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Polyvinyl butyral-based composites with carbon nanotubes. Efficient dispersion as a key to high mechanical properties

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Abstract

Even if carbon nanotubes and derivatives are commonly used as reinforcing phase in composite materials, also in commercial products, their tendency to agglomerate generally determines a scarce dispersion, thus not maximizing the effect due to the second phase. In this paper, a perfect dispersion of highly entangled nanotubes was achieved by using a very simple approach: exploiting the dispersing effect of a low-cost polymer, polyvinyl butyral (PVB), coupled with standard ultrasound sonication. Several dispersion approaches were tested in order to develop a consistent and widely applicable dispersion protocol. The tape casting technology was subsequently used to produce 100-300 μm thick PVB-matrix composite tapes, reinforced by multiwall carbon nanotubes dispersed according to the optimized protocol. Their mechanical properties were evaluated, and a simple model was used to demonstrate that the effective dispersion of carbon nanotubes is the key to obtain significantly improved properties.

Keywords: Carbon Nanotubes; Dispersion; Mechanical properties; Polymer composite; Polyvinyl butyral.

1. Introduction

After their discovery at the beginning of the 90s [1], carbon nanotubes (CNTs) immediately started to cover a fundamental role in several scientific branches, from physics to chemistry, medicine and biology. In the material science and engineering field, a large number of studies have been conducted on carbon nanotubes, as a consequence of their extraordinary physical and mechanical properties. In particular, since 1991, a large number of attempts have been conducted in order to exploit the outstanding potential of this carbonaceous material as reinforcement in composites. The most

commonly used matrix is the polymeric one (to obtain polymer matrix composites, PMCs) [2–5], but, in the last decade, an increasing number of metal- and ceramic-matrix composites (MMCs [6–9] and CMCs [10–12], respectively) were obtained. Despite massive efforts to optimize CNTs-based composites, the full potential of these reinforcement materials has not been yet exploited, due to the difficulties associated with the dispersion of entangled carbon nanotubes during the processing steps and to the poor interfacial interaction between CNTs and the matrix materials.

The dispersion of nanotubes involves complicated phenomena, since often the carbon nanotubes are produced in bundles or bundle aggregations. Their state is affected by at least two competitive interactions: (1) the interaction of van der Waals forces among carbon nanotubes, responsible for their tendency to aggregate, and (2) the interaction between carbon nanotubes and the medium, which impacts their dispersion [13–16]. The behaviour of single carbon nanotubes or of bundles of carbon nanotubes in a composite is completely different. In fact, in order to achieve an efficient load transfer from the matrix to the reinforcement, CNTs must be uniformly dispersed to the level of isolated tubes individually wetted by the matrix. This homogenous distribution of single nanotubes results in a uniform stress distribution, and minimises the presence of stress concentration centres. Several dispersion approaches have been proposed by numerous researchers [2,17]. They are based on two different concepts: mechanical dispersion and chemo-physical dispersion.

Obtaining a good dispersion of CNTs can be quite a laborious problem in the field of composites preparation, due to several reasons. First, suitable equipment, that uses either high strain or cavitation, must be used. In literature, cavitation is the preferred approach, thanks to the improved quality of the obtained dispersion [18]. For this reason, ultrasounds are generally applied, using a probe sonicator in a suitable solvent. All the dispersion techniques that use mechanical stress to break the nanotubes aggregates entail heating, so that solvent evaporation must also be considered as an issue.

Secondly, singly dispersed nanotubes occupy a large volume, so that solutions with high concentration cannot be easily obtained. When the concentration of the nanotubes to be dispersed is too high, a sort of gel forms during the dispersion process. The origin of this gel must be sought in the fact that the nanotubes that pass from the aggregated form to the dispersed state must be kept sufficiently apart so that they do not interact with one another. If too many nanotubes are present in the same volume, the van der Waals interaction prevails, resulting in the formation of a network of interacting nanotubes that confers a gel state to the dispersion, generally impeding further dispersion [19,20].

In addition, nanotubes are damaged by the application of a mechanical dispersion, both by high shear stresses and by cavitation [21]. Thus, short dispersion times should be used, where possible, to reduce the number of defects created and to limit the observed nanotubes length reduction.

Finally, a suitable solvent must be chosen, with enough affinity with the carbon nanotubes to avoid re-agglomeration of the tubes as soon as the dispersing machine is switched off. Many studies are present in literature on how to choose the best solvent for the nanotubes dispersion [24,25]. Often, however, solvents are either toxic, expensive or have other critical issues, so that the use of a dispersant can be envisaged. Dispersants are molecules with a good affinity with both the nanotubes and a specific solvent (possibly cheap and non toxic), that create an interface layer which mediates the interaction between nanotubes and solvent. The last difficulty to overcome is the characterization of the dispersion itself. While several techniques can be used, no simple quantitative approach is found in the literature.

The present work describes a method for achieving a perfect carbon nanotubes dispersion, starting from severely aggregated tubes, by exploiting the noteworthy dispersing ability of a polymer, polyvinyl butyral (PVB). The use of CNTs in polymer matrix has already been used recently for the preparation of carbon nanotube composites [22–25], obtaining interesting results regarding the improvement of elastic modulus [26] and mechanical properties [22]. However, PVB can be also used as a simple dispersant, that remains in many cases a critical step if good quality composites are to be obtained. Indeed, the lack of dispersion can often explain the reduced improvement of the properties of composites obtained with carbon nanotubes [18,27–29].

In this paper, the dispersion was studied in a common solvent, ethanol, using standard ultrasound sonication and using PVB as dispersant. Then, to correlate the dispersion state of the reinforcement with the mechanical properties of composites, composite tapes were obtained through the tape casting technology, using PVB as a well-known binder [30–33]. The mechanical properties and the microstructure of the obtained tapes were then evaluated.

2. Materials and Methods

Since the purpose of the work was to evaluate the dispersing power of PVB, and to obtain PMCs tapes, low-cost, industrial grade NC7000 nanotubes (Nanocyl™, Sambreville, Belgium) (**Figure 1)** were used. These nanotubes have an average diameter of 9.5 nm, average length of 1.5 μm, 90% carbon purity, and a surface area around 250-300 m^2/g. As shown in Figure 1, the multiwall carbon

nanotubes (MWCNT) have a rather small diameter, and are extremely agglomerated, which was considered a positive feature in this work, since the ability to disperse nanotubes must be evaluated versus a difficult material. Two aggregation levels are observed: small snake-like aggregates, with diameter in the 1 μm range, that, in turn, agglomerate in spherical aggregates in the 100 μm range.

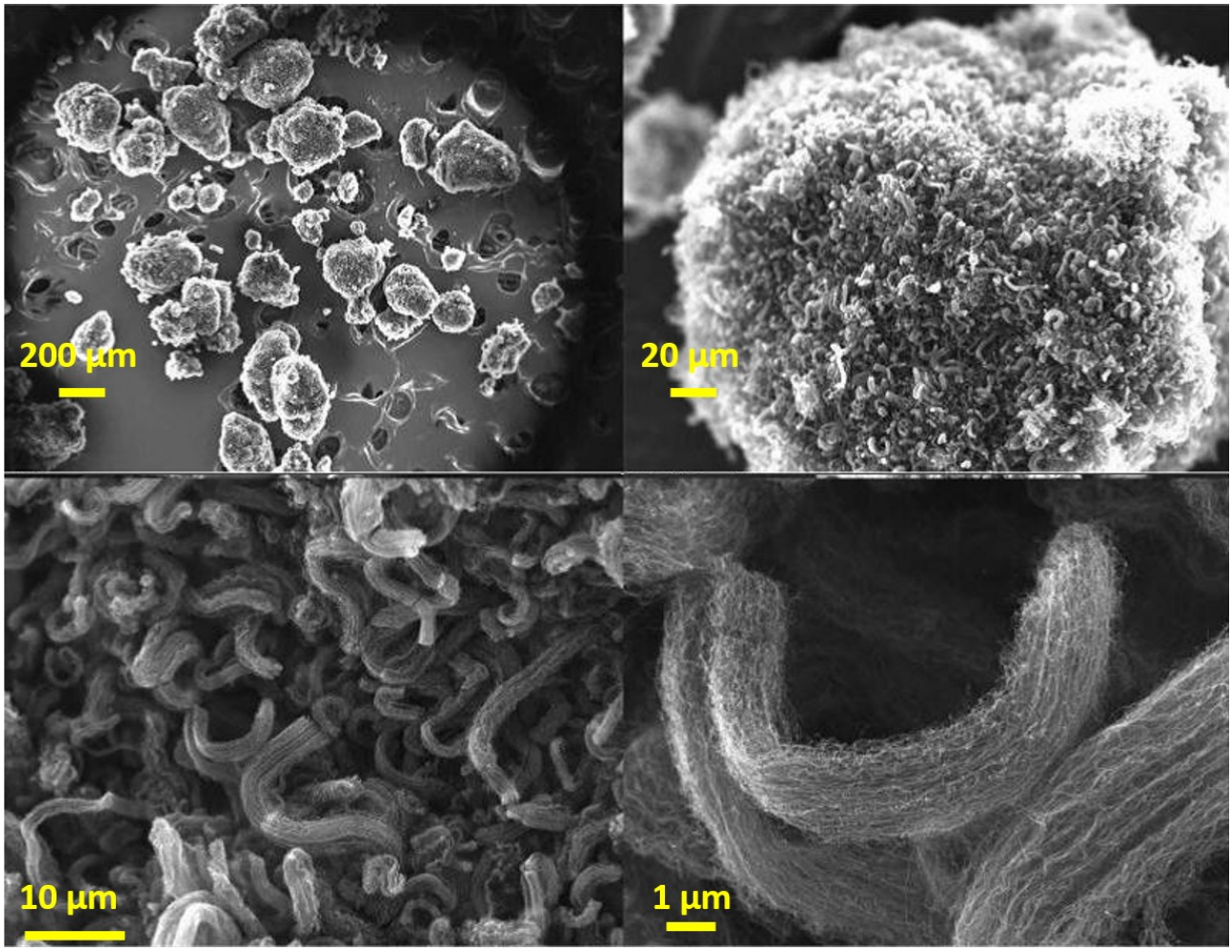


Figure 1 – Micrographs showing Nanocyl™ NC7000 nanotubes and their different aggregation forms collected at different magnification.

Ethanol (>99.8% purity, Sigma Aldrich, Milano, Italy) was used both as a dispersion medium for the dispersion tests and as solvent for the preparation of the slurries for tape casting. Polyvinyl butyral (PVB) was used in the form of the commercial Butvar product (produced by Solutia, Kingsport, Tennessee, U.S.A.). To evaluate the effect of the PVB properties on its dispersing power and on the mechanical properties of the composites tapes, two kinds of PVB were used : PVB-98, containing between 18 and 20% of polyvinyl alcohol (PVA) with a molecular weight between 40000 and 70000;

PVB-76, containing between 11.5 and 13.5% PVA with a molecular weight between 90000 and 120000. Both PVBs contain no more than 2.5% of polyvinyl acetate (PVAc)[34]. In all the dispersion experiments 30 mg MWCNTs were dispersed in 30 g of ethanol.

All the analyses conducted to estimate dispersion were carried out using the PVB-76; the weight ratios for the six samples prepared to study the polymer effect are shown in **Table 1.**

Two different sonicators were used: a probe ultrasound sonicator (SONICS®, Newtown, CT, U.S.A.) Vibra-Cell VCX 750 (maximum power 750 W) and a low energy bath sonicator SONICA Ultrasonic cleaner by Soltec™ Milano, Italy (maximum power 130 W).

CNTs (mg)	PVB (mg)	Ratio CNT/PVB
30	0	
30	30	1:1
30	150	1:5
30	600	1:20
30	2400	1:80
30	5010	1:167 (slurry)

Table 1 – PVB and CNTs content expressed in weight and CNT:PVB weight ratio for the six samples prepared for the polymer effect study

To evaluate the dispersion state of the MWCNTs, several analysis techniques were employed: microscopic observation, UV-visible spectroscopy, optical microscopy and visual observation of diluted dispersions. For the microstructural characterization of the materials and of the samples produced during the experimental work, a Scanning Electron Microscope FEG ASSING SUPRA 25 was used, in the case of PVB-CNTs composites after metallization of the samples. Optical Microscopy (OM Leica DMI 5000M) at different magnification was used to evaluate the dispersion of CNTs in the composites. UV-Vis spectroscopy was used in order to evaluate the dispersion grade of carbon nanotubes/PVB diluted solutions, using a UV–Vis double beam spectrophotometer Shimadzu UV-2600. The spectra were collected between 210 and 800 nm of wavelength.

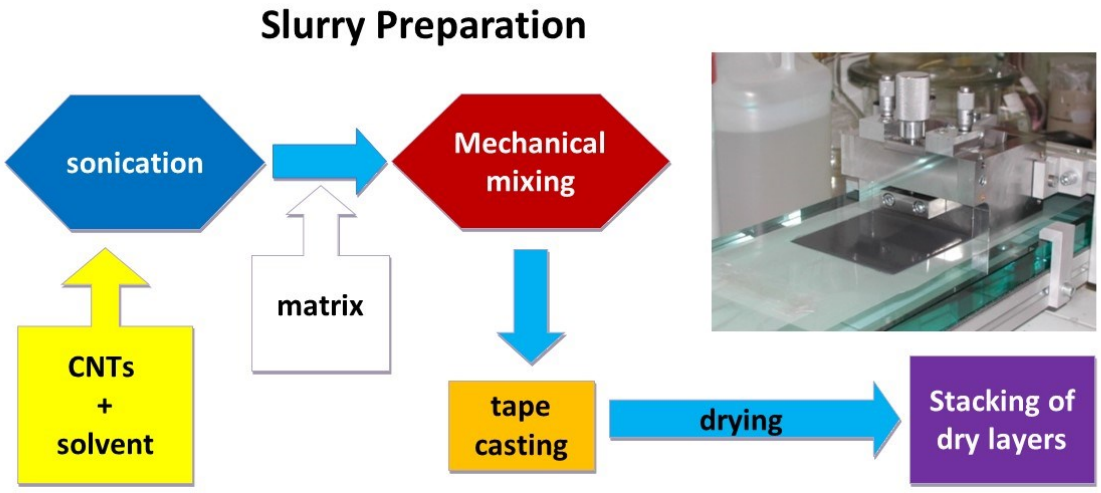


Figure 2 - Tape casting procedure to produce CNTs-PVB composites

The tape casting process, schematically reported in **Figure 2**, required the preparation of a slurry containing the matrix material, the reinforcement and a proper solvent, evaporated after the casting. The PMCs preparation consisted in the dispersion step of the carbon nanotubes in ethanol, followed by the addition of polyvinyl butyral up to the required quantity, and thus by a homogenization step (agitation by magnetic stirring for 24 hours). The procedure called for an ulterior step of probe sonication for 15 minutes, at power of 100 W, with CNT:PVB 1:4 ratio. The system was then placed on a magnetic stirrer that provided a mild but continuous agitation, and the remaining PVB added slowly (about 2 g/h). During the processing, the beaker was kept covered in order to prevent solvent evaporation. The solution was stirred overnight before being processed. 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 by the slurry viscosity. Once cast, the PVB-CNTs composite strips were dried in a specially designed chamber at room temperature for at least 12 hours, up to complete evaporation of the ethanol solvent. Different samples were prepared by modifying the ratio between CNTs and polymer, in order to study the reinforcement concentration effect on the final properties of the material. The dispersion of carbon nanotubes inside the polymer was studied mainly through SEM observation.

Finally, mechanical performance of the tape cast PVB-CNTs composites were measured by tensile tests following the ASTM D882[35] methodology, on a Sintech 10D Dynamometer, on strips with 100 mm length and 10 mm width. Both maximum tensile strength and Young's modulus were calculated. The measurements were made on at least 5 specimens for each concentration of CNTs.

3. Results and discussion

3.1. Dispersion study

The problem of the dispersion and characterization, as mentioned in the introduction, is however very important, because it is easy to be fooled by the high volume occupied by the nanotubes. For instance, in **Figure 3a** is reported an image of a beaker containing a typical MWCNTs dispersion obtained after 15 minutes probe sonication: at a first sight, the content of the beaker appeared black, uniform and the dispersion appeared stable for several days. Nevertheless, at the ethanol meniscus a small width of pure ethanol can be observed, as shown in **Figure 3b.** This is an indication of a bad dispersion, and indeed, if the suspension is then sufficiently diluted with ethanol, allowing a much larger volume for the nanotubes, the CNT precipitates completely in a few minutes, leaving only a few CNT bundles suspended in the solvent (**Figure 3c**).

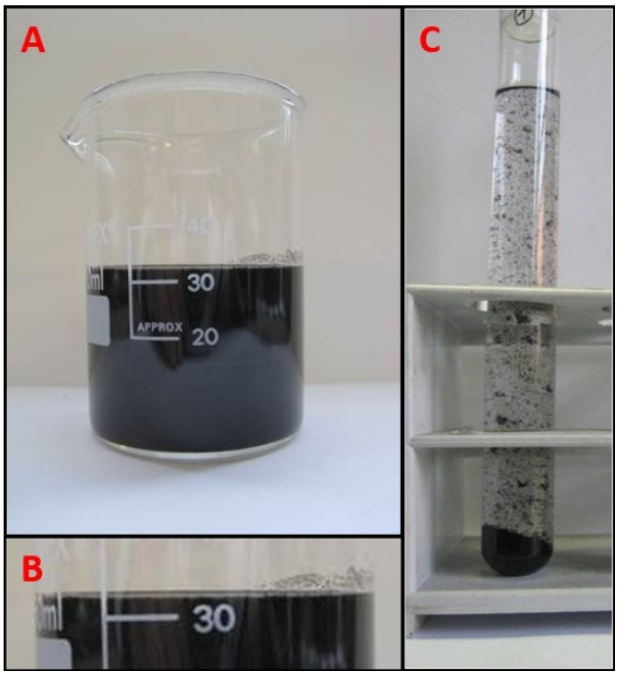


Figure 3 - CNTs dispersion in ethanol after 15 minute of probe sonication (a) and a magnification of its meniscus (b). Precipitation of the sonicated CNTs after dilution with pure ethanol (c)

To obtain a proper dispersion, thus, the main requests are: to avoid the formation of a gel by not exceeding the limit concentration of nanotubes; to keep the dispersion time as short as possible; to

use a suitable solvent or dispersant agent, so to avoid re-aggregation due to the preferred interaction among nanotubes with respect to the nanotube-solvent one. Regarding the dispersant, several polymers have been used in the literature for dispersing CNTs [15-17,19,24,25]. PVB however, even if already used as a composite matrix, [19-23,26] was not studied specifically as a dispersant [26]. The polyvinyl butyral is the common name for poly[(2-propyl-1,3-dioxane-4,6-diyl)methylene], a polymer obtained from polyvinyl alcohol by reaction with butyraldehyde. It is characterized by the presence on its structure of a 1,3-dioxane, a cyclohexane ring with two substituent oxygen atoms in positions 1 and 3. A typical commercial polyvinyl butyral contains some polyvinyl alcohol and polyvinyl acetate units, as shown in Section 2 for Butvar PVB products.

The dispersant accessibility to the nanotubes must also be considered. Indeed, if nanotubes are ultrasonically dispersed without the use of the PVB dispersant, long subsequent stirring times are needed to obtain a proper dispersion. This is demonstrated in **Figure 4**, where the SEM images of composites tapes obtained by first dispersing carbon nanotubes in ethanol, followed by the addition of PVB and stirred for 1, 24 and 72 hours respectively are shown. The SEM observation of CNT composites is a good technique to evaluate the dispersion state of carbon nanotubes; in fact, if CNT bundles are observed in the composite, this is a sure sign of lack of dispersion in the suspension. After 1 h stirring (**Figure 4a**) the composite tape is still very defective, showing bundles and aggregates of nanotubes, while 24 hours of stirring (**Figure 4b**) are needed to obtain a proper dispersion. Longer times (72 h, **Figure 4c**) do not further modify the dispersion state observed at SEM.

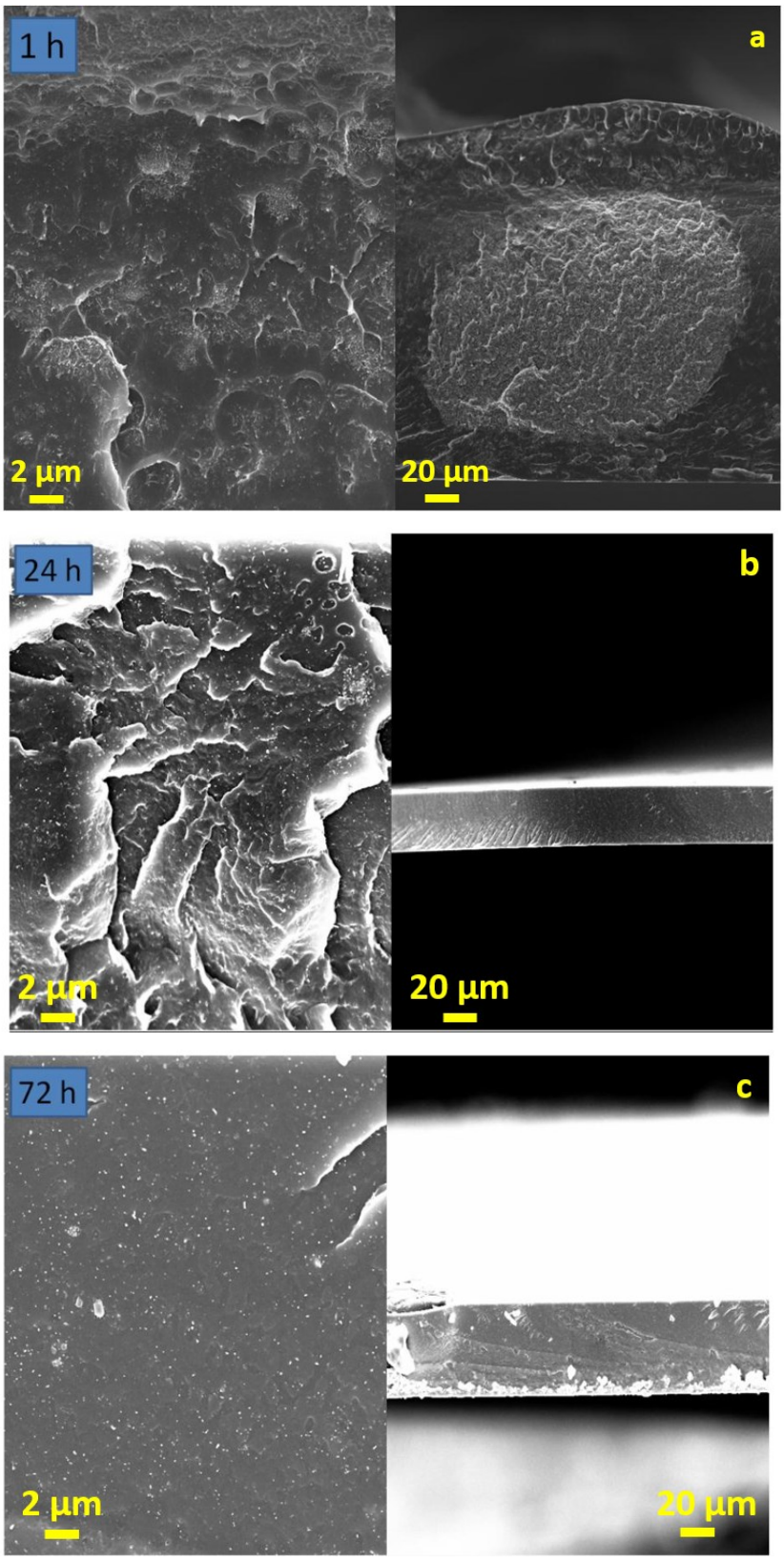


Figure 4 - Fracture surfaces (two SEM magnifications) of tape cast CNTs- PVB-76 composite after **a)** 1 hour of magnetic stirring, **b)** 24 hours of magnetic stirring, **c)** 72 hours of magnetic stirring.

Moreover, when the dispersant is added after the sonication treatment, higher quantities are needed, as shown in **Figure 5.** In this case, carbon nanotubes were dispersed in ethanol (0.1%wt. CNTs) and sonicated for 15 minutes. Then six different PVB amounts, shown in **Table 1**, were added, and the solutions stirred for 24 h. To verify the extent of the dispersion, all the samples were then diluted 40 times with ethanol and put in test tubes for a better observation of possible precipitations. The visual observation of highly diluted CNT suspensions is also a good approach to verify the dispersion state. In a diluted environment, carbon nanotubes are not blocked in a network structure by the CNT-CNT interaction and thus can freely precipitate if the CNT-CNT interaction is stronger than the interaction with the solvent. In **Figure 5** the diluted carbon nanotubes suspensions are shown. As expected, the sample prepared in absence of polyvinyl butyral resulted not dispersed, and the CNTs completely precipitated to the bottom of the vial in few hours. By adding PVB, the dispersion improves, yet very high amounts (CNT:PVB 1:80 ratio) are needed to complete disperse the nanotubes. In fact, in the bottom of the test tube observed in the **Figure 5**, a small deposit can still be observed on samples 1:1, 1:5 and 1:20. The slurry sample corresponds to a CNT:PVB 1:167 ratio, used for casting the PVB-CNTs composites.

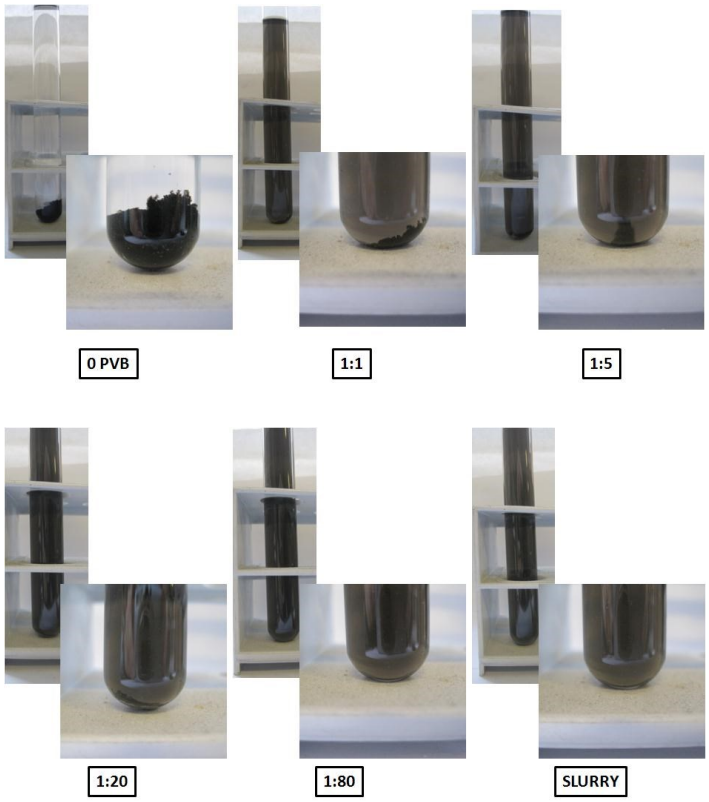


Figure 5 - Dispersions of CNTs in presence of different amounts of PVB-76 after sonication, mechanical stirring and dilution with pure ethanol (1:40 vol)

Instead, a very small amount of polymer, corresponding to a CNT:PVB 1:1 ratio, allowed to obtain a more homogeneous solution when the PVB was added directly during the sonication, allowing the obtainment of a good dispersion in a single 15-minutes step. This is shown in **Figure 6,** where no precipitate can be observed, and the supernatant ethanol remained black and not uncoloured as in the case of not effective dispersants. This confirms that a strong dispersion treatment in the presence of the dispersant is always needed to allow both the dispersion of the nanotubes aggregates and, at the same time, the penetration of the dispersant inside even the smallest bundles of nanotubes.

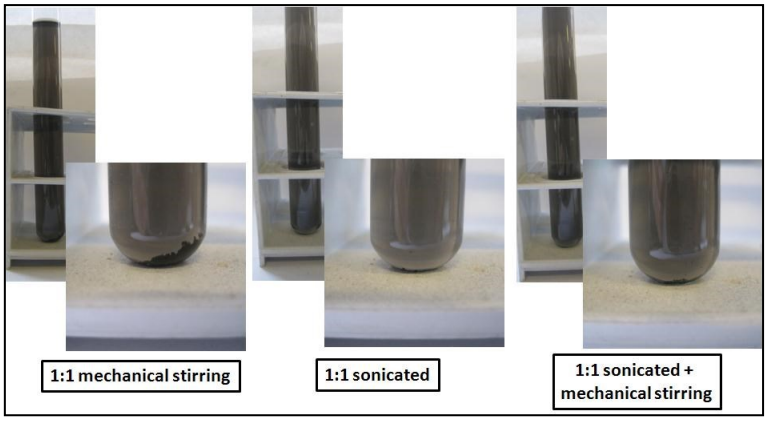


Figure 6 - Test tubes of differently treated CNTs-PVB-76 samples. The left one corresponds to a dispersion in which the polymer was added after sonication, in the mechanical stirring step; the central picture shows a dispersion in which the PVB is added during the sonication step and the mechanical stirring step is eliminated; finally the picture on the right displays a dispersion made adding the polymer during the ultrasonication and stirring for 24 hours.

The are many possible reasons for the outstanding dispersion ability of polyvinyl butyral in dispersing carbon nanotubes. First, the polymer wrapping effect, that is a well-known interaction between carbon nanotubes and polymers [24–26]. It is generally considered a non-covalent functionalization and involves the modification of nanotubes interfacial properties. The suspension of CNTs in the presence of some polymers leads to the wrapping of polymer around the CNTs to form supramolecular complexes. The polymer wrapping process is supposed to be achieved through the Van der Waals interactions and π-π stacking between CNTs and polymer chains containing aromatic compounds.

To verify the quality of the dispersion of carbon nanotubes containing low PVB concentration, UV-visible spectrometry was employed. In fact, the scattering of light from 210 nm to 800 nm of

wavelength can be used to evaluate the presence of single dispersed carbon nanotubes, since the light scattering is higher when the nanotubes are singly dispersed than when bundles are present [36–38].

The samples for UV-visible spectroscopy were left in the test tubes for two weeks without any agitation or vibration, in order to precipitate all the larger agglomerates and thus to avoid interferences during the scattering test. A small amount of the supernatant was taken from the test tube and further diluted ten times in pure ethanol.

The results are reported in **Figure 7** where UV/visible spectra are shown from solutions with different CNT:PVB weight ratio. In **Figure 7a** it is shown the case of the polymer added during mechanical stirring, i.e. after sonication, while in **Figure 7b** the case of the polymer added during sonication. The scattering effect is correlated with the rising of the absorbance, and when all the CNTs are dispersed the absorbance saturates. A clear increase is observed between the mechanical stirred samples and the sonicated ones. In the case of mechanical stirring, to obtain the maximum possible absorption very high concentrations of PVB are needed (the slurry one, i.e. a CNT:PVB 1:167 ratio), while in the case of sonication, the saturation of the absorbance of the solution is obtained already at low PVB concentration (CNT:PVB 1:4 ratio). UV-visible spectroscopy suggests that while at the CNT:PVB 1:1 ratio there is not an enormous difference between the dispersion of nanotubes in the case of addition of PVB during mechanical stirring or sonication, for bigger PVB quantities, adding of the polymer during sonication guarantees very good dispersions. The motivation can be found in the re-aggregation phenomenon, that occurs after sonication only when PVB is not present in the solution during the sonication phase, requiring then much higher PVB concentrations to attain high quality dispersions.

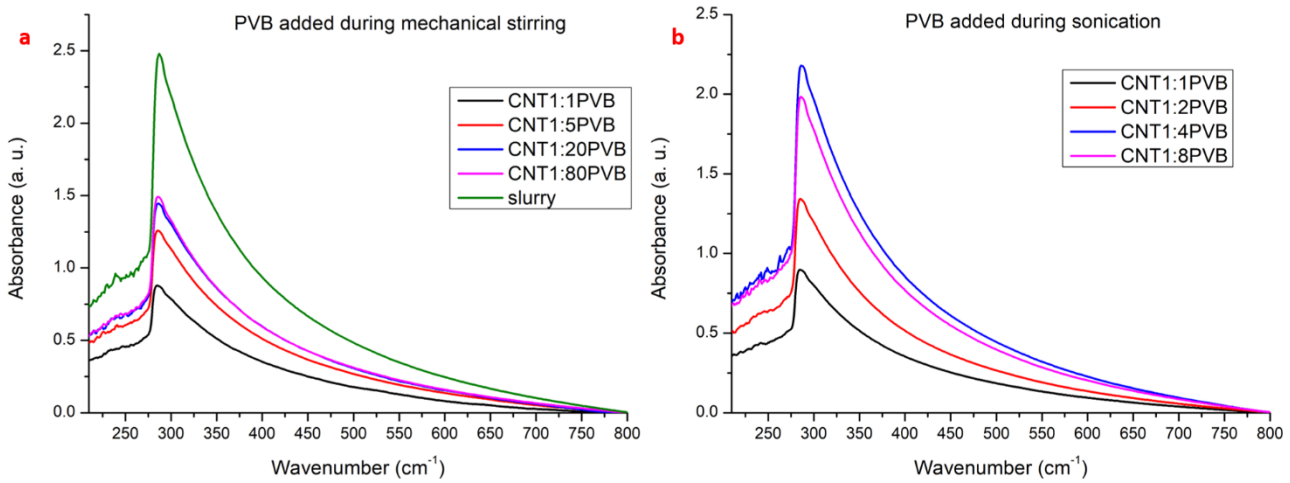


Figure 7 - UV-vis absorbance of different CNTs suspensions in PVB-76: comparison between mechanical stirring (a) and sonication (b).

3.2. Polymer matrix composites prepared by tape casting

Mechanical performance of the composites was measured by tensile tests. **Figure 8** shows Young's modulus (**Figure 8a**) and maximum tensile strength (**Figure 8b**) for PVB-CNT composites obtained with both PVB-98 and PVB-76. In the case of PVB-98, it is evident that the nanotubes were not substantially effective in reinforcing the resin, notwithstanding the very good dispersion observed in samples with low concentration of nanotubes. The Young's modulus presents a small increase up to 1% CNTs, while the maximum tensile strength has a small increase only with a very low quantity of CNTs (0.1%). Further increasing the nanotubes content causes both properties to decrease, to values even lower than the pure resin. In the case of PVB-76, instead, a substantial increase in Young's modulus and tensile strength can be observed in the sample containing 0.5% CNTs. With 2% and 10% containing samples, however, no further increase of Young's modulus was observed, and tensile strength decreased.

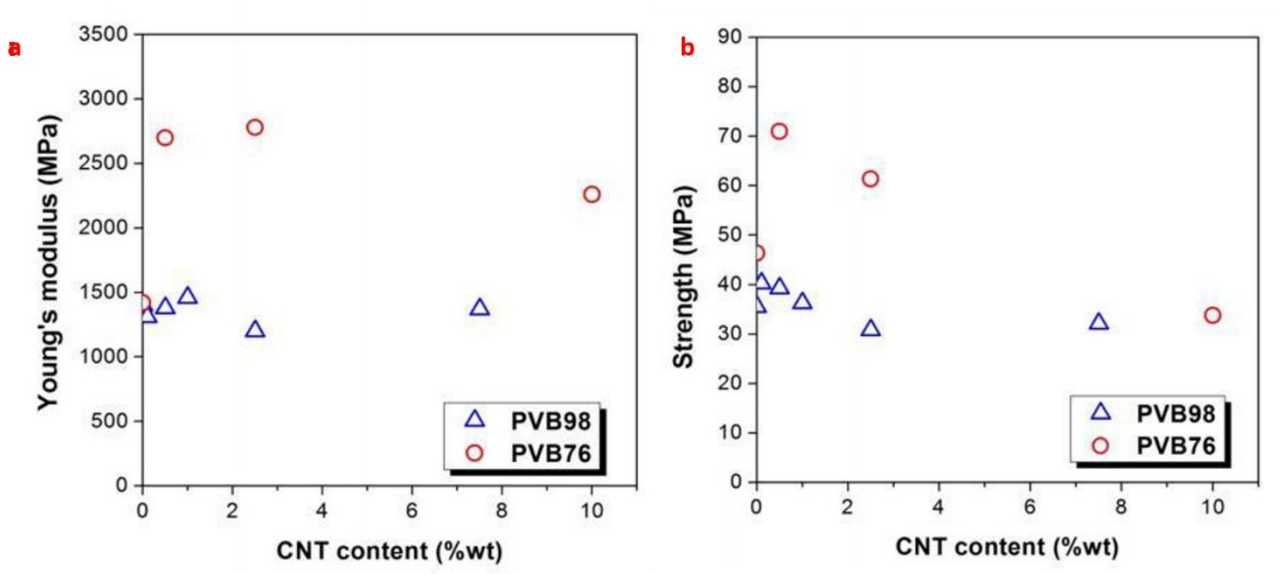


Figure 8 - Young's modulus (a) and maximum tensile strength (b) vs CNT content (%wt) for PVB-98 and PVB-76 composites

To explain this behaviour, it is necessary to consider both dispersion and stress transfer from the matrix to the nanotubes. In the case of samples with a low percentages of carbon nanotubes, the dispersion was very good, the tapes presented no defect and the nanotubes appeared partially aligned at a SEM observation, as shown in **Figure 9a**. As also observed in a previous work [5], low CNT concentrations allow a uniform dispersion of the filler in the matrix and a better exploitation of the exceptional mechanical properties of the single CNTs. When the CNT concentration increases, however, nanotube bundles tend to form. If the bundles are sufficiently big, they behave as structural defects, counterbalancing the positive effect of the increased CNT concentration in the matrix **(Figures 9b and 9c).**

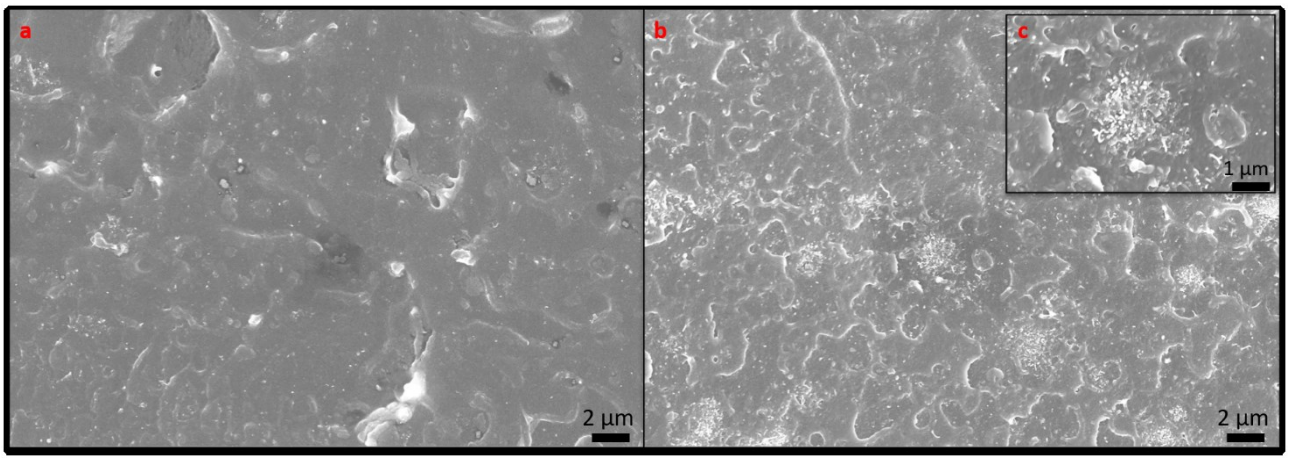


Figure 9 – a) SEM PVB reinforced with 0.1% wt. of CNTs b) SEM PVB reinforced with 1% wt. of CNTs and c) detail of an agglomeration of nanotubes in the matrix

The dispersion however cannot explain the substantial difference between PVB-98 and PVB-76 samples. In this case, interfacial stress transfer must be considered. The difference between PVB-98 and PVB-76 are related to the chain length, that is shorter for PVB-98, and to the PVA content, that is higher for PVB-98. So, PVB-98 presents less PVB groups and a shorter chain length with respect to PVB-76 (the average molecular weight is between 10000 and 11000 for PVB-76, instead of values for the PVB-98 comprised between 5000 and 6000). These two facts can explain the difference in the strength of the composites obtained with the two PVB formulations. The chain length of PVB_98 is too short for both wrapping the nanotubes and efficaciously entangling with the other polymer chains, and the lower amount of PVB groups reduces the adhesion between the polymer and the CNTs. Thus, even if the dispersion is good, the nanotubes are not effective in reinforcement. In conclusion, even if both PVBs are effective in dispersing the nanotubes, only PVB-76 is an effective matrix for the preparation of strong PVB-CNT composites.

The samples of PVB76-CNTs composites with a very high amount of carbon nanotubes show an increased value of Young's modulus with respect to the polymer, but no increase in mechanical strength. The models typically used to calculate the theoretical strength of a polymer-based composite containing carbon nanotubes [39] give a roughly linear increase in the 0-10% range. So, the increase of Young's modulus for the sample containing 10% of CNTs should be twenty-fold the increase observed for the 0.5% sample, while it is not. This suggests that in the sample containing 10% CNTs only a very little fraction of carbon nanotubes are well-dispersed and participate to the mechanical properties of the composite. Moreover, since defects in a composite are stress-concentration points, most of the nanotubes (still present in bundles) not only do not participate to the stress, but cause a reduction of strength. It must be stressed that the glass transition temperature of PVB is around 60 °C, so that at room temperature the resin has a low toughness, and the cracks propagate rapidly, bringing to fracture.

In order to provide a method for estimating the mechanical properties of the carbon nanotubes used in this work, we applied several models[40] to the composites with PVB-76 and 0.5% CNTs, both regarding Young's modulus and tensile strength.

Regarding Young's modulus, the rule of mixtures models refers to a composite with continuous aligned fibers, while the Halpin Tsai model refers to the case of aligned short fibers, and so it is more similar to this case. From both models it is possible to calculate the Young's modulus of the fibers (in this case CNTs) by knowing the composite Young's modulus. In the case of the mixtures model:

$$E_C = E_F \nu_F + E_M(1 - \nu_F) \quad (1)$$

and consequently

$$E_F = \frac{E_C - E_M(1-\nu_F)}{\nu_F} \quad (2)$$

In the case of Halpin Tsai model:

$$E_C = \frac{E_M(1+Ŧ\eta\nu_F)E_M}{(1-\eta\nu_F)} \quad (3)$$

where

$$\eta = (E_F/E_M - 1)/(E_F/E_M + Ŧ) \quad (4)$$

and Ŧ is 2 times the aspect ratio of the fibers. From these equations can be calculated that

$$E_F = \frac{E_m Ŧ(E_m - E_c)}{(1-\nu_F)E_c - E_m(1+Ŧ\nu_F)} \quad (5)$$

In the case of the rule of mixtures we obtain E_F = 250 GPa, but this is a lower bound value, since nanotubes are not continuous. By using instead Halpin-Tsai modulus, and considering the producer data for length and diameter of the fibers, corresponding to Ŧ = 316, we obtain the value of E_F = 534 GPa, which is a better estimation of the Young's modulus of CNTs.

Regarding tensile strength, instead, before choosing a model, it is necessary to make some hypothesis on the critical length of the reinforcement L_c. If the critical length is much smaller than the total length, then it is possible to roughly estimate the tensile strength of the reinforcement with a very simple rule of mixtures model, since the mechanical behaviour will not very different from the case of a composite with continuous reinforcement[40]. By applying the rule of mixtures model, we can thus calculate the fiber strength σ_F, following an equation similar to (2):

$$\sigma_F = \frac{\sigma_C - \sigma_M(1-\nu_F)}{\nu_F} \quad (6)$$

where σ_M and σ_C are the strength of matrix and of composite, respectively.

The result gives a value of 4,8 GPa, that must be inserted in the equation giving the critical length L_C, to verify that the initial assumption was good.

$$L_C = \frac{\sigma D}{2\tau} \quad (7)$$

where σ is the fiber strength, D its diameter, and τ the interfacial shear stress. The interfacial shear stress of carbon nanotubes into a polymeric matrix was estimated close to the value of τ = 140 MPa by Chawla[41], while the mean nanotubes diameter is given by the producer as 9.5 nm. With these values we can calculate a critical length of 164 nm, that corresponds to a ratio L / L_c = 9. From[40] we can see that with this ratio the strength of the composite is rather close to the value for continuous composites, suggesting that this estimation is acceptable. Thus, the mechanical strength of the nanotubes is close to 5 GPa, which is in line with the literature[40].

The increase in nanotube content is hampered by the fact that most of these nanotubes do not contribute to the mechanical performance since they are not well dispersed. This is well in agreement with the observation on the tapes, both with PVB-98 and PVB-76, where already at 1% CNTs content the presence of residual agglomerates of nanotubes is observed. Thus, the maximum effective concentration of nanotubes is comprised between 0.5% and 1%. Above this quantity, the total volume required for an effective dispersion is higher than the volume of the solution, and during the dispersion step agglomerates are not well dispersed and remain inside the tapes as defects.

4. Conclusions

In this work, a study on the interaction between carbon nanotubes and polyvinyl butyral (PVB) polymer was performed. PVB is a low-cost polymer often used as binder in the slurry formulation for tape casting technology. It was found to be not only a good matrix for composites, as already suggested in the literature, but also a noteworthy dispersant for carbon nanotubes in ethanol. However, some issues were identified when working with PVB both as a dispersant and as a composite matrix.

The dispersing ability of PVB is very good; however, when severely entangled nanotubes are used, the accessibility of PVB to the whole CNTs bundle must be guaranteed. The best way envisaged in this paper is to add directly a low amount of PVB during the sonication. If sonication is performed without PVB, then much longer times are needed for a proper nanotubes' dispersion, and higher dispersant quantity too. The characterization of the dispersed nanotubes suspensions suggested that visual observation on very diluted solution is a very fast, simple and effective way of judging the real nanotubes dispersion. A more complicated but more effective alternative seems to use UV/visible light absorption on very diluted suspension, even if in this case the sample preparation requires a long time to allow the settling of the aggregates before taking the supernatant and making the measurement.

Regarding the use of PVB as a composite matrix, first it must be considered how the total volume of solvent influences the maximum amount of nanotubes that can be effectively dispersed. It was also observed that when a polymer with shorter chain is used, the effectiveness of the carbon nanotubes in reinforcing the polymer is much lower than in the case of a longer-chain polymer. In the latter case, with 0.5% CNTs it was possible to pass from 1.5 GPa Young's modulus and 45 MPa tensile strength to 2.7 GPa Young's modulus and 70 MPa tensile strength, with a relative increase of 80% and 60% respectively. By hypothesising that in the 0.5% CNTs sample all the nanotubes are perfectly aligned

and dispersed (as suggested by SEM observations on the composite tapes), an estimation of stiffness and strength of the nanotubes was performed. The values of 534 GPa for Young's modulus and 4.8 GPa for tensile strength were obtained by using the Halpin Tsai model, that are reasonable values for the industrial nanotubes used (Nanocyl NC7000). It is also possible to observe that when higher amounts of nanotubes are used, most of the nanotubes are not acting effectively towards the improvement of mechanical properties, but instead remain agglomerated.

5. References

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