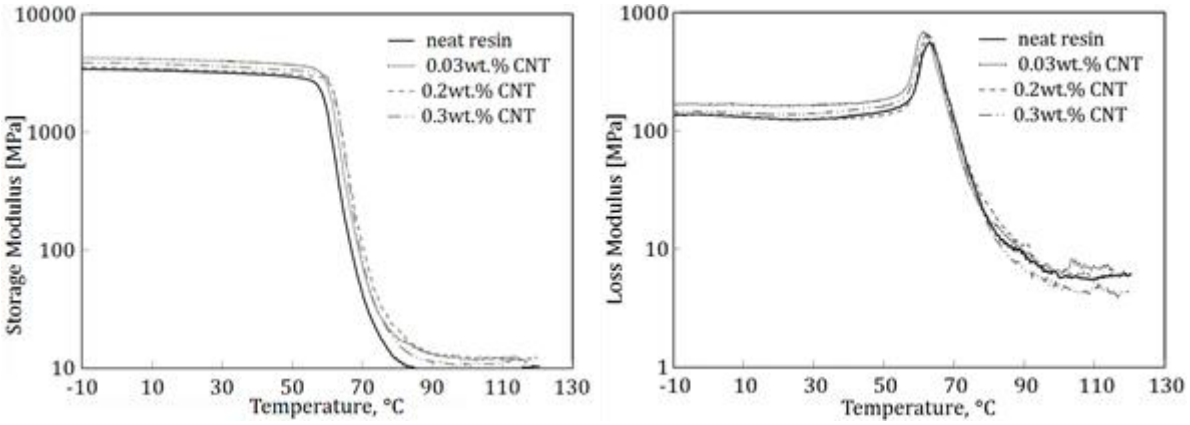

Figure 6. Storage and loss modulus vs. temperature for epoxy system #1 with different CNT content.

The interlaminar shear strength (ILSS) test was performed for a few nanocomposites containing 0.2 and 0.3 wt. % CNT. Significant increase of ILSS of the nanocomposites (~60%) compared with the neat epoxy resin was found. ILSS data are listed in Table 2.

##	Nanocomposite	CNT content Wt. %	ILSS MPa	enhance, %
1	Neat epoxy #1	0.0	29	-
2	Nanocomposite #1	0.2	47	62
3	- " -	0.3	45	55
4	Neat epoxy #4	0.0	31	-
5	Nanocomposite #4	0.2	37	19

Table 2. Results of ILSS test.

4 Conclusions

Direct mixing of MWCNT in the hardener using sonic treatment causes subsequently excellent CNT dispersion in the matrix, as observed by morphology and electrical properties. An extremely low percolation threshold of electrical resistivity, about 0.01wt. %, CNT content, was found. Significant enhancement (~60%) of the inter-laminar shear strength (ILSS) has been achieved for nanocomposite containing only 0.2 wt.% MWCNT.

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