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Pullout strength of graphene and carbon nanotube/epoxy composites

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Abstract

An atomistic multiscale modelling approach is used to simulate the nonlinear pullout behaviour of interlinked single walled carbon nano tubes (SWCNT) and single layer graphene sheets (SLGS) embedded in an epoxy polymer. The pullout forces have been computed for various configurations of nanocomposites (SWCNT-SWCNT, SLGS-SLGS and hybrid SLGS-SWCNT), also by evaluating the effect provided by three different interlink compounds. The interfacial strength due to fibre pullout predicted by the hybrid atomistic-FE model is compared against experimental and molecular dynamics results available in open literature. The results show the specific deformation characteristics (localised auxetics) that provide an increase of pullout forces and interfacial strength with the use of the links.

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Keywords: Graphene sheets; carbon nanotubes; nanocomposites; finite element; shear strength;

1. Introduction

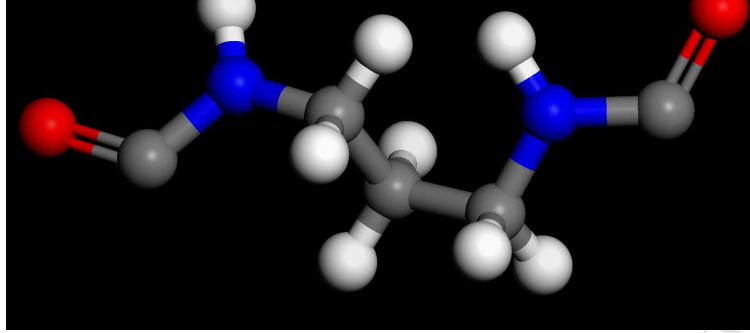
Carbon based nanomaterials such as graphene sheets and CNTs display exceptional mechanical [1–10] and electrical [11–16] properties. These nanostructures can be used to reinforce polymers and in general multifunctional composites and devices [17–24]. Graphene sheets can be mechanically exfoliated from graphite, chemically modified and then be embedded in polymer solution [25], or dispersed in an organic solution and then used as stable fillers in polymers [26]. CNT reinforced polymer composites can be produced by casting in a polymer [27], or typically by dispersing CNTs in a solvent by sonication followed by mix in a polymer liquid with ensuing evaporation of the initial solvent [28]. The demand for nanocomposites in industrial applications is ramping up [29], however some drawbacks are still present in the modern production of carbon-based structural materials. More specifically, some of the main problems are represented by an inadequate bonding between the matrix and reinforcement, the difficulty of producing an uniform dispersion within the matrix, and in general the generation of homogeneous

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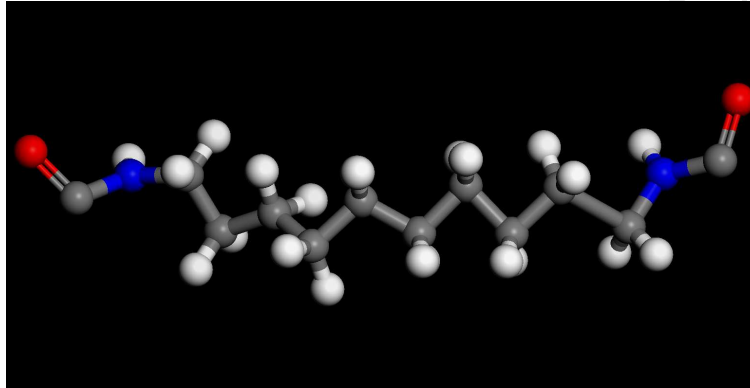
the polymer can enhance the structural performance of the composite [30] and overcome the drawback represented by the inadequate bonding strength.

To reduce the capital costs involved in the manufacturing of nanocomposites with additional chemical and functionalization groups it is essential to evaluate the aspects of fibre bridging at simulation level. The computational modelling of the mechanical properties of graphene sheets and CNTs at atomic scale has been performed by several researchers using Finite Element techniques [1, 2, 5, 6, 31–34]. The Finite Element-based atomistic simulation techniques to represent general carbon nanostructures have been used for example by Scarpa et al [1, 7, 8, 31] and Pour et al [2, 35]. Scarpa and co-authors in particular have developed a multiscale hybrid atomistic FE technique to represent the interaction existing between C-C sp^2 and sp^3 bonds, van der Waals interactions [1, 8, 36], the influence of hydrogenated bonds [37], and recently extended the technique to simulate the mechanics of DNA strands [38]. Atomistic-FE methods have also been used to describe the nonlinear and fracture properties of graphene and carbon nanotubes [39, 40], as well as the mechanical behaviour of nanocomposites and graphene reinforcements [6, 41–43]. Nanocomposites based on SLGS/SWCNT reinforcement can be considered as two-phase or multiphase materials, represented at their most basic configuration by the presence of a nanoinclusion and a surrounding matrix. At meso and nanoscales the polymer matrix can be considered as a continuous structure. Using the hybrid atomistic-FE approach the SLGS/SWCNT nanoinclusions can be represented numerically by an array of hexagonally oriented beam elements (Bernoulli [44] or Timoshenko [31]), with their nodes being the carbon atoms. The polymer matrix at micro scale can be approximated by 3D solid tetrahedral elements (see Fig. 1). The molecules of the polymer matrix are connected to carbon atoms through van der Waals forces represented by Lennard-Jones (LJ) potentials, when no functional groups are present. From the numerical standpoint, the LJ potential attractive and repulsive forces between the fibre and the matrix can be transferred through nonlinear spring elements [6, 45].

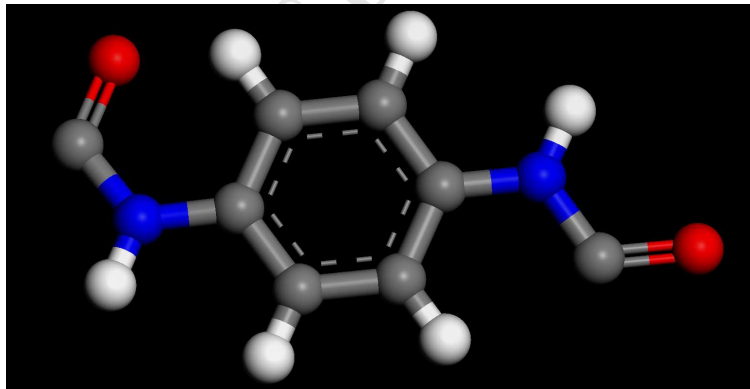
This work aims at investigating the effects due to the presence of molecular inter-linkers between different combinations of nano fillers (SWCNT/SWCNT, SLGS/SLGS and SWCNT/SLGS - Subfig. 2(a), Subfig. 2(b) and Subfig. 2(c) respectively) on the overall pullout force and strength of the composite material. The hybridization of the fillers has been done, since such composites are multiphase in nature. Exploitation of such multiphase composite systems has become a major topic of interest in recent years [46–48]. The use of aliphatic diamines and aromatic phenylenediamine as connecting functional groups between single wall carbon nanotubes within a polyethylene matrix has been observed to produce a significant increase of the pullout tensile force and the energy dissipated at the interface between the matrix and the carbon nanotubes [49]. The present work explores further the concept by using a modified multiscale approach based on the atomistic - FE approach to produce Representative Volume Elements (RVEs) that describe the polymer matrix, nanomaterial reinforcements, chemical group interlinks and van der Waals interactions within a nonlinear materials, geometry and failure criteria modelling framework. In this work we will consider three different types of inter-linkers (Fig. 1): aliphatic diamines ($(CH_2)_3N_2H_4$), long chain aliphatic diamines ($(CH_2)_{10}N_2H_4$) and Phenylenediamine (referred to as PDA). In Fig. 1 the black atoms are referred



(a) Aliphatic diamine $(CH_2)_3N_2H_4$ (Inter-linker-1)



(b) Aliphatic diamine $(CH_2)_{10}N_2H_4$ (Inter-linker-2)



(c) Aromatic Phenylenediamine (PDA)

Fig. 1. Inter-linkers used to bridge fillers in nano-composite RVEs.

to carbon, the blue atoms represent nitrogen, the white atoms are indicative of hydrogen, while the red atoms are representative of the connections between the polymer and the fillers. To the best of the Authors' knowledge, the work presented in this paper features two levels of novelty. The first is related to the multiscale model, that incorporates the simulation of chemical groups interconnecting matrix and the carbon nanostructures within an atomistic - FE method. The results of the proposed model are benchmarked against analogous data from open

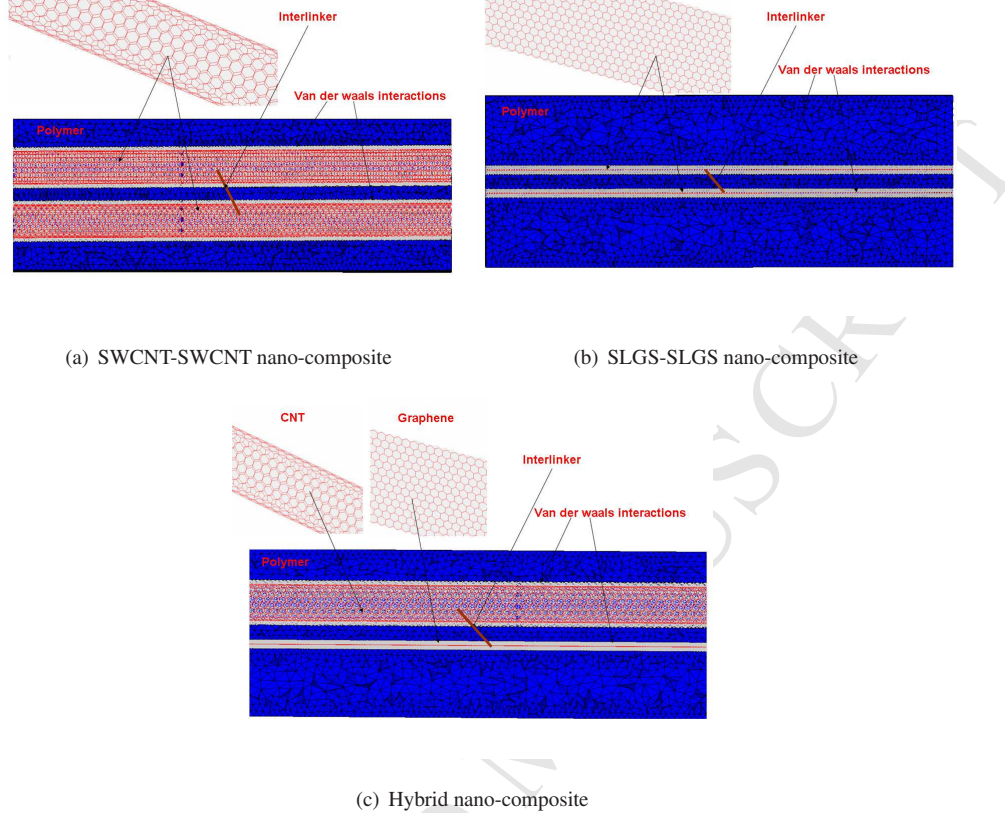


Fig. 2. Multiscale model of hybrid nano-composite with interlinkers: Three different types of inter-linkers have been simulated (refer Fig. 1)

literature produced using other molecular mechanics models. The second novelty lies within the prediction of the tensile pullout and shear strength of graphene/graphene and hybrid graphene/carbon nanotube reinforcements, and the assessment of the mechanical performance against interlinked SWCNT configurations already evaluated by other researchers. To the best of the Authors' knowledge these aspects have not been described in open literature so far.

2. Multiscale model of the nanocomposite structures

The sp^2 covalent bonds of the SWCNT and SLGS structures are represented here using deep shear Timoshenko with six degrees of freedom (3 translational and 3 rotational) beams [1, 31]. The element type B31 from the ABAQUS element library has been used to simulate covalent bonds. The length of each beam is 0.142 nm (the equilibrium length of C-C sp^2) and the diameter (thickness) is 0.089 nm [31]. The equivalent mechanical properties of the beams representing the C-C bonds are calculated based on the energy equivalence between the beams' strain

Property	Value
d	0.089 nm
l	0.142 nm
A	1.01 nm ²
E	19.5 TPa
ν	0.23
ϕ	0.37

energy and the stoichiometric harmonic potential calculated through force constant methods [31]:

$$\frac{k_r}{2} (\delta r)^2 = \frac{EA}{2L} (\delta r)^2 \quad (1)$$

$$\frac{k_\tau}{2} (\delta \varphi)^2 = \frac{GJ}{2L} (\delta \varphi)^2 \quad (2)$$

$$\frac{k_\theta}{2} (\delta \theta)^2 = \frac{EI}{2L} \frac{4+\Phi}{1+\Phi} (\delta \theta)^2 \quad (3)$$

In the above equations, k_r represents the stretching force constant and k_τ the out-of-plane torsional constant. The term k_θ represents a combined in-plane rotation (bending and torsion), consistent with the harmonic potential approach [31]. The term Φ is the shear correction factor, which becomes significant if the aspect ratio of beams is lower than 10 [50]. The numerical values of the constants mentioned in the above equations can be obtained by using the linearised Morse potential model [31] ($k_r = 84.7 \text{ nN } \text{\AA}^{-1}$, $k_\theta = 9.00 \text{ nN } \text{\AA} \text{ rad}^{-2}$ and $k_\tau = 2.78 \text{ nN } \text{\AA} \text{ rad}^{-2}$). For comprehensive understanding of this methodology, the readers are referred to [7, 31, 51]. The values of the equivalent material and the element property information for C-C bonds in SLGS and SWCNT are provided in Table 2.

In the present work the mechanical nonlinearity of the covalent bonds deformation has been ignored. The equivalent stress-strain curve for sp^2 C-C covalent bonds and graphene/carbon nanotubes can be found in various works [39, 40, 44, 52, 53]. The single C-C bond shows a linear regime under tensile loading up to 10 % [40]. Armchair and zigzag graphene sheets in graphitic state show a substantial linearity of the tensile response also up to 10 % in Molecular Dynamics models using AIREBO potential [54]. In a nano-composite with low loading (less than 0.5 % wt fraction in the present work), one can also expect larger strain levels occurring in the polymer but not in the graphene sheet. Since the maximum tensile deformation in the present simulations corresponds to around 10 % strain, the assumption of linear elastic regime with nonlinear geometric deformation for both SWCNT and SLGS can be considered justified. Similarly to the approach used for the C-C bonds, the mechanical properties of the other bonds in the inter-linkers can also be obtained applying the same energy equivalence, this time using the Universal Force Field (UFF) model [38, 55]. These equivalent mechanical properties are presented in Table 2. In order to simulate the tensile strength of interlinkers, a cutoff strain of about 20 % has been assumed. If the bonds

Bond types	Bond length (Å)	Bond thickness (Å)	Young's Modulus [TPa]
CH	1.08	1.01	6
CN	1.39	0.79	23.5
HN	1.01	0.8	16

in the interlinkers are strained beyond this value, then the stiffness of the bonds will be reduced to zero. The 20 % has been taken from the C-C bond inflection point of the curve present in [39]. However, during the simulation, the bonds in the interlinker do not get strained beyond 10 %, due to contact with the polymer.

The graphene sheets are connected to the polymer matrix by van der Waals forces described by nonlinear springs providing attractive and repulsive forces and following the force-displacement model [1, 8]:

$$F_{ij} = \frac{\partial V_{ij}}{\partial r} \quad (4)$$

Where r is the atomic displacement along the \mathbf{ij} connected carbon nanostructure/matrix atoms. The force between the atoms (ij) can also be represented by [56]:

$$F_{ij} = -12 \epsilon \left[\left(\frac{r_{min}}{y} \right)^{13} - \left(\frac{r_{min}}{y} \right)^7 \right] \quad (5)$$

Where $y = r_{min} + \delta r$, δr is the atomic displacement along the length \mathbf{ij} . The r_{min} (in Å) is given by $2^{\frac{1}{6}} \sigma$, where $\sigma = (A/B)^{1/6}$. The terms B and A represent attractive and repulsive constants. For the carbon-polymer interaction we adopt the values given in [6, 56, 57], ($A = 3.4 \times 10^{-4} \text{ eV} \times \text{Å}^{12}$ and $B = 5 \times 10^{-7} \text{ eV} \times \text{Å}^6$). The term ϵ is equal to $B^2/(4A)$. In the multiscale models we use nonlinear spring elements to simulate the interaction between reinforcement, with an equivalent force deflection curve calculated using Eq. 5. The type of element used in the ABAQUS solver is SPRINGA.

The polymer matrix has been discretized using 3D continuum elements with six degrees of freedom (C3D4 in ABAQUS). Isotropic material properties have been assumed to represent the material behavior of an epoxy matrix (Young's modulus OF 2.0 GPa and Poisson's ratio of 0.3 [58]). The nonlinearity in the mechanical behaviour of the polymer matrix has been considered by using a Ramberg Osgood approximation [58]. Relevant points of the epoxy stress-strain curve are shown in Table 3. A damage criterion based on strain (5 %) [43] has been assigned to ensure that the stiffness of the elements strained beyond that tensile threshold in the polymer becomes zero.

The dimensions of the RVEs are $60\text{Å} \times 40\text{Å} \times 110\text{Å}$. The SWCNTs used in this work are of armchair type (40,40) with a length of 98 Å. The SLGSs used consist also of an armchair type (40,40), again with a length of 98 Å. These dimensions ensure that both fillers have same surface area. As the SLGS offers a 2D surface, the contact interface with the polymer molecules occurs at both surfaces (top and bottom of the SLGS sheets). The force required to pull a fibre has been calculated by constraining one end of the nano-composite structure and applying a displacement to the end of filler in opposite side, similarly to the boundary conditions applied in [43, 49]. One end

Stress in MPa	Strain in %
15	1.0
40	2.0
60	3.0
62	4.0

of the RVE is constrained and a displacement is applied at the tab end of one of the nano-reinforcements (Fig. 3). The forces from one nanofiller are transferred to the other through the action of the inter-linker. The SWCNT-

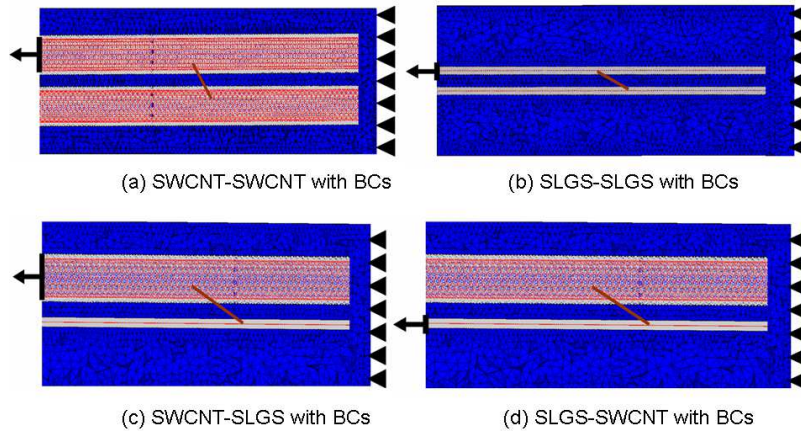


Fig. 3. Boundary conditions on four different multiscale FE models containing two fillers.

SWCNT nanocomposite contains two SWCNTs as reinforcements, with one of them being the primary filler (the one to which the end deformation is applied). A similar topology is applied to the SLGS-SLGS model. The SLGS-SWCNT model has the single layer graphene sheet at the reinforcement subjected to the external displacement. The pullout force is calculated as the reaction force measured at the end of the entire RVE where the displacement has been applied to the primary reinforcement. A node-to-element contact definition has been assigned between the nodes of the filler, inter-linkers and the surface of 3D elements in the polymer matrix. A nonlinear Newton-Raphson solver with switch on large deformation effects has been used to simulate the fibre pullout [59]. The simulation is executed until the reinforcement comes out of the matrix at a distance of 14.5 \AA . Beyond this cut-off length the elements of the reinforcement and the spring elements representing the LJ potential have been found to be unstable. During the simulation it was essential to deactivate the interface bonds between the filler and matrix if the deflection developed is higher than the cut-off distance of 0.85 nm [6]. It was also necessary to generate new bonds if a displaced carbon atom comes in contact with another atom of the matrix. Within the FE

[59]. The nodal displacements in the spring elements (interface bonds) are recorded at each increment step of the nonlinear loading. If the nodal displacement is found to be beyond the cut-off distance the analysis is stopped and restarted with an updated position of the nodes belonging to the spring elements. Another *Restart command is then issued to restart the run from the same increment. Activation and de-activation of the spring element sets are performed using the commands *Modelchange,Remove and *Modelchange,Add. This process has been referred to as the "debonding" and "rebonding" mechanism in the current work. Possible interlocking phenomenon due to the interaction between the carbon nanoreinforcements and matrix are taken into by defining a contact interaction (node to surface) between the fillers and polymer. Similar multiscale models have been developed in [45] and been used in [41]. However, these models do not describe the presence of interlinks between the nanoinclusion and the matrix as discrete functional groups.

3. Results and discussions

The pullout forces versus the tensile deformation are shown for various types of nano-reinforcement and interlinkers in figures 4 and 5. The general trend of these forces is very similar for all the four boundary conditions

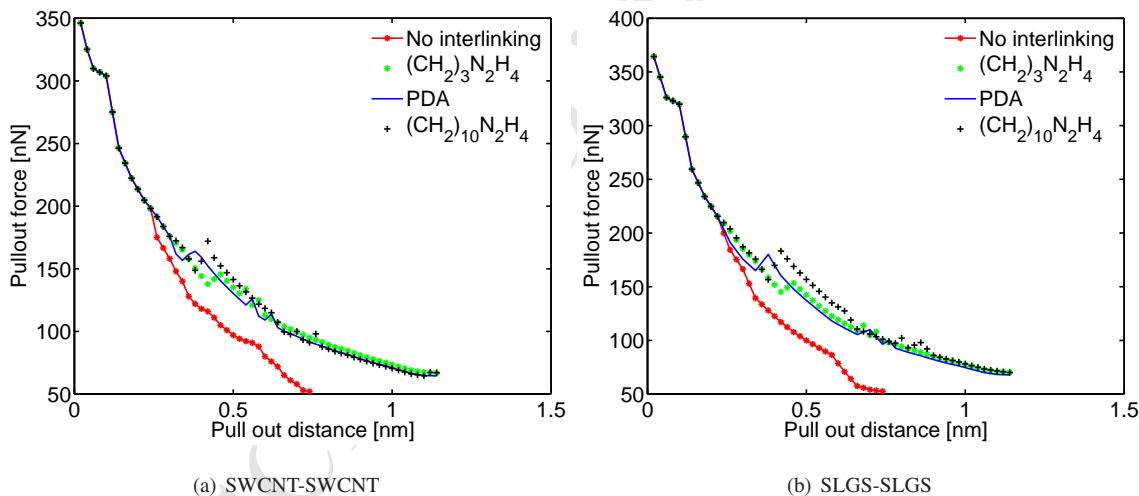


Fig. 4. Force required to pull out the fibre from the SLGS-SLGS and SWCNT-SWCNT nanocomposites.

considered, and this indicates that the two types of nano-reinforcement are quite close in terms of mechanical behaviour under the conditions assumed in this work. It is however possible to observe some differences in terms of magnitudes of the pullout forces when the reinforcements are directly compared one against the other. The maximum pullout force observed for a composite with a SLGS being the primary reinforcement is 370 nN, 6% higher compared to the case in which the single wall carbon nanotube is the primary filler (refer to Figure 4(a)). The higher interfacial strength in the SLGS nanocomposite due to the higher contact surface area between the reinforcement and the polymer is believed to be responsible for this behaviour. The same trend has been also observed in the other two nanocomposite topologies (Figures 5(a) and (b)) because the primary reinforcements in the SWCNT/SLGS

posites respectively (Figure 3). The force/displacements curves remain almost identical up to a pullout distance

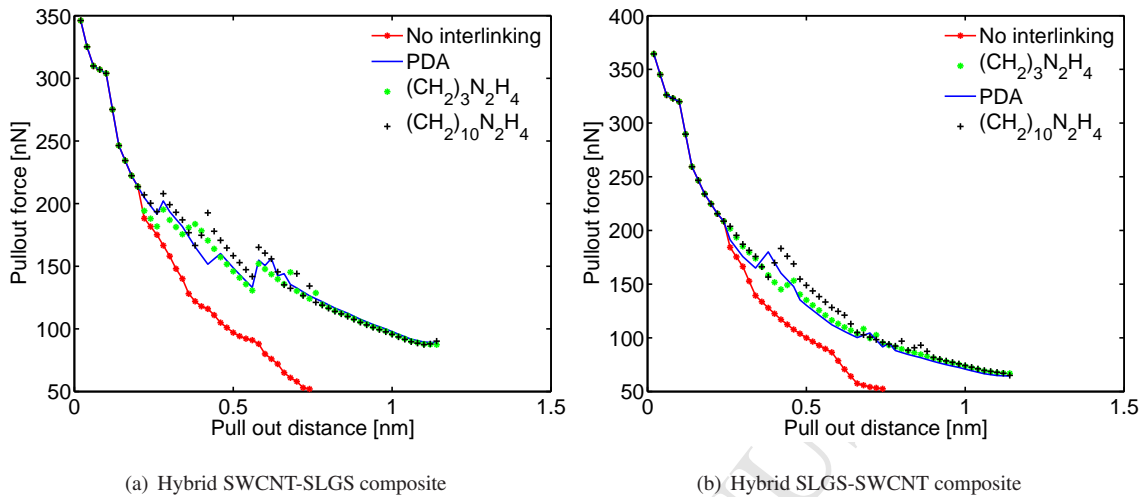


Fig. 5. Force required to pull out the fibre from the hybrid nanocomposites.

of 0.2 nm, because only the primary reinforcement is bearing the load at this stage. After this threshold distance a sudden increase in load (first peak) can be observed due to the debonding and rebonding of the van der Waals interactions in the primary reinforcement. Beyond the 0.2 nm pullout distance the curves however diverge because the load starts to be shared by the inter-linker groups. The composites without inter-linkers generate lower reaction forces beyond this distance. In the case of the nanocomposites with the inter-linkers a sudden increase in load can be observed, with its magnitude depending upon the type of inter-linker used. The model with the $(CH_2)_{10}N_2H_4$ groups generates the highest load at this point, because of its higher length that allows to transfer the load at higher tensile displacements. The PDA inter-linker also offers an increase in terms of load to pullout, since it possess a larger surface that facilitates the contact with the surrounding polymer. After the threshold distance the load will be distributed uniformly in the two reinforcements. As the load is transferred to the couple of reinforcements through the inter-linkers the walls of the carbon nanostructures distort, leading to interlocking of these walls with the surrounding polymer. Such wall distortion in the case of the SWCNT fillers can be considered a localised auxetic effect [49] (Fig. 6), similarly to what observed in auxetic polymeric fibres subjected to pullout tests [60]. As also demonstrated by MD simulations carried previously by some of the Authors [49], the auxetic effect enhances the pullout resistance of the nano reinforcements because of the fretting of the nanofiller against the matrix system due to the transverse tensile expansion (negative Poisson's ratio effect), leading to increased toughness and energy dissipation of the overall structure [61]. Further discontinuities in the load/displacement curves can be observed around 0.75 nm as a result of the debonding/rebonding occurring within the secondary reinforcement. The reaction force generated by the secondary filler in the SWCNT-SWCNT nanocomposite is around 160 nN, 12.5% lower than in the case of the SLGS/SLGS configuration, and a further indication that the single layer graphene offers an enhanced uniaxial tensile mechanical performance, also a secondary reinforcements. Similar trends can also be

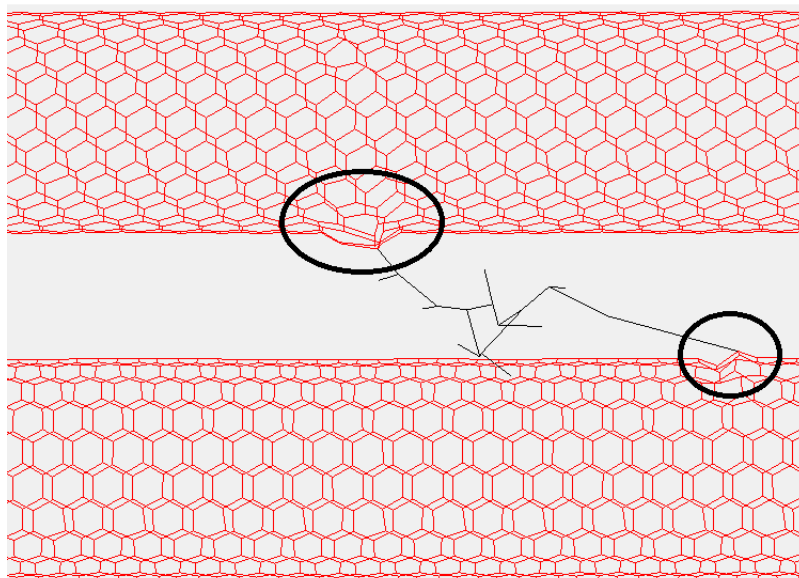


Fig. 6. Evidence of localised auxetic effect between the SWCNT reinforcements provided by the inter-linker effect.

noticed in the hybrid SWCNT/SLGS and SLGS/SWCNT nanocomposites.

The interfacial strength between the filler and the matrix can be calculated as [49]:

$$E_{pullout} = 2\pi rL\tau_i d - \pi r\tau_i d^2 \quad (6)$$

In the above equation, τ_i is the interfacial shear strength, r and L are the width and length of the reinforcements, x is the axial location in which the strength of the nanocomposite is measured and d is the deformation of the nanoreinforcement. The pullout energy in kcal/mol can be calculated by $F_{pullout} = \frac{\partial E_{pullout}}{\partial d}$, in which $F_{pullout}$ is the lowest pullout force (in nN) measured during the simulation and d is deformation expressed in nm. The interfacial strength τ_i measured in the current work and compared with the one determined by other authors is given in Table 4.

The magnitude of the interfacial strength computed in the present work is within the lower end of the reported values in open literature (44 MPa - 102 MPa). There is a noticeable scatter in the values of the interfacial shear strength, the variability attributed to the different types of force models adopted in the molecular dynamics simulations, the nature of the polymer matrix and the nanoreinforcement used. The highest interfacial strength value we have observed in open literature is 500 MPa [62]. Gou et. al. [63] have also simulated the presence of a SWCNT reinforcement in a epoxy matrix and reported 75 MPa as the interfacial strength, 75 % higher than what has been simulated in the present work with no use of inter-linker. The maximum interfacial strength recorded in the present work is 102.32 MPa (obtained by interlinking SLGS fibers with PDA). This value is very close to that of conventional/commercial carbon fibre composites [74–78]. It is also worth noticing that in the case of stick-slip damping

Table 4. Interfacial strength reported in open literature and present work. The values of present work are from SWCNT-SWCNT and SLGS-SLGS nano-composites only. The terms PEEK, MWCNT and rGO in the table refers to Polyether ether ketone, multiwalled carbon nano tubes and reduced graphene oxide respectively.

Authors	Filler type	Interfacial strength (MPa)	Inter-linker type	Matrix type	Analysis type
Wagner et al. [62]	MWCNT	500	-	Urethane based	Experimental
Gou et al. [63]	SWCNT	75.00	-	Epoxy	MD
Liao and Li [64]	SWCNT	160.00	-	Polystyrene	MD
Rahman and Haque [65]	SLGS	88.00	-	Epoxy	MD
Lv et al. [66]	FSLGS	70.00	-	Polyethylene	MD
Chowdhury and Okabe [67]	SWCNT	75.00	-	Epoxy	MD
Barber et al. [68]	MWCNT	47.00	-	Polyethylene	Experimental
Sager et al. [69]	MWCNT	86.6	-	T650 carbon-Epoxy	KellyTyson model [70]
Jang et al. [71]	rGO	136.6	-	Polycarbonate	Semi-Empirical
Tsuda et al. [72]	MWCNT	14	-	PEEK	Experimental
Roy et al. [73]	SWCNT	160	-	Polyvinylalcohol	Experimental
Present work	SLGS	49.26	-	Epoxy	Atomistic
Present work	SLGS	62.14	PDA	Epoxy	Atomistic
Present work	SLGS	95.25	$(CH_2)_3N_2H_4$	Epoxy	Atomistic
Present work	SLGS	102.32	$(CH_2)_{10}N_2H_4$	Epoxy	Atomistic
Present work	SWCNT	44.28	-	Epoxy	Atomistic
Present work	SWCNT	58.25	PDA	Epoxy	Atomistic
Present work	SWCNT	88.42	$(CH_2)_3N_2H_4$	Epoxy	Atomistic
Present work	SWCNT	98.13	$(CH_2)_{10}N_2H_4$	Epoxy	Atomistic
Zhang et al. [49]	SWCNT	46.48	-	Polyethylene	MD
Zhang et al. [49]	SWCNT	63.45	PDA	Polyethylene	MD
Zhang et al. [49]	SWCNT	90.26	$(CH_2)_3N_2H_4$	Polyethylene	MD
Zhang et al. [49]	SWCNT	100.85	$(CH_2)_{10}N_2H_4$	Polyethylene	MD

used to fit experimental modal loss factors values varies as low as 0.2 MPa - 2 MPa [79]. In the current work, the interfacial strength computed for the SWCNT-SWCNT type nanocomposites is very close to that computed with MD in [49] with similar inter-linkers and polyethylene matrix. The maximum difference is found to be around 2% (for the inter-linker $((CH_2)_{10}N_2H_4)$). In the cases of both SWCNT/SWCNT and SLGS/SLGS nanocomposites the configuration with the $((CH_2)_{10}N_2H_4)$ inter-linker offers the highest interfacial shear strength efficiency, while the $((CH_2)_3N_2H_4)$ group provides the weakest contribution due to its short length, leading to an overall lower stiffness.

4. Conclusion

The pullout and interfacial strengths in nanocomposites with hybrid inter-linker reinforcements have been predicted using a numerical nonlinear tensile atomistic-FE multiscale model. The model predicts a localised geometric distortion when the nanoreinforcements interact with the matrix because of the presence of an inter-linked (auxetic effect), as also predicted in previous works using molecular dynamics simulations. The bridging of the nanoreinforcements with a link molecule enhances the pullout strength by up to 30%. The stiffness and surface area of the inter-linkers play a role in enhancing the mechanical strength of overall nanocomposites, with the $(CH_2)_{10}N_2H_4$ interlinker found to be the most in transferring the load. The composites with SWCNT acting both as primary and secondary reinforcements show a slight enhanced pullout performance (2 % more) than the graphene layer based and hybrid nanoreinforcements. As a secondary filler the SWCNTs also offer 10% extra pullout strength when compared to single layer graphene sheets. The interfacial shear strength between the nanoreinforcements and the matrix computed with the multiscale technique shows a very good agreement with analogous configurations simulated using Molecular Dynamics, and also shows a correlation between the specific carbon nanostructure used and the chemical groups used for the inter-link. The model presented in this paper and the configurations of inter-linked nanocomposites proposed may be used to further the. The novelty of this research lies in the development of a simulation methodology that can predict the behaviour of multiphase nanocomposites at multiple length scales in which the nanofillers are bridged by interlinkers.

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