EFFICIENT DISPERSION OF CARBON NANOTUBES IN POLYVINYLBUTYRAL AND MECHANICAL PERFORMANCE OF COMPOSITES THEREOF

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Abstract
In this work polyvinyl butyral (PVB) was used both as a dispersing agent for carbon nanotubes (CNTs) into ethanol, and as the matrix for composite tapes obtained by the tape casting technology. Heavily entangled commercial CNTs were used, in order to verify the effective polymer dispersing capability and the methodology. The dispersing effect of PVB is probably due to a polymer wrapping effect, and is evident also at low concentration, even if some bundles of CNTs can remain in the suspension. A slurry of PVB containing various percentages of carbon nanotubes was tape cast to obtain composite tapes, whose mechanical properties depends on both the concentration of CNTs and the type of PVB. If the CNTs concentration is too high, undispersed bundles remain, that reduce mechanical properties. If the PVB chain is too short, no significant mechanical properties improvement is observed.

1 Introduction

Carbon nanotubes exhibit high flexibility, low mass density, large aspect ratio, and experimental data indicate both high tensile modulus and high strength for these materials. These superlative properties of carbon nanotubes make them an excellent reinforcing material for composites reinforcement for a number of applications [1-5]. However, the production of this kind of composite materials is affected by several problems: CNTs have generally a wide distribution of length, diameter, chirality, shape and conformation, and are also characterized by the presence of defects and impurities. Therefore individual CNTs embedded in a polymer only exhibit a fraction of their potential. Thus, the properties of CNTs cannot as yet be fully translated into high strength and stiffness composites. Many studies established the most suitable conditions for the transfer of the properties to individual nanotubes in a polymer composite component. Important prerequisites are the efficient dispersion of CNTs and the establishment of a strong chemical affinity with the surrounding polymer matrix [2,3].
In this paper, we present the results about dispersion of carbon nanotubes in ethanol by use of polyvinyl butyral as dispersing agent, and the use of such a polymer as the matrix in the

preparation, by tape casting, of composite tapes with improved mechanical properties. Polyvinyl butyral is a thermoplastic polymer, easily commercially available with various brands, used in many applications as adhesive, matrix, binder.
The purpose of this paper is not only to obtain carbon nanotubes-polymer composites with suitable characteristics, but also to produces them with low cost raw materials. Therefore we used for our experiments industrial grade nanotubes Nanocyl NC7000. These MWNT are produced by Nanocyl by CVD in large amounts and are currently among the cheaper CNTs on the market.

2 Materials and testing methods

Polyvinyl butyral (PVB) has been used in the form of the commercial Butvar product (produced by Solutia), and two kinds of PVB were used: PVB-98, containing between 18 and 20% of PVOH and with a molecular weight between 5000 and 6000; PVB-76, containing between 12 and 14% of PVOH and with a molecular weight between 10000 and 11000. Nanocyl NC7000 nanotubes were used, with an average diameter of 9.5 nm, average length of 1.5 µm, 90% carbon purity, 10% metal oxide residuum after burning out of the carbon, and a surface are around 250-300 m^2/g.
Tape casting process consist in casting a viscous slurry over a polymeric support, through the use of a doctor blade with controlled gap. The processing method involved the following steps: slurry preparation, tape casting and solvent evaporation. MWCNTs were dispersed in ethanol by sonication and then the polymer was added and the mixture was mechanically mixed. The slurry was then cast on a Mylar support, moving with a controlled speed, and the layer thickness was controlled by the height of the blade and the viscosity of the slurry. The organic solvents were then slowly removed by controlled evaporation in air at ambient temperature. Different samples were prepared by modifying the amount of CNTs.
The viscosity was measured by a Brookfield viscosimeter, while microscopic observations were carried out on a Scanning Electron Microscope Leo 1450 VP, coupled with an Oxford 7353 EDS. Ultrasound cavitation was applied by means of a Sonics VCX 750 Vibra-cell ultrasonic processor. Mechanical testing was carried out on a Sintech 10/D equipment. Tape casting was performed on a self-built system, using a 0,5 mm gap on a Mylar sheet, with speed of 100 mm/min.

3 Results and Discussion

The first part of this work regards the dispersion of carbon nanotubes into ethanol by using polyvinyl butyral as a dispersing agent. Dispersion of carbon nanotube is a rather important topic in literature, due to the importance of dispersion for obtaining good mechanical and physical behavior of the composites [5-8].
In Figure 1 it can be observed that the NC7000 nanotubes appears in a strongly aggregated form. Two aggregations are observed: a first one made by snake-like cylinders with a diameter around 1 µm. A second one consisting in the aggregation of the cylinders into spheroidal particles of some hundred micrometres diameter.
Clearly, any residual aggregation of CNTs in polymer composites will result in inferior properties of the materials. The effective utilization of CNT material in composite applications depends strongly on their ability to be dispersed individually and homogeneously within a matrix [2].

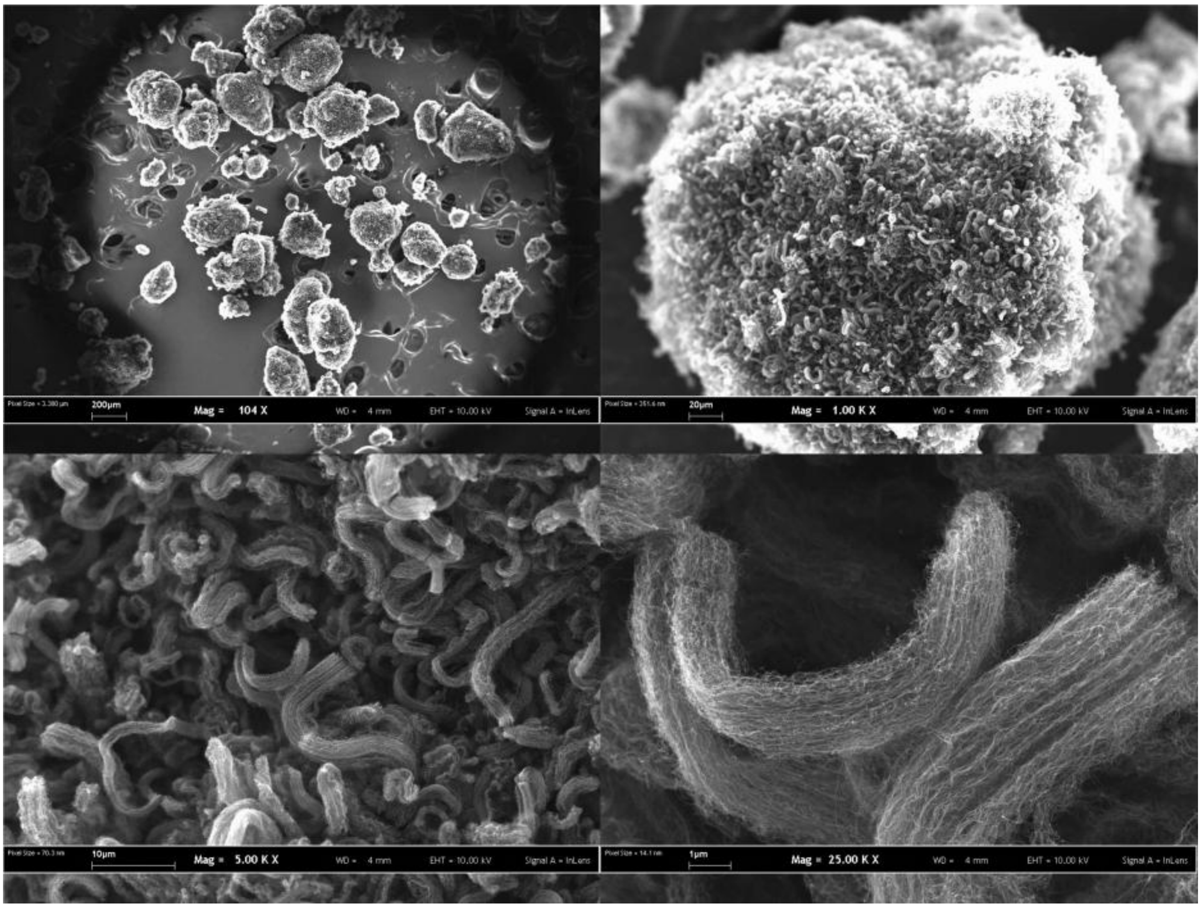

Figure 1. Nanocyl NC7000 nanotubes in their different aggregation forms.

In a first step the nanotubes were dispersed in ethanol containing a high concentration of PVB. Ultrasounds were applied to the carbon nanotubes-ethanol suspension, by using an ultrasonic tip at around 150 W power. Afterwards, PVB-98 was slowly added during mechanical stirring, and both the effect of stirring time and of PVB concentration was studied. The analysis of the dispersion was carried out mainly by SEM observation of the composite tapes.

In the case of 0.5% CNTs concentration in the polymer, when a low stirring time was used (1 hour), carbon nanotubes agglomerates were yet present inside the tape, as shown in Figure 2a. Here a light circular zone can be observed on the section of the tape, that is a bundle of nanotubes that not contains any polymer. When the time was increased up to 24 hours all the agglomerates disappeared (Figure 2b).

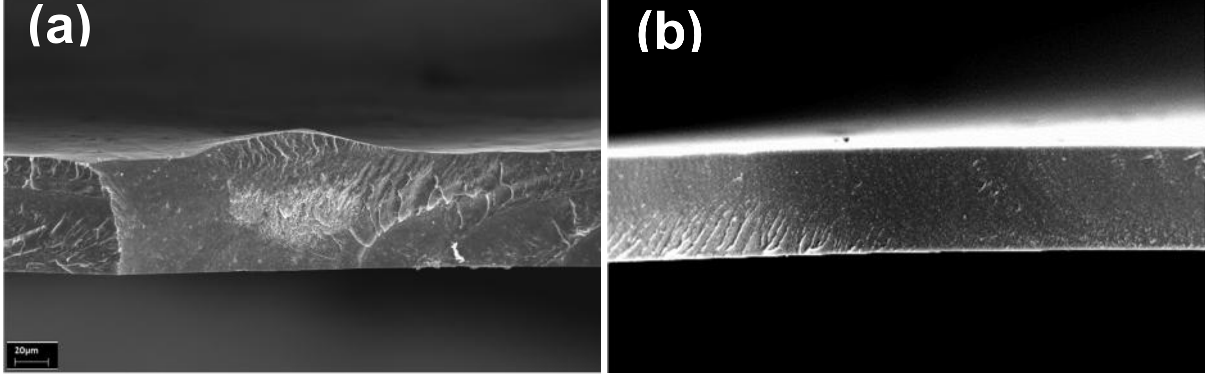

Figure 2. PVB-CNT tapes after ultrasound irradiation of 1 h (a) or 24 h (b).

The effect of PVB concentration on the dispersion was then studied for samples sonicated for 24 hours. The PVB seems to be able to slowly disperse residual bundles of nanotubes, if a previous ultrasonic strong dispersion is carried out. The question that arises is then if the PVB can be used in small amounts as a dispersant for CNTs, or if the required concentration is too high for this task. Thus the effect of PVB concentration on the dispersion of nanotubes was studied: CNT/ethanol ratio was 1/1000, while PVB/CNT ratios of 0, 1, 5, 20, 80, 160 were used. The last one, 160, is the ratio needed for a slurry that presents a convenient viscosity for tape casting. Figure 3 shows the results. The sample without PVB show no trace of dispersion, while the presence of even a small amount of polyvinyl butyral (PVB/CNT ratio equal to 1) allow the dispersion of a very significant amount of nanotubes, even if a small residuum remains on the bottom of the test-tube. By increasing the quantity of PVB it is possible to increase the amount of nanotubes in suspension, even if it is necessary to go up to PVB/CNT = 80 to obtain a complete dispersion of the nanotubes.

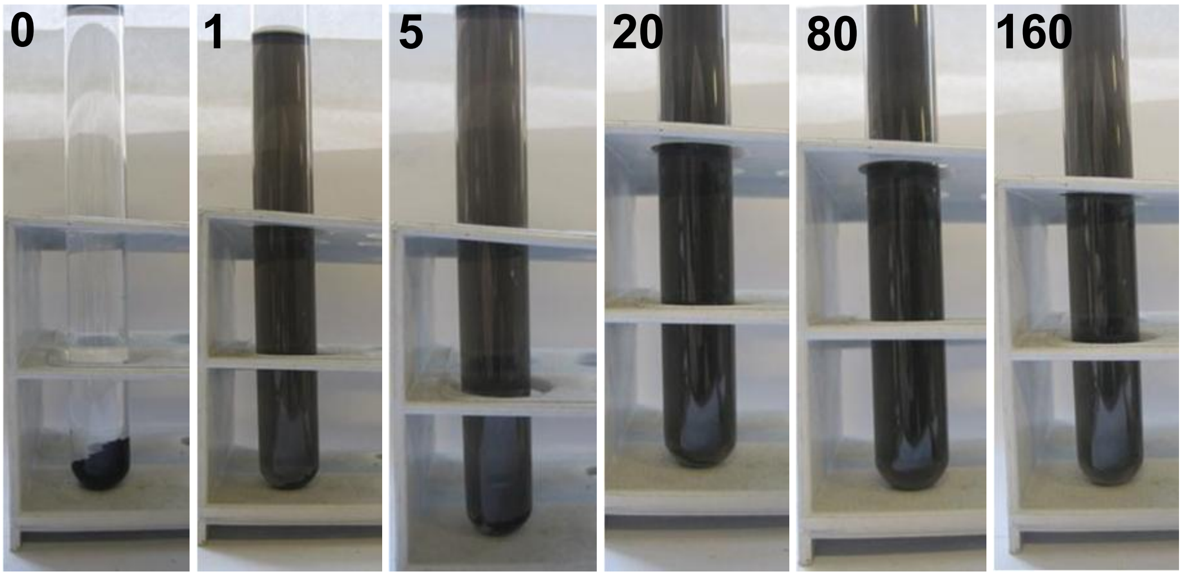

Figure 3. PVB-CNT suspensions in ethanol at different PVB/CNT ratios; from left to right PVB/CNT ratio is equal to 0, 1, 5, 20, 80, 160.

Finally, the effect of carbon nanotube concentration was studied, in the conditions of the slurry, in order to be able to cast composite tapes and to measure their mechanical performance.

In order to obtain uniform and repeatable tape, the tape casting apparatus used in this work requires a viscosity of the slurry in the range of 160-200 cP. Since the nanotube presence in suspension increases the viscosity, in this case not only the CNT/PVB ratio was varied (in order to test composite tapes with different nanotube content) but also the PVB/ethanol ratio, with the aim of keeping the viscosity close to the optimal value. Moreover, in this case two different PVB types were used, and since PVB-76 solutions are more viscous, its concentration in ethanol was slightly less than that of PVB-98.

In Figure 4 it is shown the section of a PVB-98/CNT composite containing 0.5% of carbon nanotubes. In this case the nanotubes are uniformly dispersed within the polymer matrix, and a partial orientation is observed along the casting direction.

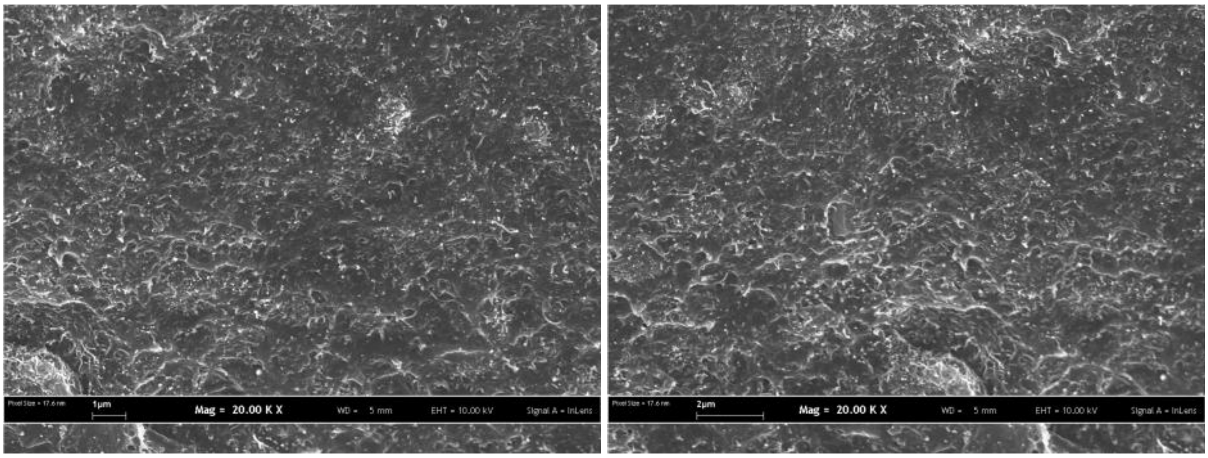

Figure 4. PVB-98/CNT composite containing 0.5% of carbon nanotubes.

In a tape containing 1% of carbon nanotubes (Figure 5) instead the dispersion is less good. Zones with CNTs agglomerates can be observed together with zones with a lower concentration of nanotubes. Small undispersed bundles can also be observed along the tape section.

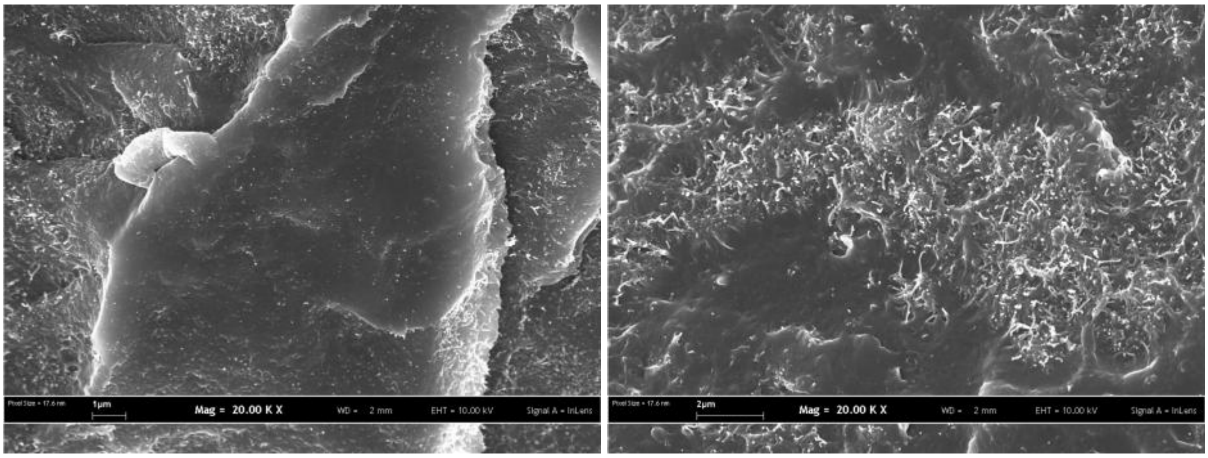

Figure 5. PVB-98/CNT composite containing 1% of carbon nanotubes.

In a tape containing 2.5% of CNTs many nanotubes are present in very large undispersed bundles, so that macroscopic defects are found, as can be observed in Figure 6.

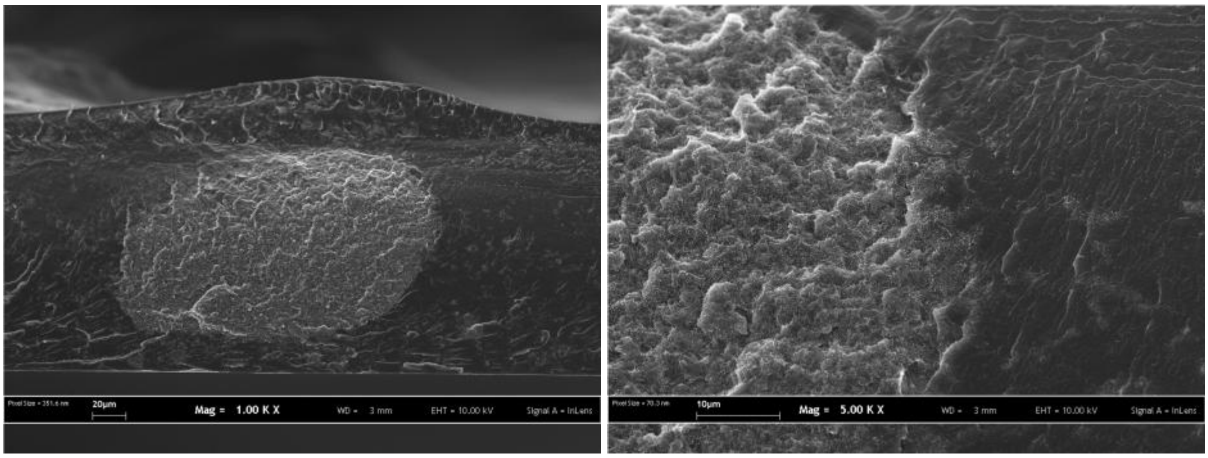

Figure 6. PVB-98/CNT composite containing 2.5% of carbon nanotubes.

The presence of larger agglomerates can be probably ascribed to the higher concentration of carbon nanotubes, that do not allow a complete dispersion during the ultrasonic irradiation step.
Mechanical performance of the composites was measured by tensile tests, and both maximum strength and Young's modulus were calculated. In Figure 7 it is possible to see a typical set of tests for a highly concentrated nanotubes solution (PVB-98, 2.5% of carbon nanotubes). The presence of defects inside the composites heavily influences the maximum strain registered during the mechanical tests. When a defect is present, a crack forms at low strains, while if no defect is present, the strain at break is much larger.

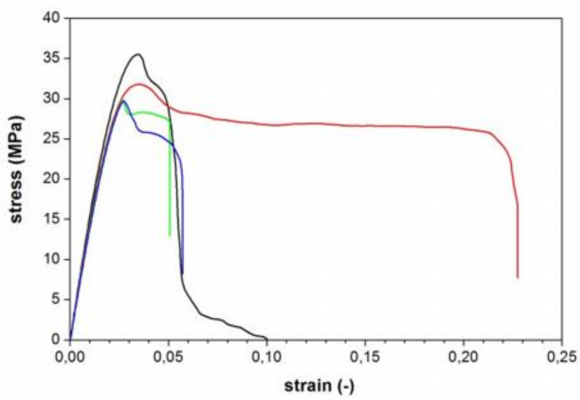

Figure 7. Tensile tests of a PVB-98/CNT composite containing 2.5% of carbon nanotubes.

The maximum strength and Young's modulus are not affected by the nanotubes concentration in composites obtained with PVB-98 (Figure 8). This is probably due to the fact that the chain length of this polymer is too short for a real wrapping of the nanotubes, so that the adhesion between polymer and carbon nanotubes is not effective. With PVB-76 based composites instead both strength and modulus increases substantially for low nanotubes concentration, where the dispersion is optimal, while strength decreases substantially for higher concentration, due to the presence of defects. Young's modulus is less affected by the presence of defects, and only at very high concentration a reduction is observed, due to the difficulties in dispersion in too concentrated suspensions. Due to the higher chain length of PVB-76 it is thought that the interaction with nanotubes is stronger, thus providing an effective reinforcing mechanism.

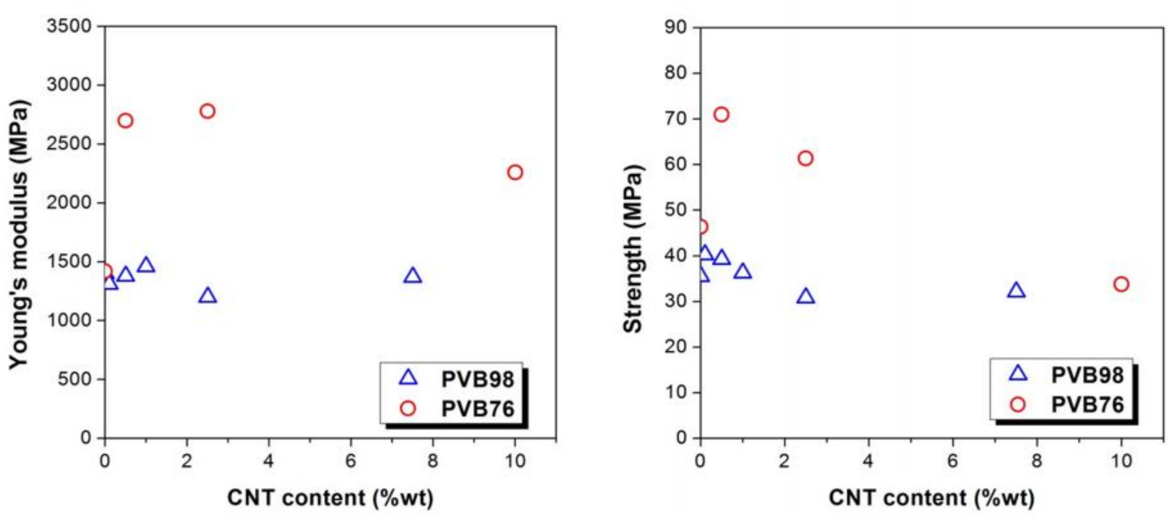

Figure 8. Young's modulus and tensile strength for PVB-98/CNT and PVB-76/CNT composites.

Starting from the data of the PVB-76 reinforced with 0.5% CNTs the modulus and strength of the CNTs was calculated, using a simple law of mixtures and hypothesising a perfect alignment of the nanotubes along the casting direction. Since the alignment is not perfect, these values are a lowest limit for the mechanical performance of CNTs. The calculated values are 260 GPa for CNTs Young's modulus and 5.0 GPa for CNTs strength, that are reasonable lowest limit values for commercial low-cost nanotubes.
By hypothesising that the CNTs are completely dispersed in the 0.5% sample, as is suggested by SEM observation, it was also possible to calculate the percentage of "active" CNTs in the different composites with PVB-76. The results suggest that the maximum concentration of well-dispersed nanotubes in the standard dispersing conditions is lower than 1%, and the other nanotubes are instead organised in bundles, that do not contribute to the overall mechanical properties, and can reduce substantially the strain at rupture by triggering crack formation.

4 Conclusions

Polyvinyl butyral demonstrated to be a good dispersing agent for carbon nanotubes in ethanol, even if heavily entangled CNTs were used (Nanocyl NC7000). If dispersion is correctly carried out by ultrasonication followed by long mechanical agitation, the majority of carbon nanotubes bundles are dissolved, leaving a uniform gray suspension of well separated carbon nanotubes. If a high amount of polymer is used no bundle is observed.
A slurry containing carbon nanotubes dispersed in ethanol with a high concentration of PVB can be used for tape casting, obtaining composite tapes with partially oriented nanotubes. If the concentration of nanotubes in the polymer is sufficiently low, all the CNTs are very well dispersed in the matrix and a significant increase in mechanical properties is observed. If the CNTs concentration increases, then some defects can be formed that avoid the full exploitation of the carbon nanotubes high strength and stiffness, since only a fraction of the nanotubes are contributing to the mechanical properties. Moreover, the strain at fracture is reduced, since the CNTs bundles act as defects.

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