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STRETCHING THE ENDURANCE BOUNDARY OF COMPOSITE MATERIALS: PUSHING THE PERFORMANCE LIMIT OF COMPOSITE STRUCTURES

Review of the role of the interphase in the control of composite performance on micro- and nano-length scales

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Abstract In fiber reinforced composites (FRCs), exhibiting heterogeneous structure at multiple length scales, the interphase phenomena at various length scales were shown to be of pivotal importance for the control of the performance and reliability of such structures. Various models based on continuum mechanics were used to describe effects of the macro- and meso-scale interphase on the mechanical response of laminates and large FRC parts, satisfactorilly. At the micro-scale, the interphase is considered a 3D continuum with ascribed average properties. Number of continuum mechanics models was derived over the last 50 years to describe the stress transfer between matrix and individual fiber with realtively good success. In these models, the interphase was characterized by some average shear strength, τ_a, and elastic modulus, E_a. On the other hand, models for tranforming the properties of the micro-scale interphase around individual fiber into the mechanical response of macroscopic multifiber composite have not been generally successfull. The anisotropy of these composite structures are the main reasons causing the failure of these models. The strong thickness dependence of the elastic modulus of the micro-scale interphase suggested the presence of its underlying sub-structure. On the nano-scale, the discrete molecular structure of the polymer has to be considered. The term interphase, originally introduced for continuum matter, has to be re-defined to include the discrete nature of the matter at this length scale. The segmental immobilization resulting in retarded reptation of chains caused by interactions with solid surface seems to be the primary phenomenon which can be used to re-define term interphase on the nano-scale. Thus, the Rubinstein reptation model and a simple percolation model were used to describe immobilization of chains near solid nano-particles and to explain the peculiarities in the viscoleastic response of nano-scale “interphase.” It has also been shown that below 5 nm, Bernoulli–Euler continuum elasticity becomes not valid and higher-order elasticity along with the proposed reptation dynamics approach can provide suitable means for bridging the gap in modeling the transition between the mechanics of continuum matter at the micro-scale and mechanics of discrete matter at the nano-scale.

Introduction

Continuum mechanics can be used to describe effects of micro-scale interphase on the stress transfer in single fiber composites considering the system a three phase material in which the individual phases, i.e., solid inclusion, matrix and interphase, can be characterized by some average properties [1–5]. Unlike at the micro-scale, extreme caution has to be exercised when selecting suitable modeling scheme at the nano-scale when the discrete molecular structure of the polymer becomes obvious. One of the main difficulties when considering nano-scale in composites is to determine the size of the representative volume in which the discrete nature of the composite structure has to be taken into account [6]. Very little has been written so far on the laws governing the transition between the nano- and micro-length scales, especially, on the reliability of classical continuum mechanics when scaled outside their validity range, i.e., down to the nano-scale [7]. Thus, it seems desirable to perform a critical review of the current

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knowledge on the structure and properties of the micro- and nano-scale interphases in polymer composites and the methodologies for their modeling in order to provide means for bridging the gap between continuum and discrete models useful for reliable design of future multiscale hierarchical composite structures.

The design of multi-length-scale composite structures, such as the fuselage of the Boeing 787 (Fig. 1), represents the state-of-the-art engineering application of fiber reinforced composites (FRCs). These large structures are designed from top to bottom using continuum mechanics methodologies and the transitions between the individual length scales are treated simply with scalling down the structural features of the greater length scale. Such multiscale continuum mechanics modeling approach was demonstrated to provide reasonable means for transforming the mechanical response of polymer composites accross several length and time scales from macro- down to micro-scale (Fig. 2) [8].

Since the FRCs exhibit heterogeneous structure at multiple length scales, the interphase phenomena are of pivotal importance for the control of the reliability and performance of multiscale FRC structures. There seems to be general agreement on using continuum mechanics models to account for interphase phenomena from macro- to micro-scale and the design schemes based on continuum mechanics, variational principles or Finite Element Analysis (FEA) have been validated [2]. The understanding of the translation of the properties of the micro-scale interphases into the response of macroscopic FRC parts is far less unambigious [9]. The greatest success have been achieved in understanding and modeling of the role of the micro-scale interphase in the stress transfer from the matrix to a single fiber in model composites [2–4, 8]. However, attempts to transfer properties of the micro-scale interphase in the performance of a multi-fiber FRC structures have generally failed.

Over the last 20 years, substantial advances were made in understanding the deformation behavior of hard tissues such as bones which can also be considered multiscale functionally hierarchical composite structures (Fig. 3) [7]. Unlike the FRC fuselage, bone is designed bottom-up

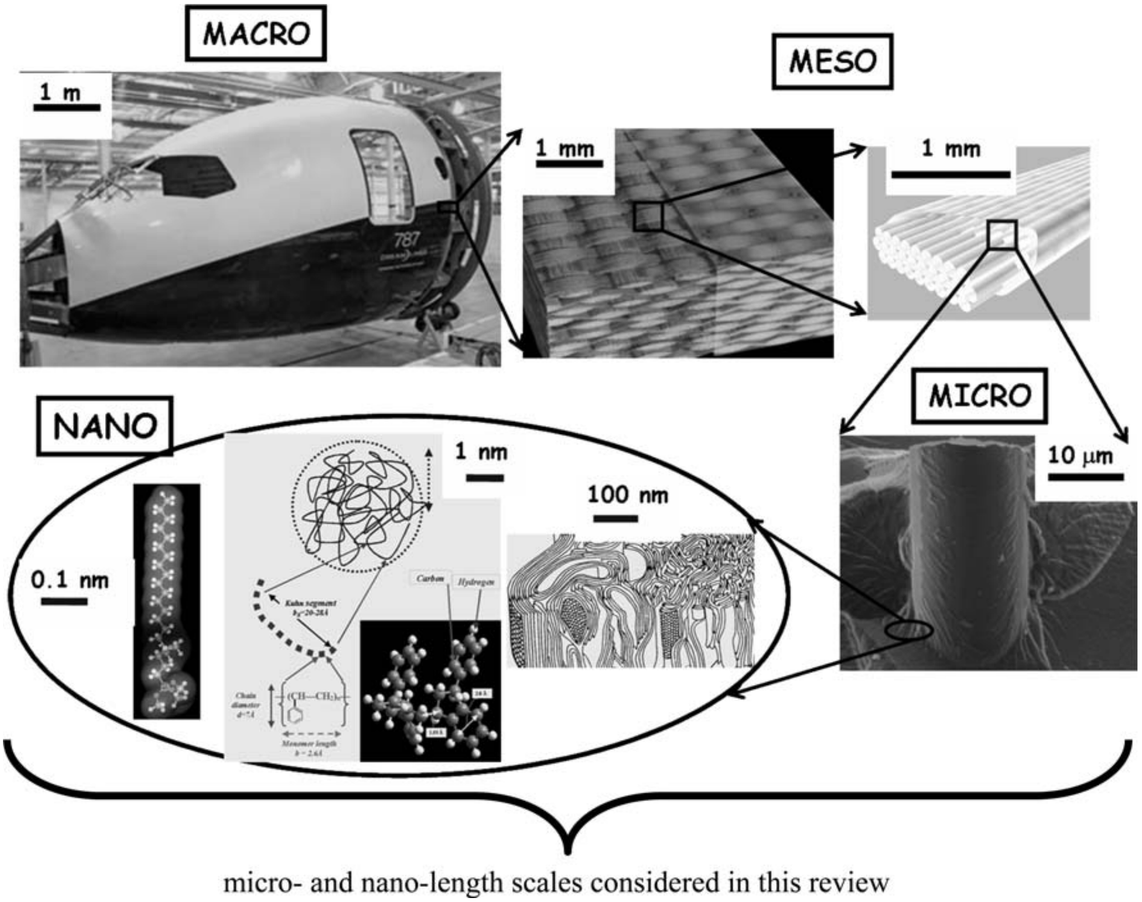

Fig. 1 Part of the fuselage of Boeing 787 Dreamliner can serve as an example of a large manmade *multiscale* composite structure. This polymer composite structure has been designed using the engineering top–bottom methodology within the framework of continuum mechanics. No functional hierarchy exists between the various length scales

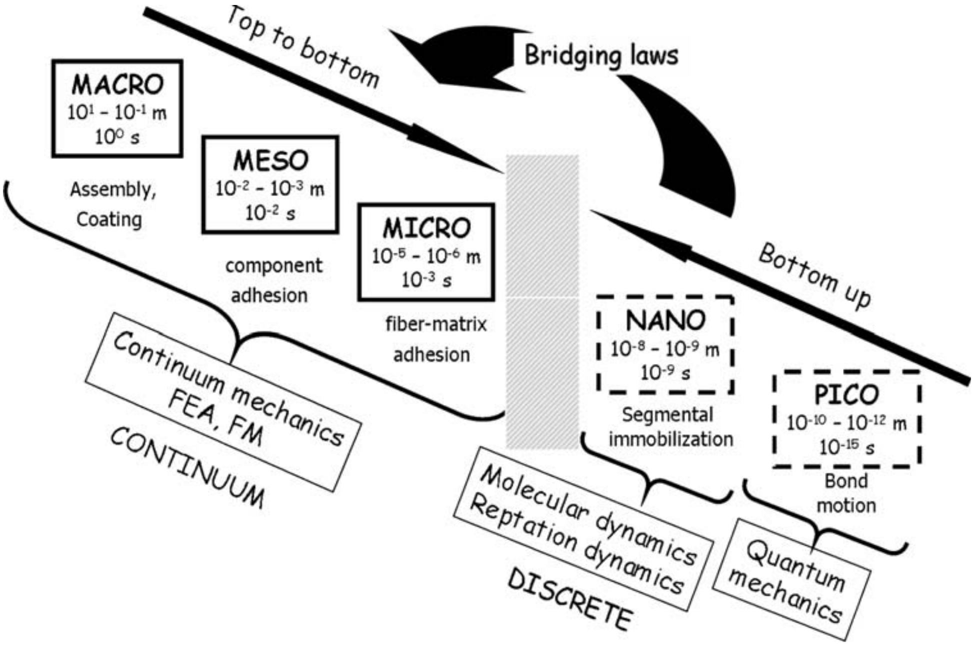

Fig. 2 Schematic drawing of the two principal methodologies in designing multiscale composite structures, i.e., the *top–bottom* engineering approach and the *bottom-up* approach observed in natural composites with the emphasis on the role of interphase phenomena at various length and time scales

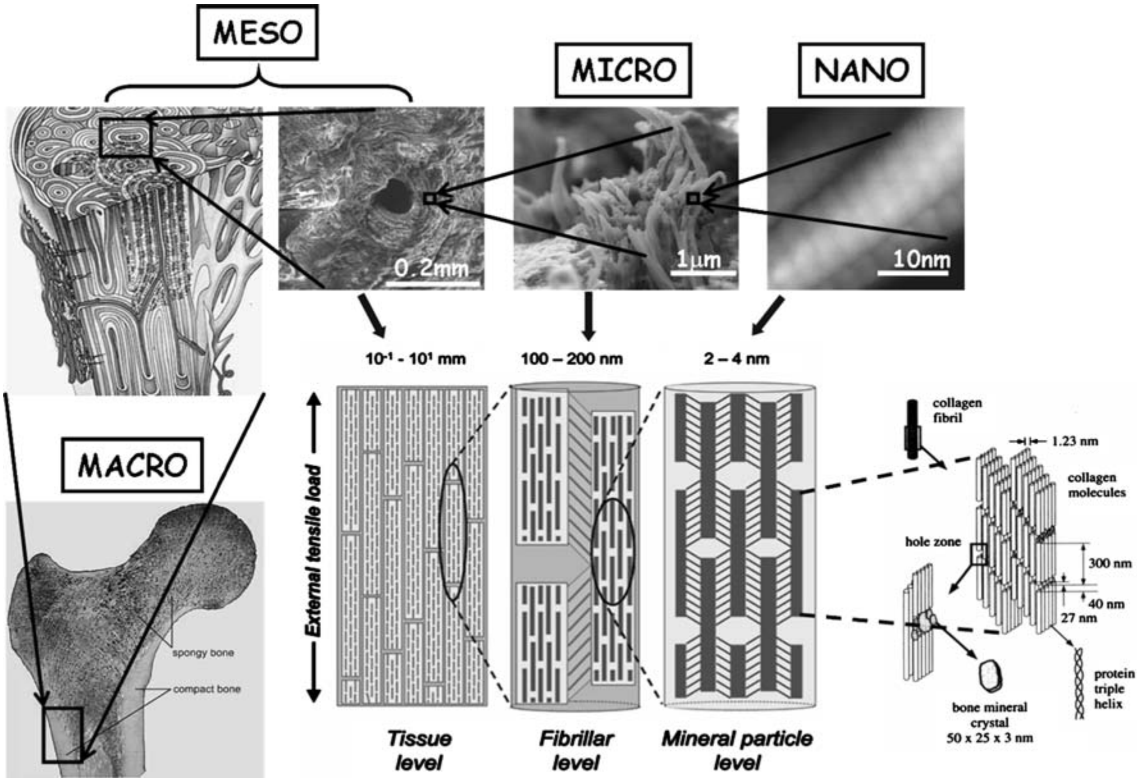

Fig. 3 Part of the femur bone can serve as an example of a large natural *multiscale, functionally hierarchical* composite structure. This polymer composite structure has been designed using the bottom-up methodology with the molecularly designed discrete interphase ensuring mechanical performance of the bone and providing means for functional hierarchy and signaling between the various length scales [assembled with help of Ref. 10]

starting from mineralized protein fibrils, to osteons up to a complete bone [10, 11] (Fig. 2). Despite of similar multiscale structure, natural composite structures differ from the man made composites, significantly. One of the main differences is in the role of the molecular interphases allowing the natural composite to be hierarchical, addaptive and self-repairable. In addition, the discrete molecular nature of the “interphases” between various length scales in hard tissues result in mechanically stiff and tough natural composites [12, 13].

In this paper, the interphase phenomena in the manmade and natural polymer matrix composite structures at the micro- and nano-scales are briefly reviewed. The bridging laws for transformation of properties of the discrete matter at the nano-scale to the continuum matter at the micro-scale, based on the combination of gradient strain elasticity and reptation dynamics of a chain above T_g, will also be outlined.

Micro-scale interphase

The research of the micro-scale interphase phenomena in composite materials has attracted considerable attention of both the scientific and engineering communities over the last 50 years. Good succes has been achieved in describing the role of the interphase in stress transfer from the matrix to the fiber using model single fiber composites (Fig. 4). From the simple Kelly-Tyson model, to the various lap shear models, to the numerical F.E.A. models, the approach based on the continuum mechanics has been employed

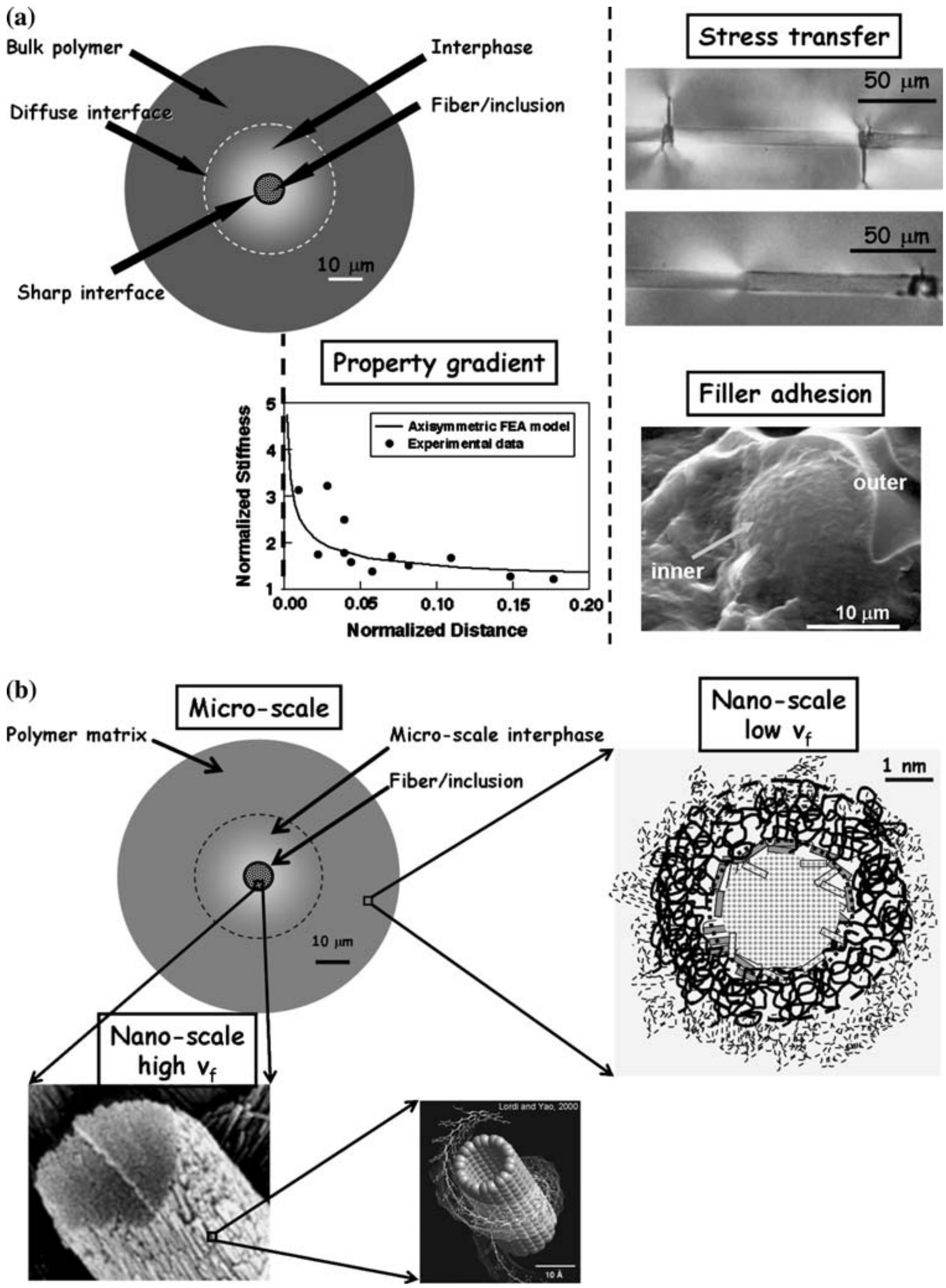

Fig. 4 (**a**) Visualizing the interphase considering only the micro-scale. Interphase is a continuum layer with a gradient properties reflecting variations in its structure. The main role of the micro-scale interphase is to provide stable and effective means for stress transfer between inclusions and polymer matrix even under adverse conditions. (**b**) Visualizing the structure of a micro-composite considering also the nano-scale structural features when the discrete structure of the matrix and inclusions becomes evident

[14]. Even though the molecular structure of the interphase has been anticipated in many papers, with some exceptions [15–17], the main effort has been devoted to the relationship between the type, thickness and deposition conditions of the fiber coating and the average shear strength of the interphase, τ_a, measured in a simple test employing model single fiber composite [18].

Mechanical properties and environmental stability of both fiber reinforced and particulate filled thermoplastic composites are strongly dependent upon the stability of the interfacial region between the matrix and fibers, especially when exposed to moist environment. This is of particular importance in glass fiber reinforced thermoplastic composites since the glass fibers are highly hygroscopic and the bond between the fibers and the thermoplastic matrix is usually weak. Hence, the tailoring of well-bonded, durable interphases between the thermoplastic matrix and glass reinforcement has become a critical concern. The use of coupling agents, chemically reactive with both matrix and reinforcement, and/or chemical modification of the surfaces of one or both constituents have been the most successful means of providing reasonably well controlled bond between matrix and the encapsulated reinforcement [19].

From the published data, it seems clear that a monomolecular interphase layer with engineered molecular structure specific for the desired combination of resin and reinforcement should result in the most favorable mix of properties in thermoplastic matrix composites. Reactive end-capped polymers capable of chemically reacting with the fiber surface or various methods of grafting matrix molecules onto reinforcement surface are the most promising candidates for further investigations [17, 20]. Thickness of the interphase can be controlled via modification of the molecular weight and chain stiffness of the constituent molecules, its mechanical properties can be varied by selecting the backbone chain constitution and configuration, and its surface free energy can also be controlled by the chain constitution and by the polarity of the end-groups. Elastic properties of these layers are controlled by the attraction forces at the interface as well as the conformation entropy of the chains forming the layer.

Organofunctional silanes are so far the most widely used coupling agents for improvement of the interfacial adhesion in glass reinforced materials [19]. Upon application of a silane from either dilute solution or the vapor phase, a highly crosslinked multilayer siloxane “interphase” is presumably formed with thickness ranging from 1.5 to 500 nm. Unlike in thermosetting matrices with extensive interpenetration between organosilane layer and the matrix monomer, long chain molecules do not interpenetrate the organosilane layers significantly. On the other hand, immobilization phenomena are of a greater importance in thermoplastic matrix composites. Moreover, processing temperatures of engineering thermoplastics ranging from 230 to 350 °C can exceed the thermal stability of the commonly utilized organosilanes.

Thickness dependence of the elastic modulus of thin polycarbonate (PC) layers deposited on a flat E-glass substrate was measured over the thickness interval ranging from 10^6 to 30 nm [9, 21, 22]. In all cases investigated, elastic moduli of the deposited layers, E_i, decreased monotonically with increasing layer thickness reaching a constant bulk value for layers thicker than 5×10^5 mm (Fig. 4). Thermally annealed PC and $SiCl_4$ grafted oligo-PC interphases, exhibited higher elastic moduli than the as received solution deposited PC interphase. No effect of thermal annealing on elastic modulus of strongly bonded oligo-PC interphase was observed. It has been shown that the shear strength of the interface, τ_a, measured in a singlefiber fragmentation test exhibited strong dependence on the interphase E_i.

Similarly to the PC interphases, elastic moduli of the deposited silane layers decreased monotonically with increasing layer thickness reaching a bulk value for layers thicker than 10^5 nm [21, 22]. Reactive chlorine containing silane formed always stiffer layers compared to its alkoxy-analogues most probably due to stronger interaction between the chlorine and glass surface and, most probably, due to less defective network structure (Fig. 5). This hypothesis was further supported by the observed strong effect of deposition technique, controlling the layer supermolecular structure, on the layer elastic modulus. Solution deposition technique yielded always layers with lower elastic modulus compared to the layers formed by rf-plasma or rf-plasma enhanced CVD deposition of the same substance. A qualitative explanation of the observed behavior was provided assuming formation of strongly immobilized layer of constant thickness, t_i, and elastic modulus, E_i, near the bonded interface. Strength of the interfacial bond and network density of the polysiloxane interphase were proposed to be the factors determining t_i and E_i for the given external conditions. Experimental data showed that the contribution of this strongly immobilized layer started to play an important role for interphase thickness below 10^3 nm. This “inner” layer has been covered with weaker “outer” layer with more defective network structure. The thickness of the “outer” layer was dependent on the concentration of the silane solution it was deposited from. The difference in E_i between the outer and inner interphase layer was increasing with strengthening the layer-surface interaction.

In order to enhance the performance and reliability of the FRC structures at the macro-scale, the results obtained for the micro-scale interphase can be used to control the stress transfer between the matrix and the reinforcement. Stiff interphases provide very efficient stress transfer, less

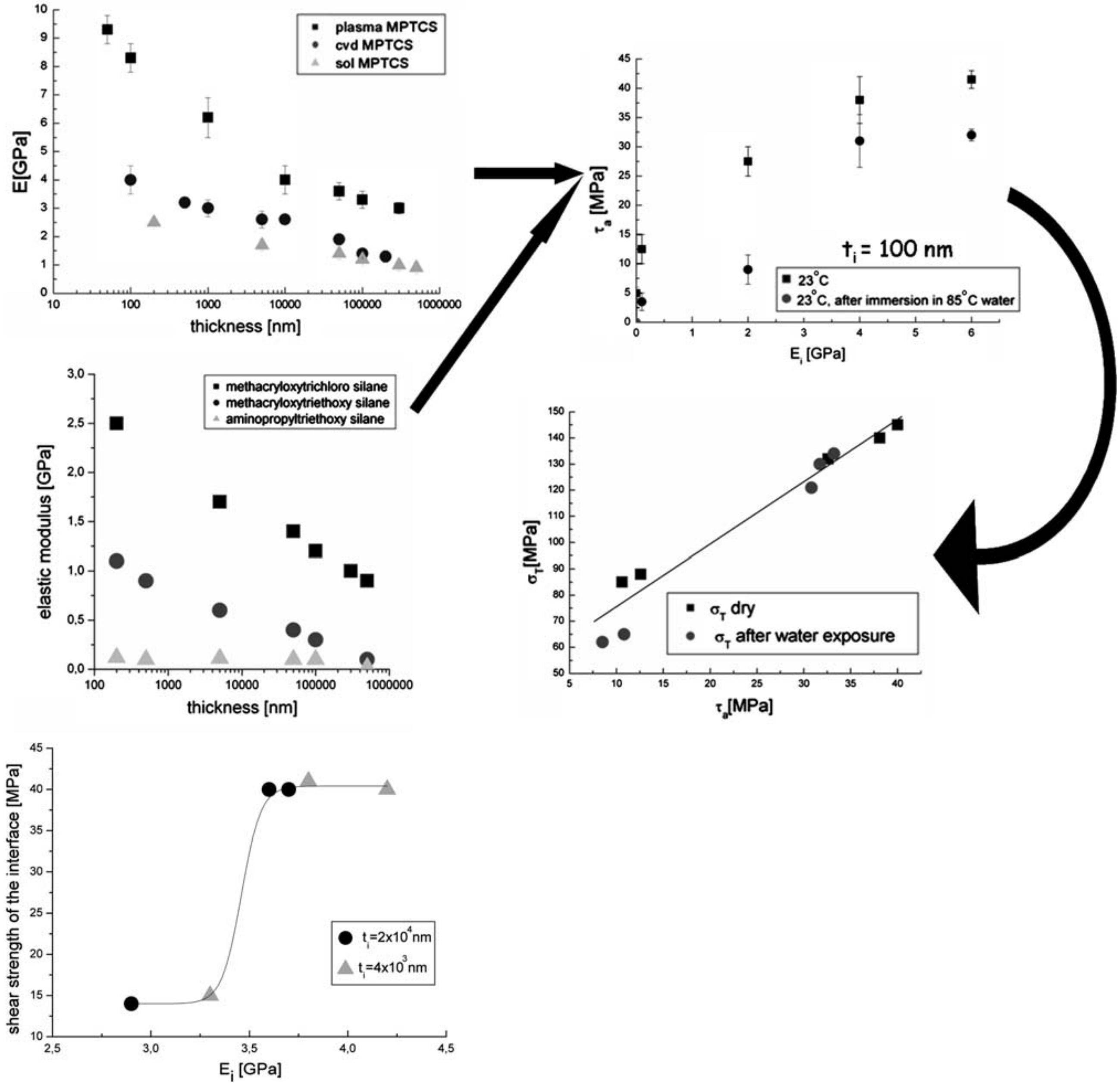

Fig. 5 A typical example of the micro-scale organosilane interphases of various composition deposited on glass fibers using various deposition techniques and translation of the phenomenological properties of the interphases into mechanical response of multifiber compsoites with unidirectiolly aligned fibers

water diffusion, however, support brittle failure, thus, limit the damage tolerance of the FRC. Tough interphases slightly reduce the effectiveness of stress transfer and may be less resistant to water attack, however, they provide significant enhancement of damage tolerance of the FRC part. Moreover, the tough interphases are less sensitive to the direction of the external loading compared to the stiff ones. As it has already been shown, one can design hybrid FRCs with reinforcing fibers coated with both stiff and tough interphases in order to tailor the performance and reliability of the final FRC part.

Nano-scale interphase

One has to bare in mind, however, that when the length scale considered reaches few nanometers, which is equal to the size of individual polymer chains, the very term "interphase" becomes un-umbigious due to the fact that the discrete nature of the matter has to be taken into account. Originally, the term interphase has been defined in the framework of continuum mechanics. However, the continuum mechanics in the Euler form may no longer be valid on the nano-scale due to very large non-locality in elastic response of systems with coordinated movement of large number of atoms, such as observed in polymer composites [23].

The role of the nano-scale "interphase" to control the performance and reliability of the FRC parts has to be considered from two perspectives: (i) low v_f nano-composites ($v_f < 0.05$) and high v_f nano-composites ($v_f > 0.85$). The (i) represents the direction to preparing new nano-structured advanced matrices while the (ii) leads to designing new nano-structured advanced reinforcements. With few exceptions, most of the published literature on the synthetic nanocomposites deals with the low v_f nanocomposites [24–31], while, on the other hand, most of the literature published on high v_f nano-composites is related to the mechanics of bio-composites such as bones, teeth and shells [10–13].

Most of the experimental evidence related to the interphase in the low v_f nano-composites were obtained at temperatures below the polymer T_g using meso-scale test specimens. Assuming the chain immobilization to be the primary reinforcing mechanism on the nano-scale, spatial distribution of the conformation entropy within the polymer phase is of primary importance. Hence, experimental data for nano-composites above the matrix T_g has to be considered. Sternstein at al [32] published interpretation of the viscoelastic response of rubbery nanocomposite above the matrix T_g, i.e., the Payne effect. Kalfus and Jancar [33, 34] analyzed the viscoelastic response of polyvinylacetate filled with nano-sized hydroxyapatite over the temperature range from −40 to +120 °C and observed strain softening similar to the Payne effect [35]. The modulus recovery experiments allowed to determine the terminal relaxation time of reptation motion of bulk and surface immobilized chains, supporting the hypothesis that there is no "interphase" per se when nano-scale is considered. In order to bridge the gap between the continuum interphase on the micro-scale and the discrete molecular structure of the matrix consisting of freely reptating chains in the bulk and retarded reptating chains in contact with the inclusions, higher-order elasticity combined with a suitable molecular dynamics model could be utilized.

It was demonstrated, that the large specific surface area of the nanosized filler is capable of immobilizing large amount of entanglements causing the steep increase of E' with small addition of nanoparticles. This observation seemed to confirm the purely entropic character of the reinforcement mechanism on the nanoscale. All the data published support the dominant role of the chain immobilization as the main reinforcing mechanism.

In the light of the existing experimental evidence, it seems that the term "interphase" defined as a continuum phase of limited extent looses its physical meaning when considering true nano-composites. Due to two orders of magnitude greater specific surface area of the true nanofillers, almost all the polymer chains are in contact with the surface at very low filler loadings above 2 vol.%. In addition, continuum mechanics has only limited validity at this length scale and the discrete molecular structure prevails resulting in strong effect of non-local character of viscoelastic response of the nano-composite matrix.

The interphases in high v_f nano-composites were studied using the abalone shells [36]. These shells represent a laminated sheet reinforced composite with over 95 vol.% of aligned 500 nm thin aragonite sheets embedded in a protein matrix in apparently mesh-like fibrillar form (Fig. 5). In the work of Hansma and co-workers [12, 13], the model of sacrificial bonds has been proposed to explain the observed high-fracture resistance of nacreous composites. It has been shown by Zidek and Jancar [37], that the hypothesis of the sacrificial bonds can also be used to simulate deformation response of lightly cross-linked long flexible chain network polymer fibril. In order to apply the model [37] to the behavior of an ensamble of chains in the vicinity of rigid weakly attractive nanometer sized inclusion, the immoilization phenomenon has to be investigated as the source of the drastic change in the viscoelastic behavior of polymers with addition of small amount of nano-scale inclusions.

Chain immobilization on the nanoscale

Reducing the size of rigid inclusions from micro- to nano-scale is accompanied by 2–3 orders of magnitude increase in the internal contact area between the chains and the inclusions. Moreover, above 2 vol.% nano-particle content, the average interparticle distance is reduced below 2 radii of gyration, R_g, of the chains. Hence, almost all the chains are in contact with the solid surface, possess reduced segmental mobility at temperatures $T \geq T_g$. Below T_g, main chain segmental mobility is frozen and only secondary low temperature side chain mobility can be affected. In addition, the conformation statistics of chains near solid surface can be altered from Gaussian random coil to Langevin coil above T_g and this phenomenon can be transformed into the behavior of immobilized chains also upon solidification below T_g.

In order to characterize the reduction in chain mobility in an entangled melt quantitatively, one can use the characteristic reptation relaxation time, τ_{rep}, introduced by deGennes [38]. The τ_{rep} is given for an entangled chain as:

$$\tau_{\text{rep}} \cong \frac{L^2}{D_c} \cong \frac{NL^2}{D_0}, \qquad (1)$$

where L is the length of the reptation path, N the number of monomer units in a chain, D_c and D_0 are diffusion constants of a chain and a monomer, respectively. The terminal relaxation time of a chain in a neat polymer melt can be expressed in a number of ways. Lin [39] has expressed the τ_{rep}, taking chain contour length fluctuation into account, in the form:

$$\tau_{\mathrm{rep}} = \frac{L_0^2}{\pi^2 D_{\mathrm{c}}} \cong \frac{b^2 \zeta_0 N^2}{\pi^2 k_{\mathrm{b}} T} \left(\frac{M}{M_{\mathrm{e}}}\right) \left[1 - \left(\frac{M_{\mathrm{e}}}{M}\right)^{1/2}\right], \tag{2}$$

where ζ_0 is the monomer friction coefficient, b the length of the statistical segment, k_{b} the Boltzmann constant, T the absolute temperature, N_{e} is the number of monomer units per one entanglement strand.

In the case of a chain interacting with a filler surface and entangled with neighboring chains, the question of primary importance is how to establish a connection between the static conformation structure and the chain dynamics. In spite of certain intra-molecular order, the chain in a melt can be considered a random Gaussian coil. If such a chain approaches a solid surface, its conformation transfers to the train-loop-tail structure and the chain conformational entropy, as well as, the chain internal energy can alter very substantially depending on the surface-polymer interaction energy, e_{fp}, under given conditions. Assuming the chain friction coefficient, ζ_{c}, in the form [40, 41]:

$$\zeta_{\mathrm{c}} = \zeta_0 N + \zeta_{\mathrm{a}} N^{1/2}, \tag{3}$$

where ζ_{a} is the friction coefficient of an adsorbed monomer unit and the number monomer units in trains is $N_{\mathrm{a}} = N^{1/2}$ for the weakly interacting surface, the terminal relaxation time is in the form:

$$\tau_{\mathrm{rep}}^{\mathrm{ads}} = \frac{L^2}{2D_{\mathrm{c}}} = \frac{b^2 N^{5/2}}{2k_{\mathrm{b}} T N_{\mathrm{e}}} \left[\zeta_0 N^{1/2} + \zeta_{\mathrm{a}}\right] \tag{4}$$

Kalfus and Jancar [33] extended the use the above Rubinstein model [40, 41] to describe the reptation time of a linear chain weakly interacting with nano-filler surface.

Friction coefficient, ζ_{a}, is very difficult to measure and it is known just for the system silica-polystyrene [42] at 153 °C. Estimation of the ζ_{a} was based on the theoretical analysis given by Subbotin et al. [43]. Thus, one can establish a relation for the reptation time of a surface adsorbed chain as follows:

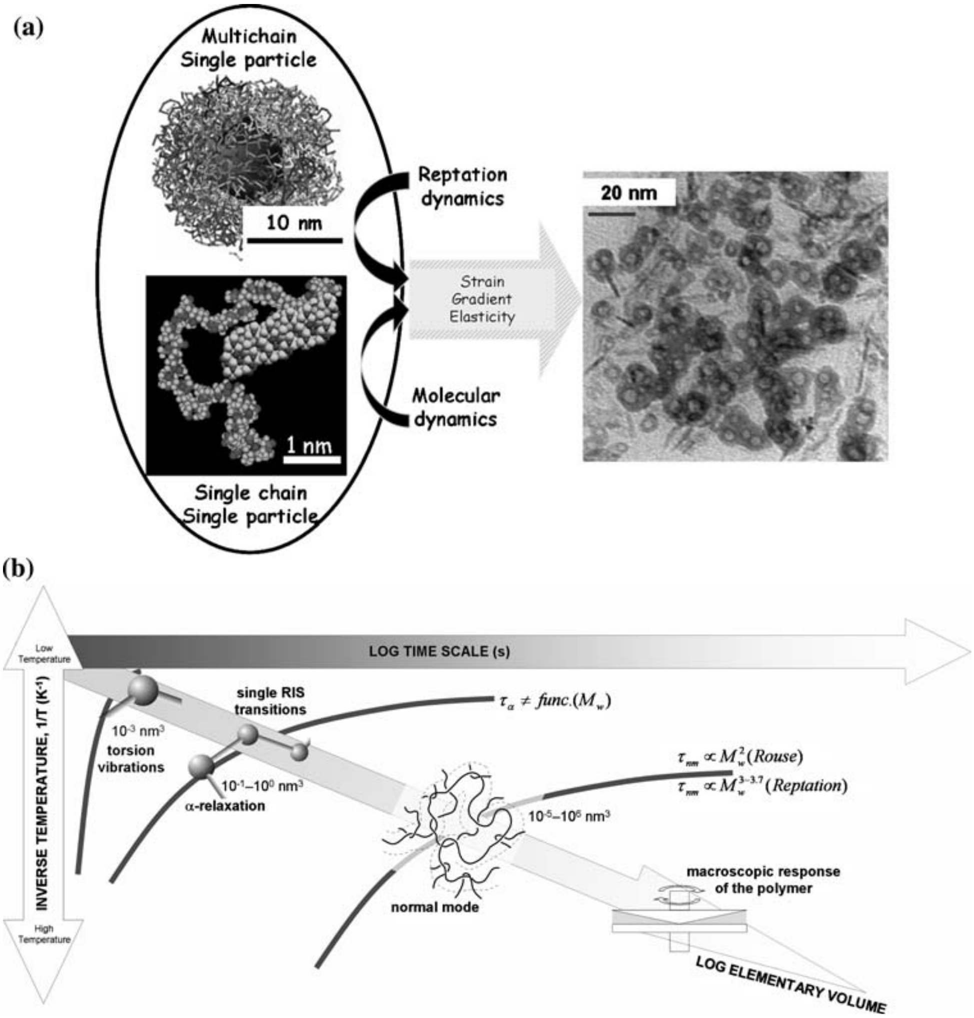

Fig. 6 (**a**) Schematic drawing of the nano-scale "interphase" and the models used to translate behavior of discrete matter consisting of molecules with segmental mobility reduced due to the presence of nano-scale solid inclusions. Crystalline inclusions surrounded by a number of long chain molecules can be modeled as a continuum while amorphous inclusions with the extent of non-locality similar to polymers has to be considered discrete as well. (**b**) Molecular relaxation processes on the background of the time, temperature and elementary volume scale [6]

$$\tau_{\mathrm{rep}}^{\mathrm{ads}} = \frac{b^2 N^2}{\pi^2 k_{\mathrm{b}} T N_{\mathrm{e}}} [\zeta_0 (N - N_{\mathrm{a}}) + \zeta_{\mathrm{a}} N_{\mathrm{a}}] \tag{5}$$

In the case that $N_{\mathrm{a}} = N^{1/2}$, the reptation time takes the form:

$$\tau_{\mathrm{rep}}^{\mathrm{ads}} = \frac{b^2 N^{5/2}}{2\pi^2 k_{\mathrm{b}} T N_{\mathrm{e}}} \left[\zeta_0 N^{1/2} + \zeta_{\mathrm{a}}\right] \tag{6}$$

To describe the change in reptation dynamics of the chains as a function of nanoparticle volume fraction, percolation model was used. At the percolation threshold, physical network formed by interconnection of immobilized chains on individual nanoparticles penetrates the entire sample volume. In this case, only physical “cross-links” are considered and the terminal relaxation time reaches the value characteristic for the life time of the physical filler-polymer bond. Thus, the relaxation time near the percolation threshold is expressed in the form [44]:

$$\tau_{\mathrm{composite}}^{\mathrm{rec}} = \tau_{\mathrm{rep}}^{\mathrm{ads}} v_{\mathrm{eff}} \left(\frac{v_{\mathrm{eff}} - v_{\mathrm{eff}}^*}{1 - v_{\mathrm{eff}}^*} \right)^b \tag{7}$$

where v_{eff}^* is critical effective filler volume fraction ($v_{\mathrm{eff}}^* = 0.04$ for PVAc-HAP at 90 °C) and b is the percolation exponent ($b = 4$ for the same system). The v_{eff}^* is a sum of the filler volume fraction and the volume fraction of immobilized chains and was shown to equal 0.04 for PVAc-HAP nanocomposites at 90 °C. In order to simplify the percolation, random clustering of effective hard spheres was considered only in the way similar to that originally outlined by Jancar et al. [45] for micro-scale composites. Percolation threshold at approximately 2 m^2 of the filler-polymer contact area per 1 g of the composite was found in PVAc-HA nanocomposite system (Fig. 6). All the chains were immobilized at the internal contact area of 42 m^2 per 1 g of the nanocomposite.

Characteristic length scale for transition between continuum and discrete elasticity in polymer composites

The classical continuum mechanics is designed to be size-independent. For nano-composites, however, size-dependent elastic properties have been observed which cannot be readily explained using continuum mechanics and, thus, prevent simple scalling down the existing continuum elasticity models [23]. Polymers are unique systems with macroscopic viscoelastic response driven by the relaxation processes on the molecular level [46]. These relaxation processes represent particular molecular motions occurring in some characteristic volume, V_{c}. The V_{c} depends on the type of the relaxation process and temperature. The characteristic volumes vary from 10^{-3} nm^3 for localized bond vibrations to 10^6 nm for the non-local normal mode of relaxation (Fig. 6) [46]. In the case of the non-local normal mode of relaxation, its characteristic volume is the upper limit for V_{c} displaying strong dependence on the chain size. Below this upper limiting characteristic volume, $V_{\mathrm{c}} \sim R^3 \propto N^{3/2}$, where R is the chain end-to-end distance and N is the number of monomer units in the chain. The characteristic time, τ_{c}, for each particular relaxation process varies from 10^{-14} s for bond vibrations above T_{g} to the infinitely long times below T_{g}. Thus, the macroscopic viscoelastic response of a polymer is a manifestation of a range of molecular relaxations localized in some characteristic volume and the rate of the relaxation mode is indirectly proportional to its locality (Figs. 7 and 8).

The physical reasons for the expected breakdown of continuum elasticity on the nano-scale include increasing importance of surface energy due to appreciable surface to volume ratio [47], the discrete molecular nature of the polymer matrix resulting in non-local behavior in contrary to local character of classical elasticity [48], the presence of nano-scale particles with the length scale similar to the

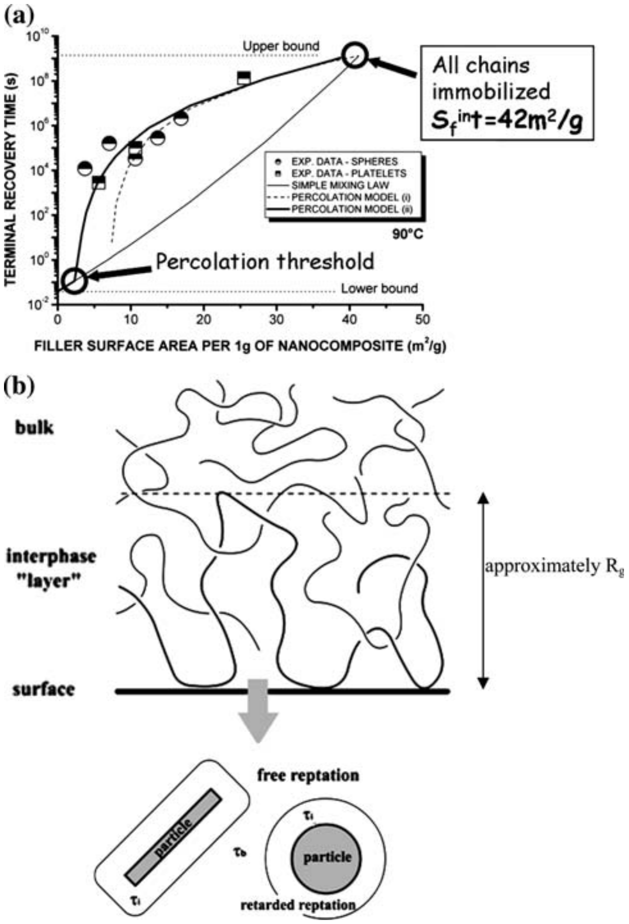

Fig. 7 Simple approach combining the reptation dynamics and percolation model to describe the retarded reptation of chains in the vicinity of solid nano-sized inclusions representing the nano-scale “interphase”

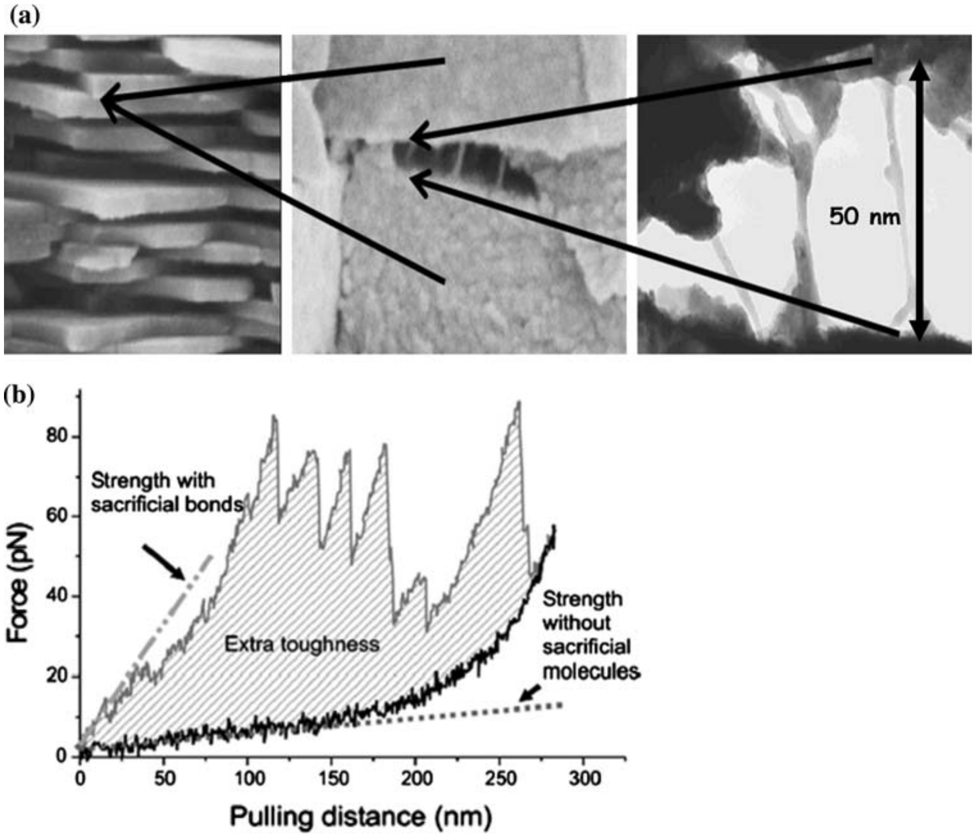

Fig. 8 (**a**) Cleavage of the abalone shell at various length scales revealing the discrete character of the "interphase" when visualized on the nano-scale [36]. (**b**) Schematic representation of the effect of sacrificial bonds on the cleavage strength of the discrete molecularly designed interphase shown in (**a**) [12, 13]

radius of gyration of the polymer chains [49, 50] and internal strain due to molecular motion within a non-primitive lattice [51, 52]. Quantum confinement effects can also play a role inducing a strain field on the nano-scale without the presence of external loading, however, its importance is limited to the size range below 2 nm [53].

In order to estimate the length scale at which the classical elasticity becomes non-valid, the MD on a polyethylene chain in a cubic simulation cell was performed under periodic boundary conditions at 50 K [23]. The corresponding length scales for the longitudinal and transverse directions were 1.85 and 3.81 nm, respectively. A recent work by Nikolov et al. [53] estimated that rubbers above their T_g should have non-local length scale approximately 5 nm. The high non-locality in polymers most probably stems from a cooperative behavior of large number of chain segments characteristic for entangled polymers. As a result, parts of the material system may undergo considerable non-affine deformation associated with occurence of high-moment stresses. Consequently, for such systems, taking strain-gradient effects into account while investigating nanoscale elastic phenomena may impart significant size-dependent corrections to the results obtained from classical continuum elasticity [23]. The magnitude of corrections that strain-gradient effects may impart to results obtained by classical continuum elasticity has recently been proposed by Park and Gao [48]. The bending rigidity of a rectangular beam was calculated for various length scales [23]. For polyethylene, the bending rigidity increased with decreasing beam dimensions and was double that of the classical Bernoulli–Euler bending rigidity at beam dimensions of 5 nm. On the basis of the arguments put forward above, the one may consider to carefully revise published data on the elastic properties of carbon nanotubes measured using classical elasticity.

Conclusions

In polymer matrix composites exhibiting heterogeneous structure at multiple length scales, the interphase phenomena are of pivotal importance for the control of their performance and reliability. In this paper, a review of the current knowledge on the interphase phenomena at various length scales has been attempted comparing multiscale manmade composite structure with natural multiscale functionally hierarchical composite structure. On the micro-scale, the interphase is considered a 3D continuum possessing some average properties such as elastic modulus, shear strength and fracture toughness. Existing continuum mechanics models provide satisfactory means to relate these properties to the stress transfer from matrix to the individual fiber. These models are far less successfull in translating the properties of the interphase on an individual fiber into the performance of a multifiber composite parts.

On the nano-scale, the discrete molecular structure of the polymer has to be considered. The segmental immobilization seems to be the primary reinforcing mechanism in true polymer nanocomposites at temperatures near and above the T_g. Reptation model and simple percolation model were used to describe immobilization of chains near solid nano-particles and to explain the peculiarities in the viscoleastic response of polymers near solid surfaces of large polymer-inclusion contact area. The "interphase" in the continuum sense does not exist at the nano-scale when relaxation processes in individual discrete chains are taken into account and the chains with retarded reptation can be considered forming the "interphase" analogue in the discrete matter. For a common polymer, all the chains in the composite become effectively immobilized when the internal filler-polymer interface area equals approximately 45 m^2.

In polymers at very low temperatures, the classical Bernoulli–Euler continuum elasticity becomes not valid below approximately 5 nm. The size of this characteristic volume increases with increasing temperature and higher-order strain elasticity along with molecular dynamics approach has to be used as the bridging law to connect behavior of the discrete matter at nano-scale with mechanical response of continuous matter at larger length scales.

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