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A parametric prediction of the Young's modulus of polymers enhanced with MWCNTs

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Abstract. In this work a multi-scale model simulating the effect of the dispersion, the waviness as well as the agglomerations of MWCNTs on the Young's modulus of a polymer enhanced with 0.4% MWCNTs (v/v) has been developed. Representative Unit Cells (RUCs) have been employed for the determination of the homogenized elastic properties of the MWCNT/polymer. The elastic properties computed by the RUCs were assigned to the Finite Element (FE) model of a tension specimen which was used to predict the Young's modulus of the enhanced material. Furthermore, a comparison with experimental results obtained by tensile testing according to ASTM 638 has been made. The results show a remarkable decrease of the Young's modulus for the polymer enhanced with aligned MWCNTs due to the increase of the CNT agglomerations. On the other hand, slight differences on the Young's modulus have been observed for the material enhanced with randomly-oriented MWCNTs by the increase of the MWCNTs agglomerations, which might be attributed to the low concentration of the MWCNTs into the polymer. Moreover, the increase of the MWCNTs waviness led to a significant decrease of the Young's modulus of the polymer enhanced with aligned MWCNTs. The experimental results in terms of the Young's modulus are predicted well by assuming a random dispersion of MWCNTs into the polymer.

1. Introduction

Different forms of Carbon have paved the way to innovative emerging technologies by developing multifunctional materials with enhanced tailored properties. Multi walled carbon nanotubes (MWCNTs) are considered to provide to polymers excellent mechanical and multifunctional properties in terms of electrical conductivity, thermal properties etc. [1–3]; features which are very important for the aircraft structures.

A large number of investigations available on the mechanical behavior of composite materials enhanced with MWCNTs has shown opposing results [4–6]; it has been found that the mechanical properties of the materials enhanced with CNTs remain almost the same, or show a moderate improvement or even undergo deterioration. It seems that a large number of CNT parameters e.g. the aspect ratio, the dispersion, the waviness the interphase bonding etc. influences the behavior of the enhanced material. By studying the mechanical behavior experimentally it is difficult to distinguish the impact of each parameter comprehensively. Many analytical studies [7–9] have been conducted in order to simulate the effect of the CNTs agglomerations as well as the waviness of CNTs by using Mori-Tanaka or Eshelby's models; however, they are limited to generalized assumptions for the shape of CNTs as well as of the agglomerations.

On the other hand, 3D modeling of Carbon nanotubes has remained up to now limited due to the advanced modeling requirements. Only primitive design of a few number of CNTs representing the agglomerations has been developed. Specifically, Chanteli et al. [10] have numerically investigated the effect of the CNTs agglomerates on the elastic properties of a CNTs/polymer material. For the modeling of the CNTs agglomerates, RUCs of 3, 5 and 10 CNTs have been developed by using one single pattern at each RUC. Furthermore, a multi-scale simulation approach for the prediction of the Young's modulus of polymers enhanced with CNTs has been developed by Rafiee et al. [11] by taking into account several parameters, e.g. the agglomerations, the waviness etc. At the micro-level, the authors have investigated the interaction between the CNT and the polymer. For the modeling, one single CNT has been used for the calculations. At the macro-level, the non-uniform distribution of the inclusions has been investigated as well as the prediction of the mechanical properties has been made.

However, MWCNTs seem to be effective in reinforcing polymers only if a uniform dispersion without entanglements has been achieved [8,11–14]; as the MWCNTs become more agglomerated and waved into the polymer, lower material properties should be expected [8,10,11,14]. The dispersion process is a crucial parameter for an effective reinforcement as the MWCNTs tend to be formed in agglomerations due to the weak Van der Waal forces between their tubes [15].

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Although several studies on the effect of the MWCNTs distribution on the Young's modulus have been conducted, limited results exist by using a more realistic RVE including a periodic geometry of multiple MWCNTs with random orientation and a more realistic waviness of MWCNTs with aspect ratio exceeding 150.
In this work a multi-scale model simulating the effect of the dispersion, the waviness as well as the agglomerations of MWCNTs on the Young's modulus of a polymer enhanced with 0.4% MWCNTs (v/v) has been developed. RUCs have been employed for the determination of the homogenized elastic properties of the CNT/polymer. The elastic properties computed by the RUCs were assigned to the FE model of a tension specimen which was used to predict the Young's modulus of the enhanced material. Furthermore, a comparison with experimental results obtained by tensile testing according to ASTM 638 has been made.

2. Description of the model

2.1 Material and mechanical testing

The epoxy matrix formulation is based on a mixture of epoxy precursors under the commercial name RTM6-2 [29]. However, the resin used in this study differs from the commercial one since only one type of hardener is used instead of a mixture of hardeners used in the commercial resin. Regarding the material properties used for the neat polymer, a Young's modulus of 3.26 GPa has been used, according to Reference [5]. The MWCNTs were modeled as isotropic materials with a Young's modulus of 1 TPa, which belongs to pristine non-functionalized MWCNTs, and a Poisson's ratio of 0.3, according to Reference [10]. The MWCNTs used were NANOCYL NC3100 series thin multi-wall carbon nanotubes, with an average diameter of 9.5 nm and an average length of 1.5 μm. The selected MWCNTs concentration was of 0.4 % (v/v). The selected concentration of the MWCNTs has been proved to offer sufficient electrical conductivity to composite aerostructures resulting to an effective dissipation of lightning currents during flight [17,18], while the mixture is characterized by good dynamic mechanical behavior [19]. An ultra-sonication for 20 min has been used in order to achieve a uniform dispersion of 0.4% MWCNTs (v/v) within the epoxy matrix. This dispersion method has been chosen among others based on the results of the dynamic mechanical properties for a similar epoxy resin [20,21].
A SEM inspection has been performed using a Zeiss SUPRA 35VP model. Concerning the technical data of the microscopy, a 1.7 nm resolution at 15 kV accelerating voltage in the high vacuum mode was used. The samples were gold coated (Baltec 005 sputer coater) in order to avoid surface charging. The elemental chemical analysis was performed in situ during the SEM microscopy.

2.1 Modeling

A multi-scale model simulating the effect of the agglomerations on the elastic properties of the polymer has been assessed by taking into account significant parameters in terms of the grade of agglomerations into the polymer, the MWCNTs dispersion quality as well as the waviness of MWCNTs. At micro-scale level, a RUC which comprises the dispersed MWCNTs into the polymer and at macro-scale level, the FE model of a tensile specimen have been developed.

Regarding the RUC geometry, the length of the side of the cube is determined according to Reference [10] and is given by the relation 1:

$$W_{RUC} = \sqrt[3]{\frac{k \times \frac{\pi \times d_n^2 \times L_n}{4}}{V_{CNT}}} \tag{1}$$

where k is the number of MWCNTs in the agglomerate, dn and Ln are the CNT's diameter and length, respectively and Vcnt is the MWCNTs volume fraction. A random distribution of Carbon nanotubes into the polymer was generated by using DIGIMAT FE (Digimat 2017.1). The periodic geometry of the RUC is generated based on a random algorithm which control the random placement of the MWCNTs into the cubic matrix. The MWCNTs were represented as solid particles and perfect bonding has been assumed between the particles and the matrix. To more realistically represent the MWCNTs agglomerates into the polymer, the RUC has been simulated by 24 MWCNTs, as shown in Figure 1.

For large agglomerates, an increased MWCNTs concentration into the polymer has been assumed as the result of strong interactions between MWCNTs. Therefore, the representation of the agglomerates into the polymer has been made by RUCs of 24 CNTs with concentrations from 1% to 5% (v/v).

A conforming mesh with an element type of tetra has been used due to the complicated geometry of the enhanced material with multiple MWCNTs. A dense mesh with higher density near the MWCNTs has been selected. As the MWCNTs concentration increases, the ratio of the MWCNTs diameter to the length of the RUC decreases. Therefore, a coarser mesh is required for RUCs with higher MWCNTs concentration. The respective meshes for all the RUCs are presented in Figure 2.

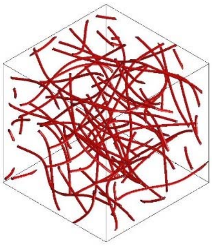

Fig. 1. RUCs patterns for the random distribution of MWCNTs into the polymer produced by DIGIMAT FE

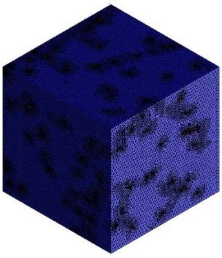

Fig. 2. RUCs meshes for the random distribution of MWCNTs into the polymer produced by DIGIMAT FE

Furthermore, the Young's modulus for aligned and randomly-dispersed MWCNTs has been predicted. The effect of the waviness taking into account the orientation of the MWCNTs on the Young's modulus has been also studied. Figure 3 shows the RUCs regarding the effect of the orientation as well as the waviness of the MWCNTs. Figures 3a-c refer to aligned-dispersed MWCNTs with increasing waviness. Figures 3d-f refer to randomly-dispersed MWCNTs with increasing waviness. A RUC comprising 24 MWCNTs has been also used for the predictions.

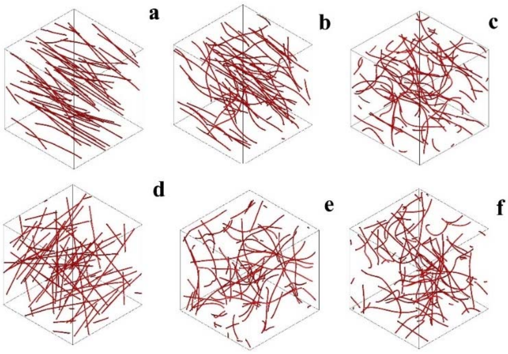

Fig. 3. Effect of the orientation as well as the waviness of the MWCNTs. a) low waviness of aligned dispersed MWCNTs into the polymer, b) medium waviness of aligned dispersed MWCNTs into the polymer, c) high waviness of aligned dispersed MWCNTs into the polymer, d) low waviness of randomly dispersed MWCNTs into the polymer, e) medium waviness of randomly dispersed MWCNTs into the polymer and f) high waviness of randomly dispersed MWCNTs into the polymer.

At macro-scale level, an FE model of the tensile specimen has been developed by means of a commercial code in ANSYS FE. The material has been represented using the 3D ANSYS SOLID185 element [23]. A typical FE mesh of the specimen is shown in Figure 4. For the tensile loading, the boundary conditions were applied at the parts of the specimen captured by the tabs. One side was fully built in, while at the other side an axial displacement was applied.

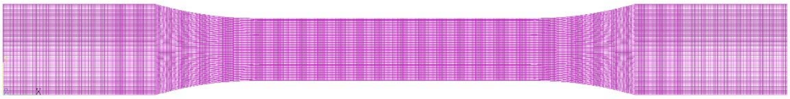

Fig. 4. Typical FE mesh of the tensile specimen

For the elements of the specimen's FE model, an isotropic material behavior was assumed except for the cases that aligned MWCNTs have been assumed. The Young's modulus of the elements was obtained by the RUCs.

The deviations from the idealized MWCNTs distribution into the polymer (Figure 5a) where MWCNTs are uniform distributed into the polymer have been investigated. As the MWCNTs agglomerations into the polymer increase, the uniform distributed MWCNTs become less (Figure 5b) till the state that all MWCNTs are formed in agglomerations (Figure 5c). A random distribution of the agglomerations has been considered, by randomly selecting the elements till the volume reaches the desired level according to the λ parameter (Table 1). The parameter λ indicates the degree of the agglomerated MWCNTs in regard to the total volume of the MWCNTs. For example when the λ value is equal to 0, it means that there are no agglomerations into the polymer and a uniform dispersion prevails. On the other side, when the λ value tends to 1 all MWCNTs are formed in agglomerations leaving a part of the polymer neat. The uniform dispersion of the MWCNTs into the specimen corresponds to 0.4% (v/v). Table 1 shows all the cases which have been studied for X and randomly oriented MWCNTs. Moreover, the concentration γ of the agglomerations is assumed to be from 1% to 5% (v/v) (Table 1).

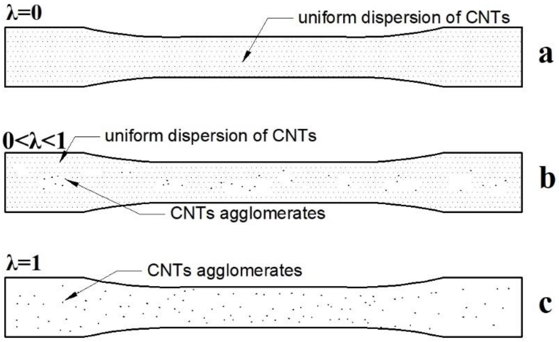

Fig. 5. Macroscopic model configuration a) λ=0, uniform dispersion of MWCNTs into the polymer b) 0<λ<1, partly uniform dispersion of MWCNTs as well as MWCNTs agglomerates into the polymer and c) λ=1, MWCNTs agglomerates into the polymer

Table 1. Study of models with different λ values for X- as well as randomly-oriented MWCNTs into the polymer. Five different cases for the MWCNTs concentration: 1-5% (v/v)

$\gamma_{agglomerations}$=1-5% (v/v)

X-oriented MWCNTs	Randomly-oriented
λ	λ
0.0	0.0
0.2	0.2
0.4	0.4
0.6	0.6
0.8	0.8
1.0	1.0

Figure 6 illustrates the FE models of the tensile specimen for different values of the λ parameter. Figure 6a shows the pattern of the FE model for λ=0.2, where only few agglomerates are embedded into the polymer; mostly a uniform distribution of the MWCNTs prevails. On the other side, Figure 6b shows the pattern of the FE model for λ=1, where only agglomerates are embedded into the polymer.

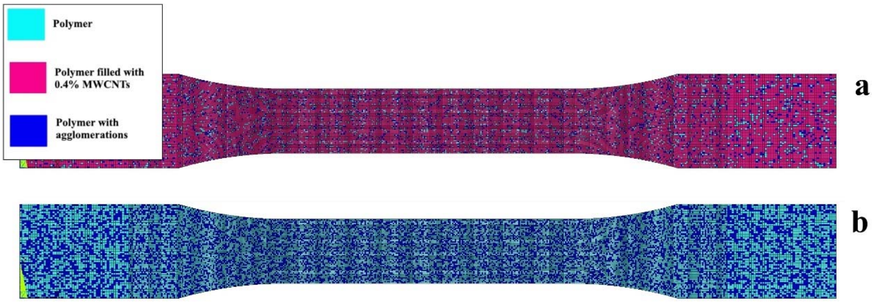

Fig. 6. Macroscopic FE tensile models configuration. a) λ=0.2, b) λ=1

3. Results and discussion

The results obtained by the SEM analysis have revealed the presence of MWCNTs agglomerates into the polymer. Multiple MWCNTs rich regions with large parts of neat polymer are shown in Figure 7. Furthermore, a deeper view at the CNTs structure revealed significantly waved CNTs randomly oriented into the polymer, as shown in Figure 8. The extreme waviness might be attributed to their high aspect ratio (~160).

Fig. 7. SEM image of a region at the fracture surface of the specimen with many agglomerations

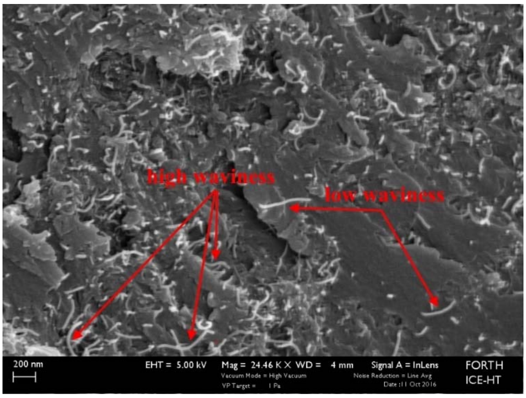

Fig. 8. SEM image of the fracture surface of the polymer enhanced with 0.4% MWCNTs (v/v)

The predicted values regarding the Young's modulus for all RUCs are shown in Figure 9. An increasing Young's modulus for an increasing MWCNTs concentration has been found for the RUCs, with values reaching up to 12 GPa for 5% (v/v) MWCNTs into the polymer.

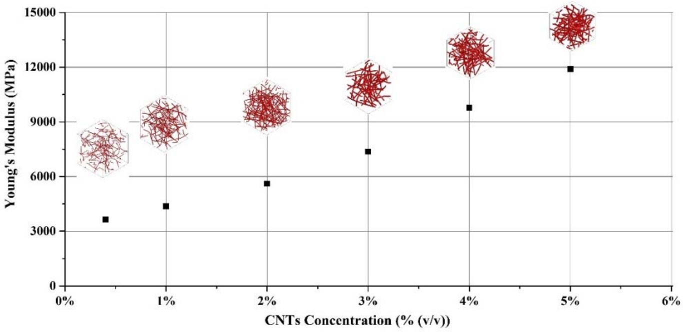

Fig. 9. Young's modulus of the RUCs for 0.4%, 1%, 2%, 3%, 4% and 5% (v/v.) MWCNTs into the polymer

Furthermore, the orientation of the MWCNTs plays a predominant role in the effectiveness of the reinforcing. The results regarding the orientation of the MWCNTs as well as the degree of their waviness are shown in Figure 10. A significant degradation of the Young's modulus has been predicted for randomly oriented MWCNTs as compared to the aligned CNTs. In addition, the waviness seems to play an appreciable role in the case of the aligned CNTs; however, for randomly oriented CNTs, the effect of the waviness is negligible. It seems that the Young's modulus obtained by the experimental results correlates very well with the case that the MWCNTs are assumed to be randomly-oriented with a high degree of waviness. This case has been also verified by the results obtained by the SEM analysis (Figures 7-8).

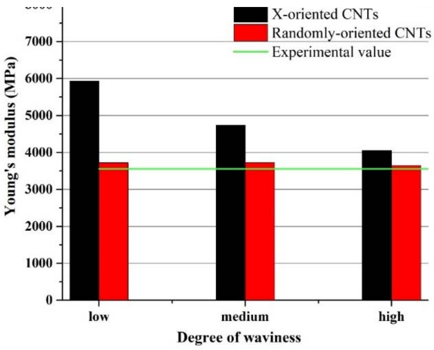

Fig. 10. Effect of the degree of waviness on the Young's modulus for aligned and randomly oriented MWCNTs into the polymer

As far as the macroscopic model is concerned, the numerical results regarding the Young's modulus taking into consideration the orientation as well as the degree of the agglomerations are shown in Figures 11-12. The results showed that there is a large deviation of the Young's modulus for the aligned uniform dispersed MWCNTs (λ=0) as compared to the experimental results found in Reference [5]. As the λ tends to 1, the numerical results converge with the experimental results. This indicates that the produced tensile specimen are governed by a random dispersion with multiple agglomerations as revealed also by the SEM results (Figures 7-8). Some previous studies have shown a reduction of the Young's modulus due to the randomly oriented CNTs, which is relative to the concentration of the CNTs into the polymer [8,12,14]. Moreover, the authors have also found that the increase of the CNTs waviness leads to reduced mechanical properties.

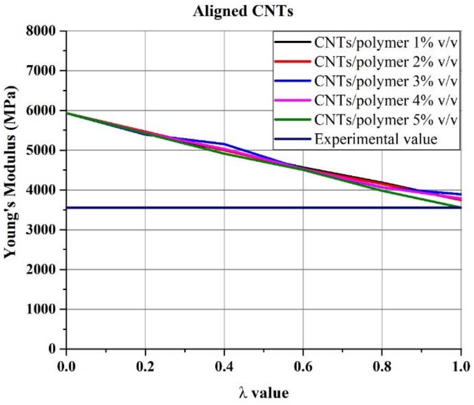

Fig. 11. Young's modulus of the polymer enhanced with randomly oriented MWCNTs

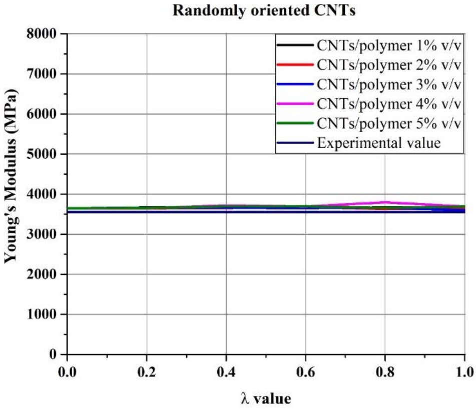

Fig. 12. Young's modulus of the polymer enhanced with aligned oriented MWCNTs

4. Conclusions

In this work a multi-scale model simulating the effect of the dispersion, the waviness as well as the agglomerations of MWCNTs on the Young's modulus of a polymer enhanced with 0.4% MWCNTs (v/v) has been developed.

- The MWCNTs orientation plays dominant role on the Young's modulus of the filled material.
- The increase of the MWCNTS waviness significantly reduce the Young's modulus value of aligned MWCNTs, whereas for randomly dispersed MWCNTs seems to play an insignificant role.
- The presence of MWCNTs agglomerations leads to random and waved dispersed MWCNTs into the polymer resulting to a large deviation from the idealized material properties.

Further research is needed in order to investigate the effect of these crucial parameters on the mechanical behavior by realistically simulating the CNTs into the polymer aiming to comprehensively understand the mechanisms which reduce their properties instead of reinforcing them.

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