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AN OBTAINING METHOD FOR CARBON NANOTUBES WITH MODIFIED SURFACE

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Abstract: *It is well-known the fact that carbon nanotubes (CNTs) contain carbon atoms in different hybridization states (sp^3 and sp^2), that generates complex structures (diamond and graphite respectively). These multiple connections generate strong interaction of forces between particular CNTs, that means Van der Waals forces and also π-π type those immediate result in the agglomerates obtaining and, singularizing the composite materials, the first effect is clusters generation process. The physical-chemical properties of nanocomposite materials are influenced by the appropriate CNTs dispersion obtaining in the matrix. This fact is efficiently obtained when the interactions energy between CNTs themselves is lower than the dispersion energy cumulated with the interactions energy between CNTs and the matrix. The dispersion energy considers CNTs blending techniques inside the matrix and the interactions energy between CNTs and the matrix supposes the chemical bond obtaining and physical-chemical interactions between CNTs and the matrix. The aim of this paper is to present some techniques of oxidative chemical treatment in order to obtain a CNTs functionalized surface as well as some techniques of coating with ceramic materials molecular layers in order to increase the chemical bond energy and the physical-chemical interactions between CNTs and the matrix. We used simple treatment methods of CNTs in acidic solutions ($HNO_3 – H_2SO_4$) and basic solutions (NH_3) having hydrogen peroxide as the oxidant agent (H_2O_2 30%). CNTs coating process with ceramic materials was made by using the precipitation method of their components (Fe_2O_3) from the supersaturated aqueous solutions.*

Keywords: *nanoparticles, functionalization, ceramic materials, multi wall carbon nanotubes (MWCNTs).*

Introduction

An increased CNT – matrix interfacial bond can be obtained due to nanocomposites cracking resistance improvement that represents one of the most important aspects ensuring the shear stress transfer to the reinforcement. The use of this functionalization process in order to obtain an improved connection between matrix and nanotubes was largely presented by Frankland and co. They showed that the mechanical properties improvement can be obtained if less than 1% of carbon atoms from CNTs make reactive bridges to the matrix.

A great discovery in CNTs reinforcing composites development was made by CNTs chemical functionalization with multifunctional amines.

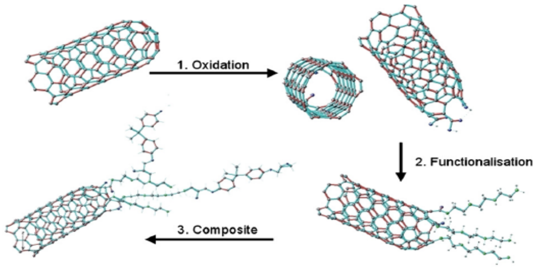

Fig.1 CNTs functionalization process [1]

An oxidative treatment on CNTs was made in order to obtain the carboxylic groups attached to their surfaces. This carboxylic group obtaining process is combined with CNTs ends opening (Fig.1). This phenomenon would allow a direct connection between different nanotubes ends, process that facilitates the mechanical reinforcement. In the next step, the carboxylic groups would react with the multifunctional amines in order to make chemical links (ionic or covalent in this case) due to the acid – base reaction. Once the resin is added, the free amino functions on CNTs surface would react with macromolecules contributing to the new links obtaining process that improves the matrix – nanotube interface.

Excepting the direct chemical functionalization, another simple method of CNTs and matrix polarity assuming is the use of surfactants. The advantage of this procedure is the physical adhesion that is not affecting the CNTs structural quality. The functional groups covalent integration is always reported to the structural modifications of the graphitic layers. [2]

The surfactants use is a general method that represents some licensed procedure base [3], [4], [5]. Surfactants can make the CNTs dispersion into polymeric matrix, so that the attraction forces between them are surpassed. The dispersion mechanism is made by the multiple interactions between surfactants and the two main components of the nanocomposite, which are: the matrix and CNTs. The conjugated polymers of the main resin can be physically linked by CNTs, so that being used for CNTs – matrix compatibility improvement. Anyway, the covalent bond is stronger than the physical interactions and the assumptions anticipate an insignificant influence on CNTs mechanical performance. Thus, the final conclusion is that CNTs surface chemical functionalization process is a key point in CNTs / polymer composite development.

Materials and methods

The aim of this paper is the presentation of carbon nanotubes treatment methods for their compatibilization with the polymeric matrix in order to obtain an efficient dispersion. [10], [11]

The method consists in carbon nanotubes dispersion insurance through chemical processes of surface functionalization due to a controlled oxidative attack, followed by a coupling process of the chemical compatible groups with the polymeric matrix. It is also used a covering method with a particles molecular layer obtained after a crystallization process from a saturated solution. [8]

The modified nanotubes after this process are more efficiently dispersed by a mechanical, ultrasonic and vibrant magnetic field stirring in the polymeric matrix. [12]

We applied the oxidative method using chemical agents like: HNO_3, H_2SO_4 and H_2O_2 as well as functionalization agents, like: NH_3, in order to break the C-C bonds from the multi-wall carbon nanotubes surfaces and to create new functional groups covalently bonded with them. It was used three functionalization methods of the multi-wall carbon nanotubes surfaces.

The first surface functionalization method is made by using a mixture of HNO_3: $H_2SO_4 = 1:3$ (HNO_3 65% and H_2SO_4 98%) for 24 hours at 295K.

It follows a step to step washing process of the functionalized nanotubes with bidistilled water till pH = 1 because above this pH value the carbon nanotubes free sedimentation from the solution can not be efficiently made, so that another separation technique should be applied. Under these conditions, nanotubes' cleaning from the solution lasts 10 minutes. The fair liquid is separated and follows a step to step washing process of the functionalized nanotubes with bidistilled water till pH = 6. Under these conditions, nanotubes separation from the solution is efficiently rmade by a centrifugation process at 6000rpm. In order to obtain sustainable drying, we applied a step to step washing process of the functionalized nanotubes using anhydrous ethylic alcohol. It follows an oven drying of 8 hours at 378K and finally the dry milling process.

The second surface functionalization method consists in carbon nanotubes functionalization achievement by using a mixture of H_2O_2: NH_3 = 1:4 (H_2O_2 30% and NH_3 25%) for 48 hours at 295K, followed by step to step washing process of the functionalized nanotubes with bidistilled water till pH = 8 because above this pH value the carbon nanotubes free sedimentation from the solution can not be efficiently made, so that another separation technique should be applied. It follows the nanotubes' separation from the solution that lasts about 15 minutes, a step to step washing process of the functionalized nanotubes with bidistilled water till pH = 7, nanotubes centrifugation from the solution at 6000rpm. The step to step washing process of the functionalized carbon nanotubes using anhydrous ethylic alcohol contributes to the fast drying process efficiently ended by an oven drying for 8 hours at 378K. Finally, the obtained powder is dry milled.

Another method of modifying carbon nanotubes surface for an increased compatibility with the polymeric matrix consists in covering technique with a molecular layer of Fe_2O_3 [6], [7]. The first step of this method is represented by carbon nanotubes dispersion using a solution of 1% sodium dodecyl sulphate (SDS) as surfactant agent followed by ultrasonication process for 10 minutes with BANDELIN HD3200 Electronic GmbH & KG Berlin Germany as presented in fig.2, having 40% amplitude. Subsequently, a solution of $FeCl_3$ 1mol/L was quantitative added under a magnetic stirring for 5 minutes and the resulted solution is ultrasonicated for 10 minutes using the same ultrasounds generator, at the same parameters.

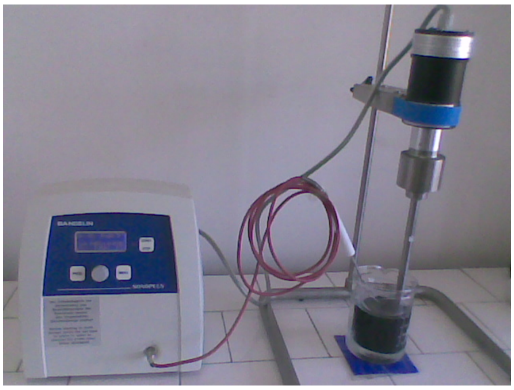

Fig.2 CNTs suspension ultrasonication using BANDELIN HD3200 as generator

After that, a solution of NH_3 1mol/L till pH = 8.5 was quantitatively added, followed by the same ultrasonication process. The final stage consists in a step to step washing process of the nanotubes covered by a molecular layer of Fe_2O_3 particles using bidistilled water till pH = 5.5, followed by a centrifugation process of the nanotubes from the solution at 6000rpm, the final washing with anhydrous ethylic alcohol, the oven drying for 8 hours at 443K and finally the dry milling process.

Results and Discussion

The obtained materials complying with these methods presented above were analyzed in order to show the modifications appeared in comparison with the initial CNTs. For this reason, we used analysis techniques of the functional groups from CNTs surface level as the oxidative decoupling result of C-C bonds localized at MWCNTs external tube level. The un-oxidized inner side tubes maintain the MWCNTs initial properties and the functionalized or covered with a molecular layer of Fe_2O_3 external tube makes a better compatibility between matrix and nanotubes.

Fe_2O_3 molecular layer has an important function to interpose to the adhesion forces between carbon nanotubes creating a coating while the deposit is forming on their surface. The nanotubes' analysis by X ray fluorescence presents the primary modifications due to the chemical treatments of surface modifications (Table 1).

Table 1

XRF analysis

CNT Elem.	Pure	F_1	F_2	F_3
Fe	1120.15	640.67	1093.34	55167.66
Ni	7185.23	4612.44	6775.87	4109.67
Co	157.55	126.15	160.15	27.85
Mn	47.47	35.67	55.61	244.58
Cr	1302.86	593.27	1242.42	610.21
V	424.23	38.16	300.37	437.52
Ti	1027.25	41.11	755.16	3277.15
Ca	1901.15	507.16	672.23	1255.14
K	225.16	353.85	281.93	2889.62

In order to present the modifications suffered by CNTs surfaces after these three different treatments applied, we performed an XRF analysis with NITON XLt 793 Thermo Fischer Scientific USA and the results were presented in table nr. 1.

It can be observed that considering the samples covered with a molecular layer of Fe_2O_3 (coded with F_3), Fe concentration is about 5.52 %. This covering layer represents a consistent deposit of Fe (III) oxide enough for generating in the composite material structure some magnetic properties utilized also in the obtaining step represented by the dispersion process in a vibrant magnetic field as well as subsequent at the general properties of the composite material. [9]

Referring to Ni and Co presence, the variations are not very important meaning that in the functionalization and covering process there are not losses or accumulations due to the chemical reagents. It does not happen the same thing at Mn, resulting in an increased value about four times for the samples covered by a molecular layer of Fe_2O_3.

Considering Cr value, this one maintains quasi-constant referring to the second method of functionalization and decreases at a moiety in the first functionalization method as well as in the covering process with a molecular layer of Fe_2O_3.

Titanium and K present a spectacular increase in F_3, this value representing a result of the chemical reagents influence.

At calcium there are no significant variations excepting the functionalized samples by method 1 or 2 as a result of frequently washings as well as chemical reagents attack.

Moreover, the nanotubes were analyzed referring to their behaviour in the polymeric matrix, so that we analyzed their concentration influence on the rheological properties. We analyzed the influence of pure carbon nanotubes (coded CNT-pure) concentration and modified by functionalization and covering process (coded CNT-F_1, CNT-F_2 and CNT-F_3 respectively).

The aim of this study was to determine the optimum value of carbon nanotubes concentration in the polyester resin in order to correspond to the technological requests for a nanocomposite material obtaining process. CNTs optimum concentration value in polymeric matrix can be determined using a viscosity variation study in relation to nanotubes concentration from the polymeric resin, in accordance with scientific literature.

Experimentally the optimum concentration value is determined at an important viscosity increasing moment, after that a constant value is registered or even a decreasing value is possible. The experimental values are synthetically presented in fig.3.

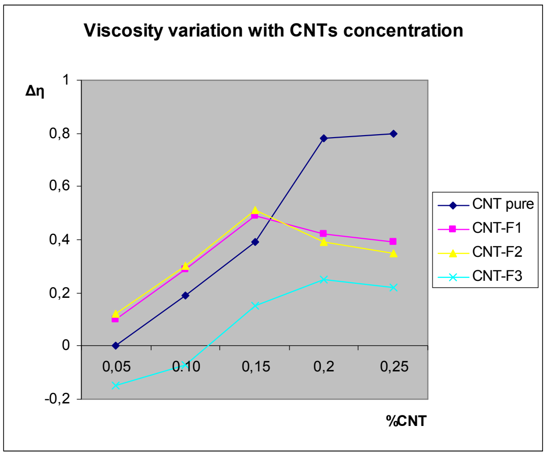

Fig.3 Viscosity variation depending on CNTs concentration

It can be observed that CNT-F_1 and CNT-F_2 respectively present wide equal variations and their plots are similar and the experimental viscosity variation data are quite higher than CNT-pure data. This can be explained by carbon nanotubes dispersion improving at CNT-F_1 and CNT-F_2 respectively in polyester matrix at the same concentration and under technological experimental conditions. This result is an expected one, considering the increased energy value when between the polymeric matrix and the functional groups the strong covalent bond is present. [13]

In the CNT-F_3 case, Fe_2O_3 presence can determine contradictory effects, which mean: Van der Waals and π-π interactions decline between carbon nanotubes due to oxide layers "arrow effect" that interpose themselves and, the most important effect would be the magnetically interactions that are responsible for clusters generation in the matrix added with covered nanotubes. That is the reason because new dispersion energy must be introduced in order to block clusters formation; this target is technological realizable due to an external vibrant magnetic field introduction. [14]

Conclusion

Considering the experimental data analysis and processing, an optimum concentration value about 0.15% CNT in CNT-F_1, CNT-F_2 and CNT-F_3 systems respectively was obtained, excepting CNT-pure system which optimum value was registered at 0.20% CNT, according to the scientific literature data concerning nanoparticles suspensions.

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