SYNTHESIS OF POLYESTER COMPOSITES WITH FUNCTIONALIZED CARBON NANOTUBES BY OXIDATIVE REACTIONS AND CHEMICAL DEPOSITION

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The paper advances a functionalization method for multiwall carbon nanotubes. It was assessed the acid functionalization with oxidizing agents, ammonia functionalization and iron oxide (III) coating of multiwall carbon nanotubes (MWCNTs). These methods were used in order to obtain polymer/MWCNT nanocomposite at different contents (0.05, 0.10, 0.15, 0.20 and 0.25 wt %). Percolation threshold of polyester nanocomposite was estimated on the basis of viscosity measurement of the unsaturated polyester resin mixed with MWCNTs. The highest relative variation of viscosity was considered as criterion for establishing the optimum content of carbon nanotubes into polyester nanocomposite. SEM analysis of nanocomposite samples with functionalized carbon nanotubes reveals dispersion efficiency in polyester matrix. The three-point bending test enables to identify the suitable method of functionalization in order to obtain a good dispersion of carbon nanotubes into unsaturated polyester matrix. It was noticed that carbon nanotubes added into polymer matrix lead to a considerable increase in surface and volume electrical conductivity.

1. Introduction

Improvement of the mechanical and electrical properties of polymer composites can be achieved by an increased MWCNTs – matrix interfacial bond [1,2,3,4,5,38]. This is one of the most important aspects concerning the shear stress transfer to the reinforcement structure. Also, the electrical properties are improved by better interface polymer-MWCNTs [6]. The use of functionalization process in order to obtain better connection between matrix and nanotubes was analyzed by Frankland et al. and also Duk et al. [7,8]. Therefore, nanotubes surface modification is an important stage in the process of obtaining advanced nanocomposite materials [9].

Attaching functional groups to the carbon nanotube ends provides a fiber-linked matrix [10,11]; thus mechanical and electrical behavior of the material are improved [4,12-18,39,40]. Attachment of functional groups can be achieved either by forming a covalent bond or by the simple adsorption through noncovalent interactions (hydrophobic, π distribution) [19,20,21,22].

Concentrated acids HNO_3 and H_2SO_4 mixed with HNO_3, H_2O_2 or $KMnO_4$ were often used to attach the acid functionalities at nanotubes surface. First, the acid groups are attached to MWCNTs open ends [23]). It was highlighted that mechanical properties can be enhanced if less than 1 wt% of carbon atoms from MWCNTs makes reactive bridges to the matrix (Desai and Haque 2005 [24,25,26]. The MWCNTs chemical functionalization with multifunctional amines was an important step in MWCNTs addition to polymer composites [10].

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An oxidative treatment on MWCNTs was applied in order to obtain carboxylic groups attached to their surfaces. The process of obtaining carboxylic group is combined with MWCNTs ends opening.

This procedure would allow a direct link between the different ends of the nanotubes and increased mechanical strength. In the next step, the carboxylic groups would react with the multifunctional amines and would produce chemical links (ionic or covalent in this case) due to reaction acid – base. Once the resin is added, the free amino functions on the surface of MWCNTs would react with macromolecules and consequently would generate new links that improve the interface matrix – nanotube .

In addition to the direct chemical functionalization, another method of polarity assimilation of MWCNTs is the use of surfactants. The advantage of this procedure is the physical adhesion which does not affect the structural quality of MWCNTs . The covalent bonding of the functional groups is always related to the structural modifications of the graphitic layers [27]. The use of surfactants is a general method that represents the starting point of several licensed procedures [8,12,13]. The surfactants can produce the dispersion of MWCNTs into the polymeric matrix, so that the attraction forces between them are overcome. The dispersion mechanism is achieved by the multiple interactions between surfactants and components of nanocomposite, matrix and MWCNTs, respectively. Therefore, the chemical functionalization of MWCNTs surface is a key approach for the development of composites based on MWCNTs and polymers.

The electrical conductivity of the composites with filler shows a nonlinear increase versus concentration, passing through the percolation threshold [28]. At lower additive concentrations, the conductive particles are separated from one another and electrical properties of composites are dominated by the matrix properties. At increasing concentration of additive, cluster formation process occurs. Near percolation threshold, the clusters form a network throughout the matrix, and an increase in electrical conductivity is expected [29]. The electrical properties of MWCNT composites are influenced by thermal and surface treatments.

The oxidative treatment yields an increased percolation threshold and lower conductivity, favoring the interaction with the polymer and a higher contact resistance [30]. The functionalization of carbon nanotubes produces an enhanced dispersion into the polymer matrix by reducing of the forces Van der Waals that occur near the MWCNTs, due to their nano size [40]. After the application of the dispersion process, the increase in mechanical and electrical properties of nanocomposites could occur. Similarly, the mechanical properties of the nanocomposites polymer-MWCNT are influenced by reaching the percolation threshold, highlighting a substantial increase in different mechanical characteristics, such as ultimate strength, bending modulus, transverse breaking effort [31].

The paper proposes treatment methods to make carbon nanotubes compatible with unsaturated polyester matrix, in order to obtain the nanocomposite polymer-MWCNT with raised mechanical and electrical properties.

2. Experimental

2.1 Materials

The unsaturated polyester matrix AROPOLTM M105 TPB Ashland, added with 1% wt. catalyst 2-ethyl-cobalt hexanoat was used, in order to obtain polymer composite. Initial catalyst was methyl-ethyl ketone peroxide 2% wt.
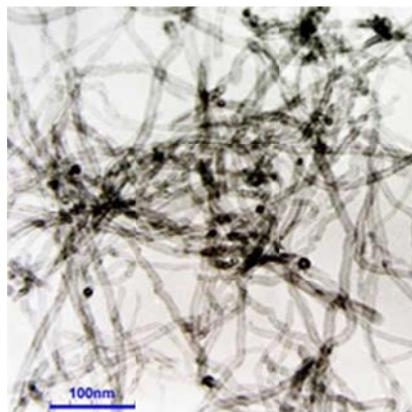
Fig. 1 TEM micrograph of MWCNTs with diameter 8 – 15 nm, length 10 – 50 μm and purity over 95% wt. (reproduced by courtesy of CheapTubes Inc)
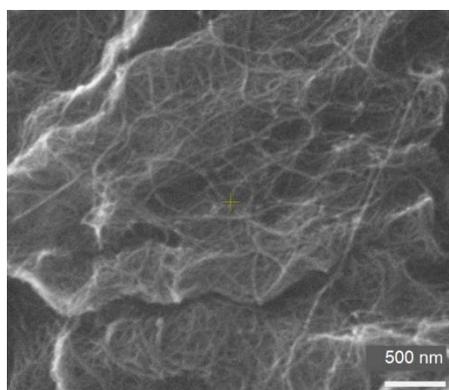
Fig. 2 SEM micrograph (x80000) of as-received MWCNTs, with the following characteristics: diameter 8 – 15 nm, length 10 – 50 μm and purity over 95% wt.

Cheap Tubes Inc. delivered multiwall carbon nanotubes (MWCNTs) with the following characteristics: diameter 8 – 15 nm, length 10 – 50 μm and purity over 95% wt. TEM and SEM micrographs exhibit high aspect ratio of MWCNTs (Figure 1 and Figure 2). In order to obtain carbon nanotubes functionalization, the following chemical reagents (from Sigma-Aldrich) were used: sulphuric acide (98% wt.), nitric acide (70% wt.), ammonia hydroxide solution (30% wt.), hydrogen peroxide (30% wt.), ethanol absolute, sodium dodecyl sulfate (>98.5% wt.), iron (III) chloride (97% wt.).

2.2 Equipment

Rheotest 2 apparatus was used to measure the viscosity of polymer-MWCNTs precursor. Images of scanning electron microscopy of the nanocomposites samples were performed using the Vega Tescan apparatus. Mechanical testing was carried out using the M350 materials testing machine (TESTOMETRIC). The electrical properties of polymer - MWCNT nanocomposite, such as volume and surface electrical conductivity, were assessed using the device DIGITAL LCR METER 9216.

2.3 Methods

The MWCNTs surface functionalization is developed through a controlled oxidative attack, followed by a coupling process of the chemical compatible groups with the polymer matrix. A coating method with a thin layer of iron (III) oxide obtained after crystallization process from

saturated solution was used. The modified nanotubes are further efficiently dispersed into the polymeric matrix by a mechanical and ultrasonic stirring.

The oxidative method was applied using chemical agents such as HNO3, H2SO4, H2O2 and NH3 solutions, in order to break the C-C bonds from the multiwall carbon nanotubes surfaces and to rise new functional groups with covalent bonds. Three functionalization methods of the multiwall carbon nanotubes surfaces were used.

i) The first surface functionalization method makes use of a mixture of acids HNO3: H2SO4 = 1:3 (HNO3 70% wt. and H2SO4 98% wt.), for 24 hours, at 295K. It follows a step-by-step washing process of the functionalized nanotubes with redistilled water until pH = 1; above this pH value, carbon nanotubes free sedimentation could not be efficiently achieved and another separation technique would be required.

The washing step was performed with 500 ml redistilled water, followed by a freely settling and then removing of clear solution. This operation was repeated for 3 times, until pH = 1.

In this case, it takes about 10 minutes to wash off the solution from the nanotubes. The fair liquid is then separated. It follows another washing of the functionalized nanotubes, with 100 ml of redistilled water for 10 times, until pH = 6. In these pH conditions, separation of nanotubes from the solution is efficiently performed by a 6000 rpm centrifugation process. In order to obtain a suitable drying, a last washing of the functionalized nanotubes is applied, with ethyl alcohol absolute. A solution based on water and absolute ethyl alcohol which is an azeotrope (95.57% wt.) with boiling point at 351.30 K, has been used to separate water from carbon nanotubes.

An oven drying, for 8 hours, at 378K, and the dry milling process end the functionalization, yielding MWCNT-F1 additive.

ii) The second method involves carbon nanotubes functionalization by using a mixture of H2O2: NH3 = 1:4 (H2O2 30% wt. and NH3 30% wt.), for 48 hours, at 295K, followed by washing of the functionalized nanotubes with redistilled water untill pH = 8.

A washing with water was applied three times with 500 ml redistilled water, followed by freely settling suspension and then removing the clear solution, until pH = 8.

It follows the nanotubes separation from the solution, lasting about 15 minutes, an washing of functionalized nanotubes with 100 ml of redistilled water for 10 times, until pH=7, and nanotubes centrifugation from the solution at 6000 rpm. The further washing of the functionalized carbon nanotubes, using ethyl alcohol absolute, contributes to the fast drying process, finished by an oven drying for 8 hours, at 378K. Finally, the resulting powder was dry milled, rising MWCNT-F2 additive.

iii) The third method of modifying carbon nanotubes surface for a proper compatibility with the polymeric matrix consists in a coating technique with a thin layer of iron (III) oxide. The first step of this method is the dispersion of carbon nanotubes using a solution of sodium dodecyl sulfate (1% wt.) as surfactant agent, followed by a 10 minutes ultrasonication, with BANDELIN HD3200 device, at 40% amplitude. Subsequently, 10 ml FeCl3 (1mol/L) is quantitatively added under a 5 minutes magnetic stirring and the resulted solution is ultrasonicated for 10 minutes. Then, a solution of NH3 (1mol/L) is quantitatively added until pH = 8.5, followed by ultrasonication for another 10 minutes. The final stage consists of an washing process of the nanotubes covered by a thin layer of iron (III) oxide, using double distilled water up to pH=5.5, followed by centrifugation at 6000 rpm.

The final washing is done by ethyl alcohol absolute. The oven drying lasts 8 hours, at 443K, followed by a dry milling that ends the functionalization, yielding MWCNT-F3 additive. The crystallization water from iron oxide (III) is removed at 443K.

These three types of functionalized MWCNTs (MWCNT-F1, MWCNT-F2, MWCNT-F3) are further used in the technology of obtaining polymeric nanocomposites, as previously discussed [32]. In order to reach an optimum content of carbon nanotubes in polyester matrix, as-received and functionalized MWCNTs at different concentrations were considered.

3. Results and discussions

3.1 Rheological analysis of precursor polymer-MWCNT

Increased viscosity of precursor solution of a nanocomposite is explained by strong interactions between nanoparticles when decisive factors like nanoparticles concentration and dispersion degree allow the percolation stage [33]. Over the percolation threshold, the properties of nanocomposite remain almost stable.

In order to identify a suitable weight ratio of functionalized MWCNTs in polymer matrix, rheological behavior of the mixture was studied at different concentrations of carbon nanotubes (0.05 wt%, 0.10 wt%, 0.15 wt%, 0.20 wt% and 0.25 wt%). The working temperature was provided by a thermosetting process at constant value of 313 K. A thin layer of resin was interposed between two mobile cylinders of the device and the friction coefficient was measured, for all working rotational speeds (from 0.5 to 30 rpm). An optimal concentration, based on viscosity measurements, can be establish through a comparative study of relative viscosity variation (Table 1). Relative viscosity variation, $\Delta\eta/\eta$, was calculated as follows:

$$\frac{\Delta\eta}{\eta} = \frac{\eta_{polymer/MWCNT} - \eta_{polymer}}{\eta_{polymer}} \tag{1}$$

Based on the errors of viscosity variation for all polymer-MWCNTs precursors, including pure and ultrasonicated polymer, an optimum working speed was determined.

The average viscosity error [%] represents the weighted average of the errors recorded for all polymer-MWCNTs precursor systems (0.05, 0.10, 0.15, 0.20 and 0.25% wt.) at the same working speed (0.5, 1.0, 2.0, 3.0, 5.0, 10, 16 and 30 rpm).

Figure 3 shows that the minimum error for the measurements of viscosity variation, on Rheotest device, is found at the working speed of 5.0 rpm. Considering the working speed of 5.0 rpm, it was also determined the viscosity variation for other precursor systems with functionalized carbon nanotubes (Figure 4).

Table 1: Relative viscosity variation ($\Delta\eta/\eta$) of the nanocomposite precursor

		Working rotational speed $\boldsymbol{\omega}$ [rpm]							
		0.5	1.0	2.0	3.0	5.0	10	16	30
		Relative viscosity variation $\boldsymbol{\Delta\eta/\eta}$							
MWCNT content	0.05 % wt	-0.240 ±0.0130	-0.011 ±0.0121	0.007 ±0.0117	0.004 ±0.0084	+0.007 ±0.0077	0.050 ±0.0080	+0.018 ±0.0108	+0.075 ±0.0125
	0.10 % wt	+0.34 ±0.0123	+0.33 ±0.0129	+0.29 ±0.0118	+0.24 ±0.0088	0.19 ±0.0073	+0.19 ±0.0093	+0.19 ±0.0104	+0.22 ±0.0128
	0.15 % wt	+0.62 ±0.0140	+0.54 ±0.0133	+0.57 ±0.0115	+0.50 ±0.0080	+0.39 ±0.0075	+0.45 ±0.0092	+0.42 ±0.0119	+0.41 ±0.0140
	0.20 % wt	+0.90 ±0.0144	+1.17 ±0.0126	+0.50 ±0.0117	+0.85 ±0.0094	+0.78 ±0.0076	+0.86 ±0.0090	+0.72 ±0.0123	+0.64 ±0.0137
	0.25 % wt	+1.19 ±0.0131	+1.17 ±0.0127	+1.14 ±0.0119	+1.12 ±0.0085	+0.80 ±0.0079	+0.98 ±0.0085	+0.75 ±0.0111	+0.68 ±0.0134

*Fig. 3 Errors of viscosity variation for polymer-MWCNTs nanocomposite precursor
at different working rotational speed*

We noticed a continuous viscosity increase for both systems polymer-MWCNTs and polymer-MWCNT-F3 until 0.20 %wt. concentration of carbon nanotubes. The increase in relative viscosity variation at a concentration up to 0.20 %wt. is explained by the increasing interactions between polymer matrix and carbon nanotubes. Over 0.2 %wt. MWCNT the viscosity remains almost stable (Figure 4). We are entitled to think that above this concentration, it is a possible to occur clusters of carbon nanotubes, that leads to quasi-constant viscosity.

In the case of precursors polymer-MWCNT-F1 and polymer-MWCNT-F2, the continuous viscosity increase occurs until 0.15 %wt. concentration of carbon nanotubes.

In other words, adding pure and functionalized carbon nanotubes at low concentration into polyester matrix, the optimum value was identified in Table 1, between 0.15% and 0.20% wt., based on viscosity variation. It can be seen that for greater concentration of carbon nanotubes, the increase of viscosity was much slowly.

Rheological analysis of precursors with increasing concentrations of both pure and functionalized carbon nanotubes underlines the percolation threshold, which is related to the maximum value of relative viscosity variation. The strong interactions between nanoparticles having a suitable concentration and dispersion degree allow for the occurrence of percolation stage.
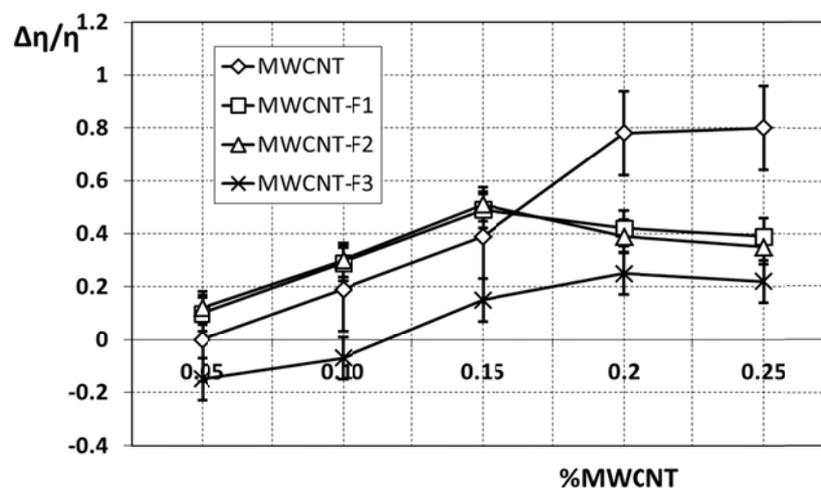
*Fig. 4 Variation of relative viscosity (Δη/ η) for different polymer-MWCNTs precursors, using
functionalized carbon nanotubes in three versions, at different concentrations,
for the working speed of 5.0 rpm*

3.2 Investigation of polyester-MWCNTs nanocomposites

SEM analysis. SEM analysis of polyester-MWCNTs nanocomposites provides information on surface structures, from a qualitative point of view. Such analysis correlated to mechanical and electrical properties gives an overview on the dispersion degree of nanoparticles into polyester matrix. SEM analysis was performed on the four nanocomposite systems: polymer-MWCNT (pure, F1, F2 and F3) at three concentrations (0.10, 0.15 si 0.20 % wt.). SEM micrographs at 0.10% and 0.15% wt., did not revealed major changes of carbon nanotubes distribution into the polyester matrix. An obvious improvement of nanotubes distribution was noticed for 0.20% wt carbon nanotubes. Therefore, SEM images were discussed for different types of MWCNT (pure, F1, F2 and F3) in case of 0.20% wt carbon nanotubes into polyester matrix of polymer-MWCNT nanocomposites.

In the case of polymer-MWCNT nanocomposite (0.20% wt. MWCNT), despite the dispersion method used for mixing the nanotubes with polyester resin, the formation of nanoparticles clusters can be noticed after polymerization, due to the rise of cohesion energy of closer nanotubes. Anyway, this happens because of increasing number of interactions van der Waals that occurs in the nanotubes proximity (Figure 5). However, the SEM micrograph shows a lower uniformity of the particles dispersion, and large polymer portions without MWCNTs.

Functionalization of carbon nanotubes allows chemical bonds formation between functional groups of the nanotubes and reactive groups of the matrix, during reticulation process.

Considering the case of polymer-MWCNT-F1 nanocomposites (0.20 wt % MWCNT-F1), it can be seen an improved distribution of functionalized nanotubes, which is related to stronger chemical interactions between matrix and MWCNTs (Figure 6). This fact can be explained by the reaction between carboxyl groups of carbon nanotubes and reactive groups of unsaturated resin, through reticulation process.

As regards the nanocomposite polymer-MWCNT-F2 (0.20 wt% MWCNT-F2), instead of carboxyl group from MWCNT-F1, there is an amino group that exhibits a great reactivity with the unsaturated polyester resin, during reticulation process. This aspect explains the suitable compatibility between functionalized carbon nanotubes and polyester matrix. Accordingly, the distribution of functionalized carbon nanotubes in polyester matrix is better than of received ones (Figure 7). As for the nanocomposite polyester-MWCNT-F3 (0.20 wt % MWCNT-F3), a better distribution of MWCNT-F3 was noticed in comparison with previous nanocomposites analysed, i.e. polyester-0.20 wt % MWCNTs, polyester-0.20 wt % MWCNT-F1and polyester-0.20 wt % MWCNT-F2 (Figure 5, 6 and 7). This fact might be explained by the wedge effect of oxidic layer chemically deposited on the carbon nanotubes surface (Figure 8).
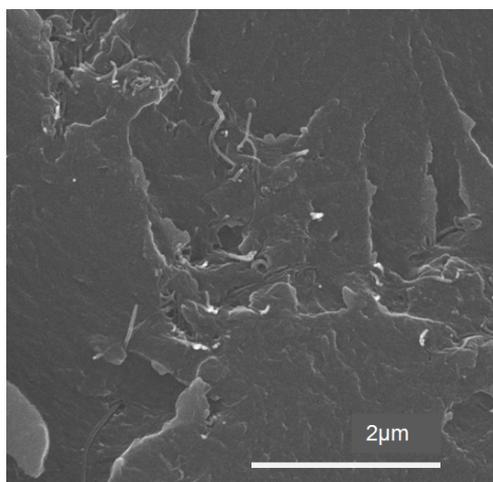
Fig. 5 SEM micrograph of polymer-MWCNTs nanocomposite (0.20 wt % MWCNTs)
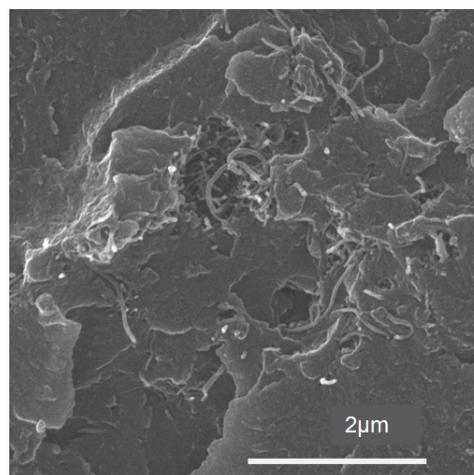
Fig. 6 SEM micrograph of polymer-MWCNT-F1 nanocomposite (0.20 wt % MWCNT-F1)
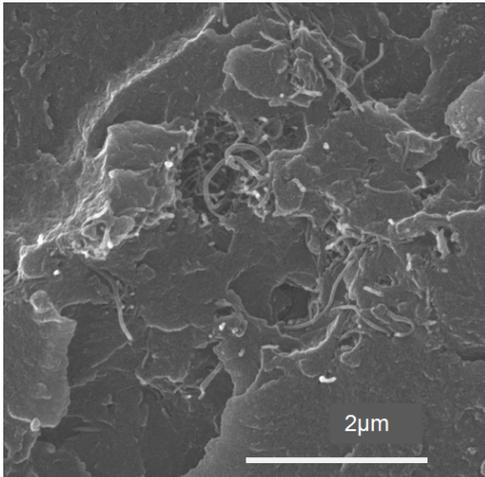
Fig. 7 SEM micrograph of polymer-MWCNT-F2 nanocomposite (0.20 wt % MWCNT-F2)
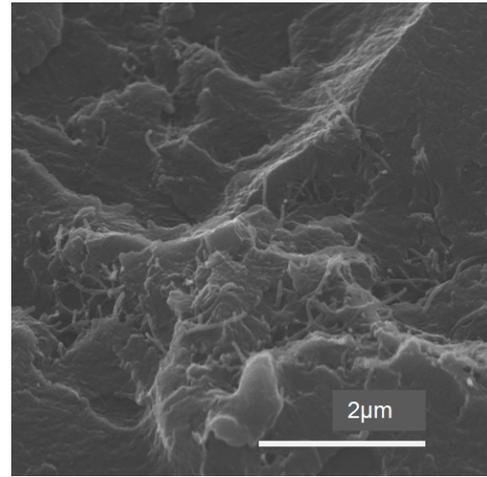
Fig. 8 SEM micrograph of polymer-MWCNT-F3 nanocomposite (0.20 wt % MWCNT-F3)

Mechanical tests. Most polymers exhibit poor mechanical properties which may be improved by adding different kind of materials [34]. Using iron oxide nanopowder a better mechanical behavior can be obtained even for small content of additive [35, 36]. Polyester-MWCNTs nanocomposite with carbon nanotubes and functionalized MWCNT-F1, MWCNT-F2 and MWCNT-F3, at different contents (0.10 wt%, 0.15 wt%, 0.20 wt%) were submitted to three-point bending test. The following characteristics are measured: σ_r - bending strength at break, and E - bending modulus.

Based on experimental data, the influence of carbon nanotubes concentration was assessed by relative variation of specified parameters from three-point bending test. Relative variation ($\Delta x/x_i$) of the characteristics measured for polyester-MWCNTs nanocomposite samples are calculated by the following equation:

$$\frac{\Delta x}{x_i} = \frac{x_i - x_0}{x_i} \cdot 100 \qquad (2)$$

where, x_i is the characteristic measured through the three-point bending test (σ_r = bending strength at break, E = bending modulus of polymer-MWCNTs sample). The subscript i is related to the concentrations (0.10 wt%, 0.15 wt%, 0. 20 wt%) of carbon nanotubes and x_0 is the characteristic measured from three-point bending test of the polyester matrix.

Table 2 contains results concerning the relative variation of bending strength at break and relative variation of bending modulus for polyester-MWCNT nanocomposites, using different types of MWCNTs (pure and functionalized, MWCNT-F1, MWCNT-F2 and MWCNT-F3), depending on concentration of carbon nanotubes.

Table 2: Relative variation of bending strength at break and bending modulus

	MWCNTs content					
			0.20%wt			
	0.10%wt	0.15%wt		0.10%wt	0.15%wt	0.20%wt
	Mechanical properties [%]					
	$\Delta\sigma_r/\sigma_r$			$\Delta E/E_p$		
Polyester/MWCNT	5.228	7.290	9.874	0.673	2.395	4.968
Polyester/MWCNT-F1	7.185	10.046	11.845	4.493	8.166	10.486
Polyester/MWCNT-F2	7.166	10.153	12.709	1.324	8.481	12.557
Polyester/MWCNT-F4	13.432	14.746	18.598	7.499	10.442	16.268

The results for bending strength at break ($\Delta\sigma_r/\sigma_r$) are shown in the first three columns of the Table 2, where it can be observed the upward trend with concentration of MWCNTs. The values of bending modulus highlight the same increasing tendency (last three columns of table 2, $\Delta E/E_p$).

It is noticed that through the functionalization of carbon nanotubes, the mechanical characteristics of the nanocomposites have increased. In the case of the first and the second type of functionalization (polyester-MWCNT-F1 and polyester-MWCNT-F2), it can be seen a rising aspect of the relative variation of mechanical characteristics, taking closer values. This is attributed to similar improved dispersion of functionalized carbon nanotubes into the polyester matrix.

Moreover, for nanocomposite polyester-MWCNT-F3, the relative variation of bending strength at break is almost double than that of nanocomposite polyester –MWCNTs, due to better dispersion of carbon nanotubes coated with iron oxide (III). Mechanical testing revealed clearly the best behavior that was obtained for the nanocomposite polyester-MWCNT-F3.

Electrical conductivity. As regards electrical behavior, it is proved that filling polymers with small content of certain nanopowders it is possible to change the electrical conductivity of the composite matrix [37]. The electrical conductivity of pure MWCNTs, is greater than 1 S/m (according to the specification of the supplier). As for the polyester used in our research, the electrical conductivity measured was about 2×10^{-7} S/m.

Accordingly, once carbon nanotubes were introduced into polyester matrix, the electrical conductivity of resulted nanocomposite exhibits an obvious increase in comparison with that of the polyester. Therefore, we examined the effect of carbon nanotubes content on electrical conductivity of nanocomposites polyester-MWCNT, depending on different types of functionalization (pure, F1, F2 and F3).

The samples of all types of nanocomposites were investigated: polymer-MWCNTs nanocomposite at three different concentrations (0.10% wt., 0.15% wt., 0.20% wt.), using as-received and functionalized carbon nanotubes (MWCNTs, MWCNT-F1, MWCNT-F2, MWCNT-F3). Working frequency of electrical measurements was 100 kHz, and the results have been summarized in Table 3.

Two types of measurements were performed, on the surface and into the volume of the material under test. Surface conductivity is calculated on the basis of resistivity measurement when the electrodes are in contact with the same side of the composite sample.

The volume conductivity is determined on the basis of resistivity measurement when the electrodes are in contact with opposite sides of the material under test and it is considered for the assessment of electrical properties of polymer composites after enrichment with nanoparticles. Electrical conductivity, resulted from measurement into the volume of the sample, for polymer-MWCNTs (0.10% wt.) has a maximum value of 2.43×10^{-4} S/m and the minimum was for the polymer-MWCNT-F1 (1.49×10^{-4} S/m) at the same concentration. Otherwise, for the polymer-MWCNT-F2 and the polymer-MWCNT-F3, electrical conductivity takes closer values (2.14×10^{-4} S/m and 2.13×10^{-4} S/m). As for surface conductivity, we noticed that the type of functionalization

has a great influence, and it takes a minimum of 1.52×10^{-3} S/m for polymer-MWCNT-F2 (0.10% wt.) and a maximum of 2.50×10^{-3} S/m for polymer-MWCNT-F3 (0.10% wt.).

Table 3: Electrical conductivity of nanocomposite samples for 100 kHz

Composite sample	Type of measurement	Electrical conductivity [S/m]		
		MWCNT content		
		0.10% wt	0.15% wt	0.20% wt
Polymer -MWCNT	Volume	2.43E-04	4.35E-04	9.64E-04
	Surface	1.85E-03	2.38E-03	5.73E-03
Polymer -MWCNT-F1	Volume	1.49E-04	1.65E-04	1.71E-04
	Surface	1.84E-03	1.44E-03	1.47E-03
Polymer -MWCNT-F2	Volume	2.14E-04	3.60E-04	3.62E-04
	Surface	1.52E-03	2.01E-03	2.01E-03
Polymer -MWCNT-F3	Volume	2.13E-04	3.25E-04	6.34E-04
	Surface	2.50E-03	2.07E-03	4.32E-03

The results for the nanocomposites with 0.15% wt. MWCNTs with different types of functionalization are shown in the second column of Table 3.

From this table, it can be noticed a maximum volume conductivity of 4.35×10^{-4} S/m for the polymer-MWCNTs, and a minimum of 1.65×10^{-4} S/m for the polymer-MWCNT-F1, in the case of a concentration of 0.15% wt. carbon nanotubes. On the other hand, for the same concentration of carbon nanotubes, the surface conductivity records a minimum value of 1.44×10^{-3} S/m for polymer-MWCNT-F1 system and a maximum value of 2.38×10^{-3} S/m for polymer-MWCNT system.

Measurements performed during the electrical tests for nanocomposites with polymer-MWCNTs (0.2 wt%) are shown in the third column of the Table 3. We noticed a quite large range for volume electrical conductivity, with a minimum of 1.71×10^{-4} S/m (polymer-MWCNT-F1) and a maximum of 9.64×10^{-4} S/m (polymer-MWCNTs). Surface electrical conductivity exhibits a maximum value of 5.73×10^{-3} S/m (polymer-MWCNTs) and a minimum of 1.47×10^{-3} S/m (polymer-MWCNT-F1).

It can be seen that the volume electrical conductivity features an rising tendency with increasing MWCNTs concentration. The nanocomposite with MWCNT-F3 provides the best value for surface electrical conductivity, 4.32×10^{-3} S/m, even if this is under the value for the polymer-MWCNTs, 5.73×10^{-3} S/m. It was clearly proved that surface conductivity takes greater values as compared to those of volume conductivity. Anyway, the samples of nanocomposites obtained in this research, feature an electrical conductivity with several orders of magnitude over the polymer matrix which is definitely insulator.

As regards the nanocomposites with pure and functionalized MWCNTs, at a concentration of 0.10% wt., it was difficult to establish a rule for surface electrical conductivity tendency. This is in agreement with viscosity measurements and SEM analysis, showing that MWCNTs dispersion for this concentration, is inadequate due to formation of agglomerations. When the concentration increases at 0.20 wt%, the agglomeration phenomenon is diminished.

In the case of nanocomposites containing as-received MWCNTs and MWCNT-F3, it can be seen that the volume and surface electrical conductivity tend to increase with rising concentration (except for polymer-MWCNT-F3, surface measurement).

In this case, for a 0.05% wt. increase of the concentration, from 0.1 % wt. to 0.15 % wt., the electrical conductivity increases almost two times. For example, for the nanocomposite polymer-MWCNTs, the volume electrical conductivity increases from 2.43E-04 S/m (0.10 % wt.) to 4.35E-04 S/m (0.15 % wt.) and finally reaches 9.64E-04 S/m (0.20 % wt.).

The same trend can be seen for the nanocomposite polymer-MWCNT-F3, when the volume electrical conductivity increases from 2.13E-04 S/m (0.10 % wt.) to 3.25E-04 S/m (0.15 % wt.) and reaches 6.34E-04 S/m (0.20 % wt.).

The nanocomposite polymer-MWCNT-F1 does not exhibit upward trend. We can conclude that in the case of nanocomposites polymer-MWCNTs and polymer-MWCNT-F3, the graphite structure of carbon nanotubes does not changes [33].

As regards nanocomposites polymer-MWCNT-F1 and polymer-MWCNT-F2, graphite structure of carbon nanotubes is affected by the opening of their ends as well as by the grafting of functional groups resulted from the oxidative reaction.

4. Conclusions

Rheological analysis reveals the increasing interactions of carbon nanotubes with polyester matrix. This is proved by an increase in viscosity. In the case of reaching a maximum rate of interactions due to percolation process, the viscosity undergoes the highest variation.

The highest viscosity values were found at different concentrations, depending on the type of functionalization, as follows: 0.15 % wt. for polymer-MWCNT-F1 and polyester-MWCNT-F2 nanocomposite respectively, and 0.20 % wt. for polyester-MWCNT-F3 nanocomposite. Therefore, it is expected to exist an optimum value of MWCNTs content in a range between 0.15 % wt. and 0.20 % wt.

SEM analysis underlines the dispersion degree of carbon nanotubes into polyester matrix at 0.20% wt. for different types of carbon nanotubes functionalization. It was observed that functionalization process assures a better dispersion of carbon nanotubes into resin. This is in agreement with the fact that functional groups are responsible for the development of strong bonds with esteric groups from polyester resin.

The iron (III) oxide layer deposited on the surface of carbon nanotubes determines the breaking of MWCNTs agglomerates through the *wedge effect*.

The attractive forces van der Waals, acting among the carbon nanotubes, are diminished by *wedge effect*, that means an easier separation of the carbon nanotubes.

Mechanical testing of the nanocomposites, enhanced with functionalized MWCNTs, shows increasing values related to the increasing concentration of the carbon nanotubes. In case of the first and second type of nanocomposites (MWCNT-F1 and MWCNT-F2) the relative variation of mechanical parameters (bending strength at break, bending modulus) increases taking closer values, due to a comparable level of the dispersion provided by the functionalizations F1 and F2.

The results demonstrate that polyester-MWCNT-F3 nanocomposite, exhibits the best mechanical behavior, and justifies the beneficial effect of the functionalization F3 on the dispersion of the carbon nanotubes.

Electrical conductivity of the polyester matrix increases with three or four orders of magnitude, when adding a small amount of carbon nanotubes. Electrical conductivity of nanocomposite with functionalized carbon nanotubes (polyester-MWCNT-F1 and polyester-MWCNT-F2) is lower than that of nanocomposites with pure carbon nanotubes.

This aspect is explained by the modification of graphite structure of carbon nanotubes as a result of oxidative functionalization. As for polyester-MWCNT-F3 nanocomposite, its electrical behavior is closer to that of polyester-MWCNT nanocomposite. This is due to the fact that chemical deposition of the iron (III) oxide does not change the structure of carbon nanotubes.

The best mechanical results were obtained in the case of nanocomposite with 0.20% wt. MWCNT-F3. As well, electrical tests, revealed good values of conductivity for polyester with 0.20% wt. MWCNT-F3, over the values obtained for MWCNT-F1 and MWCNT-F2 nanocomposites, and very closer to those of polyester-MWCNT.

This means there was obtained an adequate distribution of MWCNT-F3 into polyester matrix, that was confirmed by SEM analysis.

Finally, taking into account all tests and results discussed herein, we can conclude that by adding to polyester matrix a small amount of MWCNT-F3 it is possible to obtain improved properties of polyester composite.

References

[1] K. Liao, S. Li, Appl Phys Let **79** (25), 4225 (2001).

[2] M. Wang, K. P. Pramoda, S.H. Goh, Polymer **46** (25), 11510 (2005).

[3] E.T. Thostenson, T.W. Chou, Journal of Physics D-Applied Physics **35**(16), L77 (2002).

[4] Y. Lin , B . Zhou, K. A. Shiral, P. Liu , L. F. Allard, Y. Sun, Macromolecules
     36 (19), 7199 (2003).

[5] J. Obrzut, J.F. Douglas, S.B. Kharchenko, K.B. Migler, Phys. Rev. B **76**, 195420 (2007).

[6] O. Regev, P.N.B. ElKati, J. Loos , C.E.Koning, Adv Mater **16**(3), 248(2004).

[7] S.J.V. Frankland, A.Caglar, D.W. Brenner, M. Griebel, J Phys Chem B
     106(12), 3046 (2002).

[8] B. Duk Yang, K.H. Yoon, K.W. Chung, Materials Chemistry and Physics **83**, 334 (2004).

[9] F. H. Gojny, J. Nastalczyk , Z. Roslaniec , K. Schulte, Chemical Physics Letters
     370(5-6), 820 (2003).

[10] O.A. Shenderova, V.V.Zhirnov , D.W. Brenner, Crit Rev Solid State Mater Sci
      27(3–4), 227 (2002).

[11] J. Chen, R. Ramasubramaniam , C. Xue , H. Liu, Advanced Functional Materials
      16 (1), 114 (2006).

[12] Z. Guo, K. Lei , Y. Li , H. Wai , S. Prikhodko , H.Thomas Hahn , Composites Science and
      Technology **68** 1513–1520 (2008).

[13] P. Pötschke, T.D. Fornes , D.R. Paul, Polymer **43**, 3247–3255(2002).

[14] J. Zhu, H. Peng, F. Rodriguez-Macias, J.L. Margrave, V.N. Khabashesku, A.M. Imam,
      K. Lozano, E.V. Barrera, Advanced Functional Materials **14** (7), 643-648(2004).

[15] X. Y. Gong, J. Liu, S. Baskaran , R. D. Voise, J.S. Young, Chemistry of Materials
      12 (4), 1049 (2000).

[16] O. Rhoads, Z. Li, J. H. Harwell, L. Balzano, D.E. Resasco, Journal of Physical Chemistry B
      107(48), 13357 (2003).

[17] P. Liu, European Polymer Journal **41**(11), 2693 (2005).

[18] L.W. Qu, Y. Lin , D. E. Hill, Macromolecules **37**(16), 6055 (2004).

[19] Y. Gogotsi, Nanomaterials Handbook, CRC PRESS (Eds.), Carbon Nanomaterials, Taylor &
      Francis, USA (2006).

[20] T. Ramanathan, H. Liu , L.C. Brinson, Journal of Polymer Science Part B-Polymer Physics
      43(17), 2269 (2005).

[21] M.K. Yeh, N.H.Tai, J.H. Liu, Carbon **44** (1), 1 (2006).

[22] M. Olek , J. Ostrander , S. Jurga , Nano Lett **4** (10), 18895(2004).

[23] J.G. Yu, K. L. Huang, Chinese Journal of Chemistry, 560 (2008).

[24] A.V. Desai, M. A. Haque, Thin-Walled Struct. **43**(11), 1787 (2005).

[25] J. Sandler, M.S.P.Shaffer,T. Prasse, W. Bauhofer, K. Schulte, A.H. Windle, Polymer
      40 (21), 5967 (1999).

[26] V. Lordi, N. Yao, J Mater Res. **15** (12), 2770 (2000).

[27] S. Bose, A. R. Bhattacharyya, R. A. Khare, A.R. Kulkarni , T. Umasankar Patro,
      P. Sivaraman, Nanotechnology **19**, 335704. doi:10.1088/0957-4484/19/33/335704 (2008).

[28] S.G. Advani, Processing and Properties of Nanocomposites, World Scientific Publishing
      Company, USA (2007).

[29] C.A. Martin, J.K.W. Sandler et al., Polymer **46** (3), 877 (2005).

[30] T. Kimura, H. Ago, Advanced Materials **14**(19), 1380 (2002).

[31] M.C. Paiva, B. Zhou , K.A.S. Fernando , Y. Lin ,J.M. Kennedy ,Y.P. Sun, Carbon
      42 (14), 2849 (2004).

[32] D. Dima, M. Murarescu, G. Andrei, Digest Journal of Nanomaterials and Biostructures
      5(4) 1009-1014.

[33] S.H. Lee, E. Cho, S. H. Jeon, J.R. Youn, Carbon **45** (14), 2810 (2007).

[34] L. Deleanu, I.G. Birsan, G. Andrei, M. Ripa, P. Badea, Materiale Plastice
     44 (1), 66 (2007).
[35] D. Dima, G. Andrei, Materialwissenschaft und Werkstofftechnik **34** (4), 349 (2003).
[36] G. Andrei, D. Dima, I. Birsan, L. Andrei, A. Circiumaru, Materiale Plastice
     46 (3), 284(2009).
[37] A. Circiumaru, G. Andrei, I. Birsan, A. Semenescu, Materiale Plastice **46** (2), 211 (2009).
[38] V. Bria, D. Dima, G. Andrei, I.G. Birsan, A. Circiumaru, Tribology in industry,
     33 (3), 104 (2011).
[39] G. Andrei, D. Dima, I.G. Birsan, L. Andrei, A. Circiumaru, Materiale Plastice,
     46 (3), 284 (2009).
[40] L. Ciupagea, G. Andrei, D. Dima, M. Murarescu, Digest Journal of Nanomaterials and
     Biostructures, **8** (4), 1611 (2013).