

Modulus of elasticity & design of polymer/hydroxyapatite and other synthetic & natural polymer/ceramic composites of various geometries

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ABSTRACT

We present an overview of the subject of modulus of elasticity (E of polymer/ceramic such as hydroxyapatite (HAP) composites (for fiber/needle, platelet and low aspect ratio ceramic particles) as a function of volume fraction and, when applicable, orientation and aspect ratio; other discussed issues include packing effects (among them mesoscopic liquid crystallinity during composite processing involving preformed asymmetric particles), porosity and some scale-related effects. Selected mechanics results are discussed with emphasis on overlooked points. We adopt simplifications that allow for the easy comparison between synthetic alternatives, while what is commonly achievable (especially in terms of maximum ceramic loads) synthetically routes is contrasted with corresponding features of natural composites. We examine systematically, from the E point of view, when it is clearly beneficial to employ high modulus ceramics and when a moderate modulus ceramic can serve as a comparably effective reinforcement. Brief discussions of a number of important formation and property issues pertaining to key HAP and CaCO_3 based natural composites are also included.

Keywords: Composites, modulus of elasticity, mesoscopic liquid crystallinity, packing, hydroxyapatite (HAP).

List of abbreviations

HAP	Hydroxyapatite	E_m	Modulus of matrix
OCP	Octacalcium phosphate	E_f	Modulus of fiber
ACP	Amorphous calcium phosphate	E_{pl}	Modulus of platelets
PLLA	Poly-L-lactide	E_{comp}	Modulus of composite
HIPS	High impact polystyrene	ϕ	Volume fraction
BN fibers	Boron nitride fibers	ϵ	Porosity (= porous fraction)
LDPE	Low density polyethylene	λ	A factor for the E_{\perp} contribution to $E_{2-D,random}$ or $E_{3-D,random}$
PIPD	Pyridinylene-1,4(2,5-dihydroxy)phenylene	α	aspect ratio of the particles
H-S	Hashin-Shtrikman	ν	Poisson ratio
S-G equation	Smallwood-Guth equation	ν_m	Poisson ratio of the matrix
$E_{//}$	Axial modulus	k	Modulus enhancement factor for particulate composites
E_{\perp}	Transverse modulus	L	Length of fiber
E_o	Modulus of compact material	L_c	Critical length of fiber

1. INTRODUCTION

Calcium phosphates are among Nature's favorites for the role of reinforcing phase in structural biocomposites; yet there is a substantial variety as regards: (a) the exact function of the composite, which is vastly different for tooth enamels and bones, (b) the particle size and shape, e.g. platelet or needle, (c) the particle arrangement, which might be regular, quasi-random and, also, either isolated or network-forming, (d) the type of organism, e.g. mammal or fish etc, (e) the matrix material, e.g. collagen or other biopolymer and (f) various other features, such as the levels of porosity and moisture. In addition, artificial composites [1-12] bearing dispersions of HAP and related compounds can be and have been considered both for medical applications and other more generic structural, composite-type, uses; materials employing crystalline or amorphous apatite precursors, e.g. in the

form of bioactive glasses or ACP, also attract substantial interest. We will focus on a key mechanical property, namely modulus of elasticity (E), of, mostly compact, composites involving a polymer matrix and a dispersed ceramic phase; here HAP can be thought of as an example of dispersed ceramic exhibiting a moderate to high E value. We will describe some approaches towards attaining composites having interesting morphologies and resulting mechanical properties. Considerations span a spectrum of composite geometries exceeding that considered in most sources dealing with synthetic composites; we will only discuss briefly some actual examples and we will also skip some of the details adequately discussed in standard textbooks of synthetic composites [15-17] in order to expose overlooked important points and include original insights.

2. COMPOSITES

A ceramic like HAP might be produced in the form of particles with one (flake), two (needle) or three (low asymmetry grain) small dimensions [13-14]; the latter particles can be dispersed in a polymer matrix for the purpose of forming composites though non-composite applications of particulate HAP are possible. In addition, one might aim at generating HAP composites that do not necessitate a step of separate formation of the ceramic phase.

One of the general potential reasons to develop a composite is to replace a particular single phase (often ceramic) material B with a two phase (A+B) material that bears B phase as a dispersion within an A matrix. Those of the latter composites that are easier to process result from mixing of a B powder with an appropriate thermoplastic polymer, or an appropriate oligomer to be cured in the case of thermosets.

In the case of synthetic structural composites one employs polymer matrix/ceramic fiber composites in order to generate materials that, within a certain temperature range which is largely defined by the characteristic temperatures of the polymer resin, preserve a reasonable fraction of the modulus of the bare ceramic, attain improved strength and toughness, have a better shape control, redistribute within the material the strong bonds in a way such that reinforcement is limited to the directions (or planes) in need of reinforcement etc. Also, in certain cases it is barely

possible (though never impossible) to produce a sizable single component robust material of the ceramic of interest.

In the case of biological structural composites, Nature employs polymer matrix/ceramic (platelet or fiber) dispersions to achieve e.g. higher toughness, reduced proneness to fail catastrophically, enhanced capacity for effective healing etc. In addition, both in biological and synthetic composites selective reinforcement of particular directions or planes is frequent. Here it is possible to optimize composite shape and, further, to optimize local properties of the material, e.g. by local adjustment of the orientation of asymmetric elements such as nanoplatelets etc.

Ashby plots [18] having as axes $\log \rho$ (ρ = density) and $\log E$ suggest that when the weight of the material is one of the optimization parameters ('minimum weight designs') some of the composites in consideration can compete with ceramics for some types of loads and can compete-with or even be better-than key metals for certain types of loads; however high aspect ratio ceramic particles with E values higher to substantially higher than those of HAP are needed for strong competition of the latter kind. Further focus on tough polymer matrix/ceramic composites might create further interest in HAP (or related ceramics)-based composites even outside the field of materials of obvious medical interest (e.g. composites such as PLLA/HAP).

3. NATURAL AND SYNTHETIC COMPOSITES WITH A POLYMER MATRIX

3.1. Natural composites with a polymer matrix.

Organisms of all five kingdoms include a total of more than 60 ceramics; often the bioceramics are the dispersed phase of structural composites with a biopolymer matrix. However, organisms also include ceramics for other uses (e.g. arrays of minute (40-250 nm) magnetite or greigite single crystals detecting earth's (or any other) magnetic field, calcite otoliths detecting the direction of gravity and calcite single crystals serving as micro lenses in certain sea animals); in addition, several important natural structural composites exist with little or no ceramic phase (e.g. wood, skin).

The natural polymer/ceramic structural composites normally employ a biopolymer matrix having an elaborate primary structure while the usually embodied ceramics are calcium carbonate (also Mg-substituted calcite, dolomite etc), carbonated-HAP and fluorapatite and other phosphates, silica and some iron compounds. It is of interest that the ceramics encountered in natural composites are compositionally simple and only moderately hard & stiff; the lack of top-level stiffness is not a key issue as toughness is often more important than stiffness in the case of biological structural materials. Even in the case of non-structural natural composites the bioceramics frequently associate with 'elaborate' organic molecules; for example, magnetite crystals of the magnetotactic bacteria are surrounded by lipid bilayers and proteins [19]. The reasons behind the choice of *particular* simple ceramics for natural structural composites are

difficult to determine as they correspond to local optima of complex and partly unknown maps of parameters. Even the comparison between two potential choices is a difficult task and those more experienced in the field usually prefer to make clear that they only refer to *simple* guesses. For instance, it is often suggested that calcium carbonate is preferred over silica for sea shells as dissolved calcium ions are abundant in sea water while silica is highly insoluble. In the case of calcium cation and with an emphasis on the calcium carbonate choice, it has been noted that in the late Precambrian period the ocean was highly saturated in calcium ions; hence living species were probably secreting substances capable of preventing accidental deposition of CaCO_3 while, subsequently, inhibition was turned into tightly controlled deposition [20].

Coming now to the case of mammals, calcium cation becomes immediately available to the next generation through milk; yet, overall, absorbable calcium is not abundant outside water. In any case, why does calcium in mammals combine (in tooth and in bones) with (hydroxy)phosphate rather than with carbonate anions? The enhanced hardness of HAP over calcium carbonates is a reasonable basis for a simple handwaving argument as regards the constitution of tooth enamel. However, the tooth enamel is, apparently, just the 'crown' of the HAP of certain organisms and not the starting point of the whole biological-structural HAP 'idea'. Currey [21] notes two speculative suggestions of other authors as regards the preference

of various organisms for HAP: (a) HAP single crystals tend to be smaller than calcium carbonate single crystals and, hence, nanocrystals, favored for toughness etc reasons, can be formed more easily in the former case, (b) HAP resists better than calcium carbonates dissolution in internal acidic environments of vertebrates. Pasteris et al [22] consider the same issue more systematically and also point out that: (a) HAP constitutes a major 'safe reservoir' of Ca and P necessary for other functions of the organism, (b) desirable nanocrystalline features can be controlled (or, at least, stabilized) through the extent of incorporation of carbonate species. The original work [22] should be consulted for some details and additional suggestions; also the crystallographic role of carbonate and other species in HAP crystals is considered in further detail by Wopenka & Pasteris [23]. Here we note that biological HAP is a partially carbonated one; while potential benefits, such as control of crystallite dimensions, resulting from the latter substitution are known [23], one might also wonder if the partial carbonization had as an evolutionary precursor some full carbonization version.

In the case of natural polymer/ceramic composites, is the involved heteropolymer (protein) primary structure necessary for the achievement of the observed medium to very high ceramic loads (e.g. with 0.35 to 0.9 volume fraction)? While this is what the data might suggest at a first glance, a word of caution is necessary. The natural composites in consideration are not plain materials but tissues which are not only self-formed but they are also often self-renewed/self-repaired and, in addition, they have non-structural functions as well. Consequently, the chemical complexity of the primary structure of matrix polymers need not serve only an ordinary-type fabrication role. For example, Vincent [24] has suggested that while glycine, proline and hydroxyproline suffice for the formation of the collagen triple helix, collagen includes various other monomers because bone healing involves dissolution and some of the additional aminoacids of actual collagen might accelerate dissolution and, hence, ultimately, healing. We might also note that the mechanics of natural polymer/nanoceramic composites might be affected not only by the geometry and scale of the nanoparticles but from the fine details of the chains as well; elaborate monomer sequences might be needed for elaborate (device-like rather than 'simple material'-type) mechanical responses as well.

Further, another characteristic of proteins (including non globular proteins), namely monodispersity, might also allow for a more 'simple geometrical' control of ceramic domains via generation, upon proper chain packing, of regular openings/pockets (to be occupied by the ceramic nanoparticles); as regards some vagueness of the term 'control' see below. We might also refer to a more obvious example of a different natural composite, i.e. skin (which contains no ceramic); its main structural role is that of, say, a sturdy plastic bag but part of the complexity, as regards chemistry and spatial arrangement, of its substances aims at affective: (i) healing (when needed), (ii) moisture exchange (continuously), (iii) blocking the entrance of certain types of substances etc. Finally it is possible that for each non-globular protein involved in a natural polymer/ceramic composite there are parts that do not serve (at least in an optimum

manner) present 'interests'; this in partial analogy to the (possibly *simplistic*) concept of 'junk DNA-parts'.

Sometimes in literature there are references to the biomineralization of simple homopolymers, such as chitin which is a relative of cellulose. Certainly, it is not impossible that a simple homopolymer 'alone' can be the architecture-controlling polymer for a natural biocomposite with a ceramic nanoparticle dispersion. However, it is often the case that the presence of another, more elaborate as regards primary structure, macromolecule is crucial. For example, chitin in nacre is sandwiched between fibroin-like protein layers while acidic protein is located between the latter protein(s) and the layers of ceramic platelets; hence, chitin is not in direct contact with the ceramic CaCO_3 platelets and its contribution to the geometrical features of the bioceramic might be limited. However, indirect, through a domino of interactions, effects are still possible; for example, A_3 might organize on A_2 which, in turn, has been properly organized by A_1 ; also, see below for stress-related effects etc. A work claiming an enhanced biomineralization role of chitin is that of Falini and Fermani [25]. Of course the fact that simple biological homopolymers can combine with HAP, CaCO_3 etc, under certain *in vitro* (coprecipitation etc) conditions, to give, in some cases, interesting and occasionally rather elaborate, composite architectures might tell us little or even nothing that is safe as regards the role of the same homopolymers in biomineralization processes.

For each case of biomineralization and at least in principle one should consider the possibility of substances controlling (either favoring or inhibiting) nucleation and substances controlling (e.g. directing by favoring or blocking particular crystallographic directions of the ceramic crystal) growth. Even if *plain* homopolymers are excluded, one cannot exclude equally easily e.g. chitin-protein complexes as affecting in some manner the crystallization of biominerals. Many authors are prone to distinguish between:

- (a) main matrix/framework macromolecules that might play no fine role in the crystallization of bioceramics, though the macromolecules in consideration compartmentalize the tissue and, thus, broadly speaking, control various basics of biomineralization, including crystal sizes and
- (b) organics strongly affecting the fine details of nucleation and/or growth of the bioceramics; here one enlists glycoproteins, proteoglycans, various low volume fraction proteins, some lipids capable of supramolecular organization etc.

As regards the biopolymers that are viewed/described as 'matrix/framework biopolymers' there is much uncertainty as regards their biomineralization role; at the one end of the spectrum 'they exert much of the biomineralization control' while at the other end 'they have [almost] nothing to do with the geometry (shape, size and, possibly, the arrangement) of the dispersed ceramic particles'. Statements of the type found at the first aforementioned end are overly vague ones. Statements of the type found at the second end appear to be oversimplified ones; for example, one might note that in case asymmetric (e.g. needle or platelet-like) crystals grow and the matrix is not quasi-isotropic at the scale of crystal size there might be an alignment between long

directions of growing crystals and particular directions of the anisotropic matrix.

In order to be more specific, we will overlook/bypass (possibly quite unwisely) the cell-related details and limit ourselves to suggestions based on ordinary materials science. For the evolution of two-phase systems materials science suggests that matrices often affect, during precipitation and coarsening, the geometry of the dispersed phase via stresses; for example: (a) precipitates might be directed to form strain-energy minimizing quasi-ordered arrangements, (b) elastically soft matrix directions might preferably host precipitates and (c) small size precipitates might be favored over large size ones (this is related to the so-called ‘inverse Ostwald ripening’); for some careful pertinent descriptions see two articles by Su and Voorhees [26] and for an early suggestion of an anisotropic polymeric matrix inducing a quasi-regular spatial arrangement of nanoprecipitates see Beltsios and Carr [27]. Finally, a characteristic example of a more *mechanistic* view of a potential ‘*matrix control*’ of biomineralization is offered by a simple adaptation of the arguments of Jäger & Fratzl [28] as regards the allowable, by the collagen matrix microstructure, geometry of bone HAP. While the latter authors only attempt to deduce HAP information from what is known about the geometry of the organic and geometrically complementary part of the bone, simple rephrasing allows for statements of the type that can support the broad but vague claim that the collagen matrix ‘controls’ the biomineralization in consideration. As regards the biomacromolecules found in natural composites, the issue of chain conformation also requires attention; for example more or less the same chains (e.g. these of solid collagen and those of soluble gelatin) do not affect crystallization in the same way when packed in a certain quasi-fixed solid state arrangement and when found in solution; in the latter case they are capable of new conformations upon adsorption on the faces of growing bioceramic crystals. Consequently, statements of the type ‘biopolymer X favors nucleation (and/or anisotropic growth etc) of ceramic Y’ might not be valid under a broad range of conditions; a partial exception might be encountered in the case of *globular* proteins exhibiting a frequently fixed physical chemical surface landscape.

Nucleation is another thorny issue and we will consider a generic example of HAP biomineraliation. Some authors favor a ‘chemical’ description; calcium ions from solution move towards certain nucleation sites of an organic (e.g. protein-based) landscape. Other, more materials science oriented, authors attempt to identify sites where HAP (exhibiting a particular crystallography) will preferably nucleate heterogeneously. At the same time some authors claim that the HAP biomineral almost always nucleates as HAP while some other authors claim that it often nucleates first as OCP [19] or ACP [29,30]. For the case in consideration there is no problem when one talks ‘chemically’ and, here, broadly enough about nucleation in terms of calcium ions alone but for a ‘materials science’-type of description one cannot resort to an equally broad description, as different alternative first phases (ACP, OCP, HAP etc) might not nucleate equally well at the same sites. Incidentally the precursors of natural ceramics can be reasonable ones, e.g. ACC or vaterite for aragonite or calcite, but they can also be surprising ones; e.g. a

disordered phosphate-rich ferric hydroxide converts to ferric oxyhydroxide and the latter is partially reduced and yields the Fe₃O₄ of a magnetotactic bacterium [31].

Finally we should note that the description ‘natural structural biocomposite with nanoceramic reinforcement’ is not specific enough, as, for example, in tooth alone the same description applies to enamel and dentin, i.e. two totally different composites, despite the fact that they are both part of a tooth and the ceramic is the same, i.e. HAP. Different structural functions/roles are served best by different optimizations; for example a sea shell and a bird’s egg-shell are both structural composites with a high CaCO₃ load but the egg-shell should break easily from the inside, while it does not need to grow in size or heal.

3.2. Synthetic composites with a polymer matrix.

Composites fabricated with a low modulus polymer matrix and a high load (≥ 40 vol. %) of medium to high modulus (≥ 70-100 GPa) fibers are usually described as ‘fiber reinforced polymers/composites’. Compact polymer matrices are normally isotropic or statistically isotropic and usually exhibit 0.15 GPa ≤ E ≤ 5 GPa (Table 1; presented in two parts). Well below the latter range one finds elastomers (e.g. with an E = 2 MPa), while above to well-above the same range (e.g. E = 5-10⁺ GPa) one finds some specialty polymers, mainly thermosets and some polyimides. Rigidity percolation concepts suggest that *isotropic* polymer samples cannot exhibit a substantial (e.g. > 40 GPa) modulus of elasticity as the 3-D percolation threshold corresponds to an average connectivity of ca. 2.6 ± 0.2 while even to most heavily crosslinked polymers of some practical significance exhibit a connectivity of ca. 2.2 ± 0.1. Much higher modulus values (even well in excess of 100 GPa) are possible for polymers that exhibit strong long-range *orientation*; E values at the latter level are exhibited *only* in a *particular* direction, which is the chain axis direction and they are the basis of high modulus reinforcing polymer fibers (e.g. Kevlar®, Spectra® and so forth).

Table 1. Typical room temperature (RT) values for the modulus of elasticity (E) of selected isotropic and statistically isotropic polymer matrices. For families of polymers (e.g. epoxies) the usual range is also indicated. tp: thermoplastic, ts: thermoset, el: elastomer. d/w: dry / ‘wet’ (= at high moisture levels). sc: ‘semi’crystalline, lc: low crystallinity (< 10%), a: amorphous, np: non-plasticized, bd: biodegradable.

Polymer	E (GPa), RT	Polymer	E (GPa), RT
a-PS, a, tp	2.9-3.5	PET, sc, tp	1.9±0.6
a-PMMA, a, tp	2.4-3.5	PC, kinetically a, tp	2.5
a-PVC, lc, np, tp	2.9-3.0	PEEK, sc, tp	3.9
LDPE, sc, tp	0.20 ± 0.05	PES, a, tp	2.6
HDPE, sc, tp	1.1 ± 0.3	Epoxies, a, ts	3-6/(10)
UHMWPE, sc, tp	0.76 ± 0.07	Novolacs (PF), a, ts	4.2±0.3
i-PP, sc, tp	1.38 ± 0.35	Polyesters (uns.), a, ts	1.3-4.5
Nylon-6, sc, d/w, tp	2.9/1.5	Torlon (PAI)	5.2
PLLA, sc, tp, bd	2.7 (1.2-4.5)	NR, el	0.0010-0.0025
PDLLA, a, tp, bd	1.9	Polybutadiene (BR), el	0.001-0.005
PCL, sc, tp, bd	0.4	SBR, el	0.001-0.002
PHBV, sc, tp, bd	1.4-2.3	PDMS, el	0.0006-0.006

In the perpendicular to the chain axis plane the E value is low (e.g. 1-5 GPa); conceivably a sizable effective modulus (> 20 GPa or even >> 20 GPa) in the latter plane is possible only in some cases of polymer/ceramic nanocomposites with the chains

found within subdomains that have a width not exceeding 2 nm and are located between stiff (ceramic) asymmetric nanoparticles.

A *common* polymer matrix largely serves as glue, especially when the achieved modulus of the polymer/ceramic composite is of the order of 20-30 GPa or more. On the other hand when the second phase has the form of near-symmetric particles the modulus of elasticity of the composite is often 8 ± 5 GPa (regardless if the dispersed material exhibits a moderate, e.g. 30 GPa, or a substantially higher, e.g. > 100 GPa, modulus). A ceramic second phase in the form of near symmetric particles is described as a 'filler' and the material is rarely given enough consideration as a 'true' composite. On the other hand, it is actually in the latter case when it is fully proper to describe the material as a heterophase-modified version of the matrix material.

Reinforcement with chopped glass fibers showing orientation that is random or quasi-random in 2 or 3 directions leads to E values falling within a range that shows some overlap with E values achieved with near-symmetric fillers. Yet, *uniaxially* oriented composites with glass fibers and a load of ca. 50 vol. % show an attractive E_{axial} of ca. 35-40 GPa. We will now consider the idea of employing HAP in synthetic composites with a polymer matrix. In some ways the most common natural and synthetic structural composites with a ceramic dispersion are worlds apart. For example, while some of the most impressive natural structural composites are loaded with CaCO_3 , synthetic polymer/ CaCO_3 composites are common simply because CaCO_3 is the humblest of the fillers. Certainly humans are bound to pay more attention to HAP as the key ceramic phase of their bodies is HAP and not calcium carbonate and this is why all sorts of HAP related materials for medical applications exist. Beyond medical applications, HAP as a potential reinforcement of synthetic composites can be compared to glass fiber reinforcement. Silicate glass accounts for the 98 % of medium or better modulus synthetic fibers for composites and there is no need to aim at impressive claims for an overall-striking superiority of HAP-based composites; HAP-based composites are *not* the potential leaders of the composite industry of the future. What can be safely claimed is the following: 'even outside the medical field and for certain low to medium scale applications, HAP-based composites with appropriate polymer matrices are synthetic materials of some

potential interest and further pertinent research is of practical significance'.

Examples of strong points of HAP compared to glass reinforcement are as follows:

(a) Properly designed composite materials, such as those with non-toxic biodegradable polymer matrices, might have a high added value in view of their biological application potential.

(b) HAP is better suited for formation through precipitation routes appropriate for certain types of *nanocomposite* fabrication [27,32].

It is also possible to manipulate solution precipitation as to lead to aggregates having geometries that simplify processing and allow, e.g., for an enhanced randomness/isotropy when the latter is a target. However it should be noted that *plain* solution processing usually cannot lead in a simple manner to robust composites having large ($>> 1\text{mm}$) all three of their dimensions. In any case, a crystalline ceramic compared to an amorphous ceramic such as glass might be better manipulated at the nanoscale to produce desired shapes (platelets, needles and so forth); one might also take advantage of the possibility of HAP shape control at the nanoscale by judicious incorporation of carbonates etc [23].

(c) Most glass fibers exhibit an E of the order of 70 to 80 GPa (and also a density of 2.5 to 2.7 gr/cm^3) while apatite exhibits an E somewhat in excess of 100 GPa and a density of ca. 3.2 gr/cm^3 . In terms of modulus (E), apatite shows a value higher by ca. 35 ± 15 %; yet in terms of specific modulus (E/ρ), which is an important parameter when the weight of composite is also a concern, the reinforcements in consideration approach each other.

(d) Phosphate fibers, such as HAP, will biodegrade faster than silicate fibers, such as glass; hence accidental inhalation of fragments of the former might constitute a lesser health hazard.

Examples of weak points are the following:

(a) It is difficult to produce continuous HAP fibers (this is not impossible, e.g. by chemical conversion of a continuous glassy precursor, in the spirit of fabrication of, e.g., carbon and boron nitride fibers); electrospinning [33] appears to be a simple way to generate closely related products while it might also be noted that high aspect ratio particles can serve well many of the desired purposes.

(b) HAP needles will normally necessitate a fabrication cost higher than that for ordinary grades of chopped glass fibers.

4. MISCELLANEOUS ISSUES

This is loose set of issues gathered here for convenience; we will refer to these issues again at various points of subsequent sections.

4.1. The parameter of the modulus of elasticity.

The modulus of elasticity (E) is the, ill-named, initial slope of the stress-strain curve; its alternative name, stiffness, is, at least qualitatively, a more appropriate one.

While there is no single property of polymer-matrix/ceramic-dispersion composites that represents adequately their mechanical characteristics, the modulus of elasticity is among the key ones and, also, it is less sensitive to accidental details (e.g. scratches); hence the emphasis on E allows for a relatively brief presentation of sufficient generality. E reflects a single (and initial) mechanical response of the material, while some other mechanical properties such as strength and toughness

result from a continuum of responses. In the case of materials acting as mechanisms, which is something that can be claimed for a number of *natural* composites, an E value might constitute an even poorer representation of the *full* mechanical characteristics of the material. An example is offered by the case of partially mineralized collagen tissues. The less mineralized the collagen the more pronounced is an initial low-slope ('toe & heel' part) stress-strain portion of the axial extension curve that corresponds largely to the straightening/unfolding etc of certain parts of the collagen hierarchical structure. Consequently, there is a slope of the 'toe part' of the curve, a range of slopes for the 'heel part' of the curve and a higher slope of the subsequent elastic part of the curve. While the latter third part is usually described as the E of partially mineralized collagen, all three regimes relate to important mechanical functions of the tissue / 'mechanism' in consideration;

see Vincent [24] for an attempt to supply the involved pertinent details. E depends on the structure (e.g. aragonite and calcite exhibit a different E despite their chemical CaCO_3 identity) and the direction (this is very important in the case of macroscopically highly anisotropic materials); E is affected by porosity (see below) but it is *not* affected by any reasonable level of accidental scratches etc. It must be emphasized that while maximum E is often a material mechanics target it is not a universal one. For example, HIPS is a, *softer* than polystyrene, popular polystyrene/rubber composite prepared for the purpose of toughness enhancement of polystyrene. In addition, rubber itself, one of the key engineering materials in view of its immense capacity for *elastic* deformation, has one of the lowest E values for a compact material.

We will focus on the modulus of elasticity of composites as a function of the ceramic load (volume fraction) and geometry (particle aspect ratio and orientation). Regularity in the arrangement of the second phase and particle scale are parameters of lesser importance in the case of E (though not for other properties) of *macro*composites. Even when the exact particle arrangement is expected to affect E somewhat (as for example in the case of ceramic spheres in an isotropic polymer matrix) stresses are thought to depend only on reduced and not on absolute dimensions and, hence, scale, is not a relevant parameter. However, during the recent years it has become obvious that for *nanocomposites* with a polymer matrix the modulus of elasticity can also be affected *substantially* by the scale in some cases (see below).

4.2. Modulus of Elasticity and Second Phase Connectivity.

In the case of a second phase having the form of asymmetric particles the orientation of the long dimension of the latter points towards the direction of maximum offered reinforcement (in terms of E). Scale is often of minor importance. The connectivity of the second phase is important in the case of modulus of elasticity only in case the connections are robust ones (as for example in the so-called rigidity percolation). E is *not* among the material properties of composites that are affected substantially by the formation of a percolating network through plain particle-particle contacts. Contacts of the latter type suffice for the drastic modification of the response of the composite material only in the case of transport-related properties such as electrical conductivity (charge transport) and diffusivity (material species transport), provided that, compared to the matrix, the second (dispersed) phase allows for a more effective transport (of charges or species etc).

4.3. Modulus of Elasticity and Porosity.

Pores are 3-D domains of zero E but they are not necessarily unwanted structural features. In our case, porosity must be viewed as design option/parameter, for both natural and

synthetic composites. Gibson & Ashby [34] offer a systematic guide for the mechanical properties resulting from a substantial range of types of porosity.

Pores in the form of parallel tubes lead to a reduction of the corresponding (directional or non-directional) modulus in the tube axis direction that equals to the void polymer fraction, i.e. $E_{//} = E_{o, //} (1 - \epsilon)$. The result in the *perpendicular* direction is often $E_{\perp} \approx a (1 - \phi_f)^3 E_m$, where a is usually between 0.5 and 0.8; in brief, in the case of an array of tubular pores the axial loss of stiffness is limited while the loss is substantial in the perpendicular direction. In the case of open pores with a near symmetric shape the result is typically $E = k E_o (1 - \epsilon)^2$, where k can be near 1 or substantially smaller and the result applies better in the case of high porosity levels, e.g. $\epsilon \geq 0.7$. In terms of modulus-density Ashby diagrams [18] pertaining to minimum weight designs, it is obvious that for loads where the Ashby exponent is 2 or 3 it can be conditionally preferable to use a material having parallel tubular pores, while random open pores are best appropriate for application corresponding to an Ashby exponent of 3.

4.4. Moisture/water and mechanics.

In natural composites an amount of water, with mechanical and other roles, is almost always present. For example, water acts as plasticizer of certain protein and other biopolymer matrices; plasticization tends to reduce modulus but can enhance toughness. It has also been suggested that water is part of an energy dissipation mechanism in enamel [35]. For a range of polymers, water is an excellent plasticizer, yet a volatile one (as, for example, it becomes obvious within a couple of days in the case of bread); hence other less volatile plasticizers (e.g. glycerine etc) should be used when a plasticizing effect is desirable for materials that will not be used in an environment with a fixed moisture level.

4.5. Free nanoparticles (for nanocomposite fabrication or otherwise) - a health issue.

A widely accepted industrial practise is that the small dimension of free particles should exceed 2 to 3 microns; otherwise the particles remain suspended in the air for times long enough for inhalation. While ultrafine particles tend to cluster, the latter effect usually becomes weak beyond a size on the order of 0.5 micron and, hence, between ca. 0.5 microns and ca. 3 microns a problem exists. Overall, particles under 2 to 3 microns, and this includes all nanoparticles, should not be handled in the open. Then, in the case of nanoparticles, one might favor options such as the development of robust nanoparticle clusters (with a cluster diameter $d > 5-10$ microns) or the formation (via precipitation etc) of nanoparticles *within* a matrix; in addition there must be no danger of accidental release of large amounts of nanoparticles upon destruction of the composite material and this leads (or, at least, should lead) to additional concerns.

5. THE MODULUS OF ELASTICITY AND OTHER PROPERTIES OF COMPOSITES

We will discuss the modulus of composites and other important issues such as the packing of the dispersions.

5.1. Modulus of elasticity for a 1-D composite with a fibrous phase.

5.1.1. Axial Modulus of an 1-D Composite.

1-D composite refers to a sets of parallel fibers embedded in the matrix (a 'unidirectionally reinforced lamina (etc)'). Arranging *chopped* fibers well enough in a single direction is often difficult while substantial deviations from good alignment

are often detrimental; hence most 1-D synthetic composites involve *continuous* fibers.

For 1-D composites $E_{\text{com},//}$ is the modulus of elasticity along the fiber axis direction and it is to a good approximation:

$$E_{\text{com},//} = E_f \phi_f + E_m (1 - \phi_f) \quad (\text{Eq.1})$$

Both phases are assumed to stretch equally (and in an elastic manner) and this is more or less true for reasonably coherent polymer matrix interfaces and reasonably long fibers (see below). As regards interfaces, an overly weak interface will limit load transfer from matrix to the fibers and $E_{\text{com},//}$ will be substantially lower than expected, especially if the interface strength is below a certain limit (for details, in the case of a metal/ceramic 1-D model composite, see Tzounis et al [36]). The latter problem becomes clear when one considers the limiting case of chopped fibers resting in a cavity within the matrix without any attachment to it; in the latter case it is clear that uniaxial extension of the matrix does not lead to any load transfer to the fiber; hence the space hosting the fiber acts as an empty cylindrical cavity and leads to a drop of the modulus; in the case of the cavity the modulus is lower to that of the pure compact matrix while in the case of weakly attached stiff fibers the modulus can still be higher than that of the pure matrix.

For moderate ϕ_f values (e.g. ≥ 0.3) and $E_f \gg E_m$ (as it happens in the cases of ordinary polymer matrices and ordinary ceramic fibers) it is obvious that:

$$E_{\text{com},//} \approx E_f \phi_f \quad (\text{Eq.1a})$$

For example, for alumina fibers with $E_f = 400$ GPa and an a-PS matrix with $E_m = 3$ GPa and a-PS/alumina = 1/1 (: vol./vol.) the $E_f \phi_f$ term contributes 200 GPa while the, omitted in (Eq.1a), $E_m (1 - \phi_f)$ term contribution, equals just 1.5 GPa.

5.1.2. Transverse Modulus of an 1-D Composite.

There is a second ('transverse') modulus of elasticity that pertains to the application of stress in a direction perpendicular to 1-D oriented fibers and it is often approximated as:

$$E_{\text{com},\perp} \approx E_f E_m / [E_f (1 - \phi_f) + E_m \phi_f] \quad (\text{Eq.2})$$

Equation (2) is derived upon adoption of an, often, moderately equivalent and easy to handle, as regards calculations of mechanics of materials, geometry: matrix and fiber materials are assumed to behave as if they have the form of alternating plates and, hence, the two phases are arranged serially and experience the same stress (while the same strain is assumed in Eq.1).

The E_m in Eq.2 is usually more or less the same as the E_m in Eq., at least in the case of synthetic composites with usual polymer matrices. The same is not necessarily true in the corresponding case of fibers, as some of the fibers exhibiting high axial modulus (e.g. carbon fibers, BN fibers and also certain polymeric fibers such as Kevlar®, Spectra® etc) are, unlike glass and apatite fibers, highly anisotropic ones and exhibit a low radial modulus frequently comparable to, or even substantially lower than, that of the polymer matrix.

Implications of Eq.2 :

(a) For a medium level of fibers (i.e. for a fiber/matrix ratio of ca. 1/1 (vol./vol.)) the outcome of Eq.2 is dominated by the value of the component with the lower modulus; a simple manipulation

suggests that for equal volumes of the two phases and $E_m \ll E_f$ (lateral) the expected modulus is of the order of $2 E_m$. That is:

$$E_{\text{com},\perp} \approx 2 E_m \quad (\text{Eq.2a}),$$

for $E_m \ll E_f$ (lateral) and $\phi_f \approx 0.5$.

The factor of 2 in Eq.2a means that if the one phase is very stiff and the other is very soft then limited axial extension will basically lead to stretching of the soft phase alone; as the latter is only half of the soft/stiff alternating array, the composite material will stretch only half as much as the pure soft material and, hence, the modulus will be twice that of the soft material. This, revealing and overlooked, Eq.2a result is compatible with literature data about 1-D composites involving isotropic fibers (e.g. glass fibers, boron fibers etc). The same type of geometrical argument can be used for the interpretation of the prediction $E_{\text{com},\perp} \approx 3 E_m$ for $\phi_f = 2/3$ (see below).

The Eq.2a result $E_{\text{com},\perp} \approx 2 E_m$ for $\phi_f = 0.5$ can be contrasted with the Eq.1a result $E_{\text{com},//} \approx E_f/2$ for $\phi_f = 0.5$ (though the ranges of conditions for which the two results hold are not identical): the modulus for each of the two major directions of the 1-D composite depends largely on the modulus of a different phase. A related interesting result, which holds for $\phi_f = 0.5$ and isotropic components (e.g. m = epoxy, f = glass), is the following:

$$E_{\text{com},//} E_{\text{com},\perp} = E_m E_f \quad (\text{Eq.2b})$$

We obtain Eq.2b readily from Eq.2 upon noting that the denominator of the right side of Eq.2 is equal to $E_{\text{com},//}$ (for $\phi_f = 0.5$ and isotropic components); here it is not necessary that $E_f \gg E_m$.

We also note that when $E_f(\text{lateral}) \approx E_m$, a condition approximately correct for some anisotropic fibers, there is no need for any approximations or calculations: regardless of the ϕ_f value, the transverse modulus will be:

$$E_{\text{com},\perp} \approx E_m \approx E_f \quad (\text{Eq.2c})$$

In the case of $\phi_f = 0.5$ if we start with $E_m \ll E_f(\text{lateral})$ and gradually soften the 'plates' of fiber material then the fiber-part of the material will also start to stretch substantially during transverse extension and the modulus will start dropping from ca. $2 E_m$ to ca. E_m (: for $E_m \approx E_f(\text{lateral})$). For $E_f(\text{lateral}) < E_m$ the validity of equation Eq.2 gradually diminishes; the actual transverse modulus drops with $E_f(\text{lateral})$ more slowly than equation Eq.2 predicts.

(b) If the modulus of either of the two phases goes to zero then, according to Eq.2, $E_{\text{com},\perp} \rightarrow 0$. The latter prediction of Eq.2 is correct for $E_m \rightarrow 0$ but incorrect for $E_f \rightarrow 0$; when fibers are replaced by 'air' / tubular holes, the actual material shows a non-zero modulus, as, for example, is the case for a tubular brick in a direction perpendicular to the long axes of the holes. Eq.2 is based on the assumption that the two phases are topologically equivalent, i.e. both are assumed to be discontinuous in the transverse direction; when the actual continuity of the matrix becomes crucial (i.e. when $E_f \rightarrow 0$) Eq.2 fails completely. Incidentally, when $E_f \rightarrow 0$ (tubular holes in place of fibers) the *actual* transverse modulus varies as :

$$E_{\text{com},\perp} \approx a (1 - \phi_f)^3 E_m, \quad (\text{Eq.3}),$$

where a is usually between 0.5 and 0.8.

Eq.3 suggests that for $\phi_f = 0.5$ the actual lower bound of the transverse modulus, corresponding to axially oriented tubular holes in the place of axially oriented fibers, is ca. $E_m/10$.

(c) Case of $\phi_f \leq 0.5$ while $E_f \gg E_m$.

Eq. 2 suggests the further approximation:

$$E_{\text{com},\perp} \approx E_m / (1 - \phi_f), \text{ (Eq.2c)}$$

For $\phi_f \ll 0.5$ the latter result simplifies further to the linear equation:

$$E_{\text{com},\perp} \approx E_m (1 + \phi_f), \text{ (Eq.2d)}$$

These approximations are attractive because of their simplicity; they might not be applicable in the case of strongly *anisotropic* fibers as, then, the E_f (lateral) $\gg E_m$ condition does not always hold.

A comparison between Eq.2a and Eq.2c also shows that in the case of anisotropic fibers it pays little, at least in terms of modulus and for 1-D composites with a moderate fiber load, to try hard to orient (reorient or add) strong, E raising, bonds in the radial direction of fibers; on the other hand it is highly profitable to do so in the corresponding *axial* direction of fibers (Equation 1a). However this is only part, the E part, of the story and, for example, much of the current interest for the PIPD polymeric reinforcement fiber stems from the capacity of the PIPD chains for a multiplicity of lateral hydrogen bonds and resulting high compressive strength etc.

(d) Case of $\phi_f \gg 0.5$ while E_f (lateral) $\gg E_m$. For high enough ϕ_f it becomes eventually inappropriate to ignore the $E_m \phi_f$ contribution to the denominator of the right side of Eq.2; the result ceases to be of order $2E_m$ (as for $\phi_f \approx 0.5$) and starts approaching E_f . However, for the usual ϕ_f range ($0.1 \leq \phi_f \leq 0.67$) of well-fabricated synthetic composites and E_f (lateral) $\gg E_m$, the value $E_{\text{com},\perp}$ is essentially only a function of E_m and ϕ_f . As it can be easily verified by simple manipulation of Eq.2 and its approximations, the results are:

(i) $E_{\text{com},\perp} \approx 1.2 E_m$ for $\phi_f = 0.20$

(ii) $E_{\text{com},\perp} \approx 2 E_m$ for $\phi_f = 0.50$

(iii) $E_{\text{com},\perp} \approx 3 E_m$ for $\phi_f = 0.67$

In the case of common synthetic composites one cannot easily prepare robust composites with $\phi_f \gg 0.5$ to 0.6 and, hence, the lateral modulus remains low; on the other hand robust composites having $\phi_f > 0.7$ or even $\gg 0.7$, and, hence, exhibiting attractive $E_{\text{com},\perp}$ values, are possible in Nature.

Improvements. A slight improvement [15] for moderate to high ϕ_f values results when E_m in Eq.2 is replaced by $E_m / (1 - \nu_m^2)$ but this does not deal with cases of fundamental failure of Eq.2 (as in the case of $E_f \rightarrow 0$). One can attempt to deal with some of shortcomings of Eq.2 by using the highly popular Halpin-Tsai equation [15-17]; it heals almost everything but at the cost of limited transparency, as the approach is often used as a convenient fitting method disguised as theory. Among the popular attempts for a more transparent description of the Halpin-Tsai type the attempt of Spencer [37] can be noted.

5.1.3. Nature of the 1-D polymer/ceramic composite material.

In the *axial* direction the polymer matrix largely serves as glue, especially when the achieved composite modulus is on the order of some tens of GPa or more. For the axial direction, as well as for any direction of the 1-D composite, the selection of the matrix polymer is as important as the selection of the appropriate polymeric glue for a demanding application; as a matter of fact

epoxies serve both as common matrices and common glues. In the case of the composite:

(a) The viscosity and surface free energy of the [pre-]polymer at the liquid state affect greatly various processing and matrix-fiber interface features.

(b) elongation-to-break of the solid polymer matrix (compared to that of the fibers) affects the mode of failure under tension.

(c) If UV affects strongly the matrix it also affects strongly the lifetime of the composite in the open (and so forth).

Yet, the frequently expressed or implied view that e.g. a unidirectional composite with a $E = 3$ GPa polymer matrix and 50 vol. % carbon fibers with $E = 600$ GPa (leading to a $E_{\text{com},\parallel} = 300$ GPa) is an 'improved (/reinforced etc) version of the *matrix (/polymer)*' is not unlike the view that an artwork consisting of a desired arrangement of thin metal rods embedded in Plexiglas is an 'improved version of Plexiglas'.

It is probably best to state than in the axial direction we encounter a *new* type of material which requires a careful selection of both components but its desired performance depends largely on the properties imparted by the fiber component, mainly as a result of the levels of axial E_f and ϵ_f^* (elongation to fracture) and certain fiber surface features.

It is true that unless both the ceramic fiber content and radial fiber modulus are very high the material in the *transverse* direction is indeed, at least modulus wise, a version of the polymer matrix and we have seen that the transverse modulus has little to do with the exact modulus of the ceramic fibers. In addition, the dominant role of the resin in the transverse direction, for low to medium fractions of second phase, is also clear from the substantial drop of $E_{\text{com},\perp}$ in *slow* tests allowing for resin's creep. As data collected in Fig. 5.2 and 5.4 of Hull [15] show, $E_{\text{com},\perp}$ values drop by a factor of 2 or more when $E_{\text{com},\parallel}$ values drop just by few percent. However, this transverse softness is a recognized *weak point* (frequently handled by the proper joining of successive laminae etc; see below) and not among the reasons for the fabrication of 1-D polymer matrix/ceramic fiber composites.

5.1.4. Packing issues.

Theoretically one can add fibers up to a fraction just below that for close packing. For same cylindrical fibers the fraction for close packing is $\phi_f = 0.785$ for a tetragonal array and $\phi_f = 0.907$ for a hexagonal (triangular) array. Experimental data for good quality synthetic 1-D composites usually do not extend beyond $\phi_f = 0.64 \pm 0.04$; the latter can be viewed as a typical safe upper limit for carefully fabricated robust *synthetic* composites containing same cylindrical fibers in a regular arrangement.

When the parallel-fiber arrangement does *not* exhibit regularity, the difficulties to produce a robust 1-D composite often start at $\phi_f \approx 0.5$ because of a 2-D percolation problem. The latter problem has been considered by one of us for a different but geometrically equivalent problem [38]; groups of rods act as vessels limiting motion/exchange of liquid (e.g. a prepolymer) in a direction perpendicular to the rod axis. It is also perceivable that in special cases the 'vessel geometry' can favor enhancement of $E_{\text{com},\perp}$; the composite should be well fabricated (i.e. it should

contain no voids etc) while groups of fibers will frequently encase portions of the matrix. Then the ‘vessels’ (with fiber walls and matrix material as a content) will exhibit an effective transverse modulus that will be lower than that of the neat ceramic but it can still be substantially higher than E_m . On the other hand, the transverse effective volume of the matrix will be reduced (as the non-continuous parts will be excluded), i.e. the effective second phase load will be higher, and, hence, the transverse modulus can be raised.

Finally same fibers having appropriate prismatic shapes (e.g. exhibiting tetragonal, hexagonal etc cross-sections) are in principle space-filling ones (i.e. close-packing corresponds to $\phi_f = 1.0$). Nature makes use of the latter option as it offers very high ceramic load composites with the ceramic found in 1-D arrays of high aspect ratio tiny single crystals having polygonal (e.g. hexagonal) cross sections. Synthetic options for enhanced volume fractions of ceramics in 1-D arrays include single crystal needles or fibers, fibers extruded from orifices with appropriate non-circular cross-sections. Alternatively, high loads are possible via ‘fractal’ (= multiscale particle loading) approach, which will be described below in some detail for *spherical* ceramic grains.

5.1.5. Equations (1) and (2) as bounds.

It is frequently noted that Eq.1 and Eq.2 are, at least approximately, upper and lower E bounds respectively; the upper bound can be achieved in 1-D composites in the direction of full aligned continuous fibers. In all other cases (as regards geometry and direction of extension), values between Eq.1 and Eq.2 are possible; the latter statement is in practice correct and frequently serves as a convenient black box ‘explanation’ of all kinds of E values falling between Eq.1 and Eq.2 including those for *low aspect ratio* inclusions. We will now consider briefly the case of bones from the lower and upper bounds point of view [21, 24]. A relatively compact portion of a bone with a 50 vol. % HAP shows in a certain direction a modulus of e.g. 15-20 GPa. Eq.2 appears to favor a value that is less than 2 to 5 GPa, while Eq.1 predicts a value on the order of 50 GPa; hence a bounds-based reading is that we are dealing with a ‘clear intermediate’ case. Then one might proceed to say something more about the bone by considering, e.g. the distance of its modulus from the lower bound. However the lower bound (either eq.2 or a more elaborate, such as the H-S one, to be described below) depends strongly on the value of the modulus of the matrix. In the recent years it has become obvious that the modulus (or the ‘effective modulus’) of polymeric matrices of nanocomposites (including natural nanocomposites) can depend strongly on the width of corresponding domains and, hence, on both the fraction and the size of ceramic particles; see below.

5.1.6. Modulus of composites and the nanoscale effect.

We will now add the nanoscale effects to the discussion of the modulus of polymer matrix composites with a ceramic dispersion. Unless indicated otherwise, what follows is applicable to ceramic particles of *any* shape. However the effects should be pronounced when the modulus of the composite depends mainly on that of the ‘soft’ polymer matrix, while the enhancement factor as a result of the presence of a hard ceramic dispersion is primarily a function of the volume fraction of the ceramic (and not of the

precise modulus of the ceramic). Consequently the nanoscale effects in consideration are reflected more strongly in the values of: (a) $E_{\text{com},\perp}$ of 1-D polymer/ceramic composites and low to moderate ceramic volume fractions and (b) the modulus of polymer/ceramic composites with spherical (/low aspect ratio) ceramic particles. While most of the pertinent experimental evidence comes from systems with *spherical* (/ low aspect ratio) ceramic particles in a polymer matrix, we include the discussion at this point, as this is the first section pertaining to materials that can exhibit the effects in consideration. Effects of the type in consideration were sporadically reported from at least 1965, they became the subject of detailed studies after work reported by Vollenberg and co-workers in 1989 [39,40] and attracted further attention after 2000. In addition, thin polymer films on silicon and other controlled stiff substrates show related phenomena [41]; the latter can be thought as *partial* model systems for the polymer matrix found next to platelets in polymer/platelet composites. Differences exist as there are also effects related to the presence of a free surface in the case of the thin films and Rittigstein et al [42] have dealt with the latter issue by studying polymer nanolayers that were sandwiched *between* silica plates.

In the case of an amorphous polymer and a given T_{testing} the modulus can increase or decrease if T_g does the same (T_g shifts of the order of even a few tens of Celsius degrees are possible). Now chains in the vicinity of particle surfaces can exhibit a level of mobility different from that of chains in the bulk; the mobility can be lower (hence $T_g \uparrow$), in case surface anchoring of chains is possible, or higher (hence $T_g \downarrow$) in case of unfavorable chain-surface-of-particles interactions.

For thermoplastic polymers, a degree of polymerization (N) effect/dependence is also possible; the latter effect will be much stronger than the mild molecular effect observed for the E of *non-loaded* amorphous thermoplastic matrices. The effect in consideration results from the fact that chains ending at a ceramic surface are found within a zone having a thickness proportional to $N^{0.5}$. Literature also includes descriptions that involve more zones of modified chain mobility and other descriptions, such as the Ash et al [43] adaptation of the Long & Lequeux [44] association of thin film T_g with percolating regions of modified mobility; see also Papon et al [45].

Effects of the type in consideration are expected to be present in all amorphous polymer/ceramic composites but they are probably difficult to detect for large particles, i.e. for particles having a diameter of few tens of microns or more. However if the dimensions of the particles are drastically reduced, a substantial part or even the whole amorphous matrix can be affected and the shift of T_g will cause a shift of E_m . For example, if the diameter of spheres (or rods) drops from 20 microns to 200 Å, the particle surface for a given volume fraction will be enhanced by a factor of 10^3 and the portion of matrix material found in affected zones will be greatly enhanced. In the same way, for given ceramic particle shape and size it is expected that an enhanced fraction of ceramic particles will favor a modified T_g value for a larger fraction of the matrix. In reality the results/consequences (e.g. the E and T_g shifts) from the systematic change of parameters (such as the particle size and volume fraction for a specific particle surface

chemistry or physical chemistry) are not as simple as the preceding description implies.

In the case of a semicrystalline polymer there can be a contribution from the manner and degree of polymer crystallization as, for example, some ceramic particle surfaces can strongly affect nucleation trends; here and for 1-D composites even the introduction of some E_m anisotropy is conceivable. In addition, effects of the aforementioned kind for the amorphous part of the semicrystalline polymer are expected; here it is even conceivable that T_g will shift from below a given $T_{testing}$ to above it or vice versa.

It must be noted that the connection between T_g shifts and polymer modulus shifts is not obvious in the case of supported polymer thin films [46] but, at the same time, there is no simple connection between the T_g shifts of polymer thin films and polymer matrices of nanocomposites [47]. While it is well documented that nanoparticles cause both matrix T_g shifts and composite modulus shifts, some of the details of polymer matrix T_g shifts and polymer matrix modulus shifts remain unclear.

From the above qualitative analysis we see that if we do not take into consideration physical chemical interactions between the polymer and the ceramic particles it is possible to observe positive or negative deviations with respect to the corresponding modulus equations for ordinary composites (i.e. *non nanocomposites*); conceivably it is even possible to obtain values outside the, based on particle-free E_m , window having as limits Eq.2 and Eq.1.

5.1.7. Applications of synthetic 1-D composites.

1-D plates ('plies' or 'laminæ') are frequently stacked and bonded together to form multilayer 'laminates', with the fiber orientation changing systematically from plate to plate; the larger the number of plates involved and the smaller the angle between successive plates the more in-plane (quasi-)isotropic the laminate becomes. One might also employ two or more types of plies (the case of epoxy/graphite + epoxy/Kevlar corresponds to a popular example) and the resulting multilayer composite will be a 'hybrid laminate'. *Single* synthetic 1-D plates are of practical interest only in special cases.

5.1.8. A special example of a quasi 1-D composite: Tooth enamel of primates.

In the field of *natural* composites the employment of quasi 1-D alignment (plus various special details) suffices in the case of certain plant stalks etc; also, closer to the case of present interest, is the tooth enamel of primates; a simplified view of the latter enamels is that it consists of parallel HAP nanocrystals ('needles') ca. 50 nm wide while their aspect ratio can exceed 1000; also possibly, there is a biopolymeric 'glue' at the 1 nm scale between the nanocrystals. The following are among the details of key structural interest:

(a) There is a minute amount of non-collagen biopolymeric 'glues' (ca. 1 vol. % of the compact part) and there is water in channels (ca. 12 vol. %). More specifically the organic part consists of (i) acidic glycoproteins that appear to control the growth of the ceramic crystals and tend to surround individual crystals and (ii) amelogenins which are more hydrophobic proteins and they are not in direct contact with the ceramic crystal. It is of interest that some organisms, such as fish and a number of amphibians, bear

enameloid instead of enamel. In enameloid the ceramic is either (partly carbonated) HAP or fluorapatite in very elongated nanocrystals while collagen is found in the place of amelogenins [19].

(b) The nanocrystals exhibit some simple hierarchical arrangement of the nanocrystals in the form of bundles; the nanocrystals also exhibit some branching and fusing. The latter features amount more or less to some extent of *lateral* bridging; hence, equations pertinent to the *transverse* modulus of 1-D composites are not safe to use (even if we disregard possible nanoscale effects) for the interpretation of the measured transverse enamel modulus; the latter is difficult to measure and some reports claim that is only 15-20 % lower than the axial modulus.

In the axial direction, the human enamel can be up to 80-90 % as stiff as apatite with the reduction reflecting largely the presence of channels perpendicular to the surface. For brittle materials hardness goes with stiffness and, hence, enamel is expected to exhibit a moderate hardness. Actually enamel exhibits a hardness somewhat larger than that expected on the basis of its (average) modulus because of special compositional and geometrical *surface* features; yet, even if some estimates for a hardness comparable to that of quartz are correct, it was (from the dawn of the human race) and remains a bad idea to chew food accidentally sprinkled with quartz sand.

5.2. Composites with Short Fibers.

5.2.1. Modulus for 2-D & 3-D random fibers.

The following are handy approximations for the modulus of composites with 2-D and 3-D random arrangements of the fibers:

(i) For 2-D random arrangements:

$$E_{2-D,random} \approx (3/8) E_{//} + (5/8) E_{\perp} \quad (\text{Eq.4})$$

Here $E_{//}$ is the axial modulus for the 1-D composite with same ratio of the same components and E_{\perp} is the corresponding transverse modulus. For the direction that is perpendicular to the plane of randomization direction Eq.2 applies.

(ii) For 3-D random arrangements:

$$E_{3-D,random} \approx (1/5) E_{//} + (4/5) E_{\perp} \quad (\text{Eq.5})$$

Eq.4 and Eq.5 are handy and approximate and one way to derive them is through simplification of more involved equations (e.g. [1]); a more intuitive interpretation is based on the so-called Krenchel approximation.

Herbert Krenchel, a Danish engineer (and also a very successful designer), suggested in 1964 that if full 1-D alignment corresponds to $\theta = 0^\circ$ and θ is an angle to that, the fiber contribution in the axial direction will be:

$$n E_f \phi_f = \cos^4 \theta E_f \phi_f \quad (\text{Eq.6})$$

Here n is a numerical factor that depends on fiber orientation. As an example we will deduce the n value for the 2-D random case: For in-plane fully random distribution and according to Krenchel: $n = 3/8 = (1/\pi) \int \cos^4 \theta d\theta$, for $\theta \in [-\pi/2, \pi/2]$. Eq. shows that there is also a discrete equivalent that corresponds to four equisized fibers pointing at 0° , 45° , 90° and -45° . Upon application of Krenchel's equation to each case and proper summation we find the same n value, as:

$$n = 1/4 + 1/4(\sqrt{2}/2)^4 + 0 + 1/4(\sqrt{2}/2)^4 = 3/8.$$

The second term of the right sides of Eq.4 and Eq.5 can be understood as a correction term upon assuming that the full result is a linear combination of a parallel and a series arrangement and, hence, the second term will be of the λE_{\perp} type. Two alternative further arguments based on limiting cases suggest different λ values, the difference being largely a reflection of the approximate character of the previous (linear combination) assumption: (a) For $E_m = E_f$ it follows that $\lambda = 5/8$ for 2-D random (and $4/5$ for 3-D random), (b) For all fibers perpendicular to the stretching direction, $\theta = 90^\circ$ and, hence, the Krenchel term is zero, while the total modulus is equal to E_{\perp} and, hence, $\lambda = 1$. Both the $\lambda = 5/8$ and the $\lambda = 1$ forms are found in the literature for $E_{2-D,random}$ and both the $\lambda = 4/5$ and the $\lambda = 1$ forms are found in the literature for $E_{3-D,random}$ and, in general, the exact choice is one of secondary importance.

As the discussion of examples in paragraph 5.4.4 suggest (see below), for 3-D randomness and a moderate volume fraction of short fibers the system can be at the borders of the ‘polymer matrix E’ + ‘ceramic volume fraction’ and the ‘ceramic dispersion E’ + ‘ceramic volume fraction’ cases, as regards the control of the modulus of elasticity of the composite; a very large E of the ceramic and an enhanced volume fraction of it will favor the second case.

5.2.2. Packing issues.

For an athermal ensemble of rods (including mesoscopic ones) dispersed in an isotropic fluid the equilibrium arrangement is, as P.J. Flory first clearly showed in 1956 [48], a mutually near-parallel one (nematic liquid-crystalline) when the volume fraction exceeds a level on the order of $10/\alpha$, whereas α is the aspect ratio (= length/ diameter) of rods. If we now take an aspect ratio of ca. 100 as a guide for the minimum aspect ratio of chopped fibers that offers satisfactory reinforcement, it follows that for $\phi_f \gg 0.1$ one cannot achieve a (statistically) isotropic dispersion by accident as the chopped fibers will tend to form local parallel groups (in practice the liquid-polycrystallinity is favored with groups of nearly parallel rods having a width comparable (but typically smaller by a factor of ca. 2) to the length of the rods). In turn, the latter situation implies that the supposedly isotropic composites bearing chopped fibers are usually strongly anisotropic at scales comparable to the chopped fiber lengths or lower. For $\alpha = 100$ and $d = 10$ microns, this means that for commonly processed composite with a ϕ_f equal to 0.2 to 0.4 there can be no 3-D isotropy at the *microscopic* scale; if an enhanced level of a statistical 3-D isotropy is desired for chopped fiber composites, one should develop special composite fabrication processes.

In view of the fact that higher aspect ratio fibers intensify problems of the above type and also those problems that stem from viscosity enhancement, one might be prone to reduce the fiber aspect ratio as much as possible. The case of an aspect ratio of order 10^0 corresponds to different mechanics (see below), while what happens before such drastic reductions of length is considered briefly in the next section; more detailed discussions of the pertinent mechanics can be found in appropriate reference works [15-17].

5.2.3. Composite Modulus for Fibers of limited length.

When a high modulus continuous fiber embedded in a polymeric (soft) matrix is subjected to uniaxial extension, the tensile stress is transferred to the fiber and there are no end effects if the fibers end where the matrix ends. For an axially oriented *short* fiber surrounded by matrix the tensile stress is near zero at the fiber ends and rises gradually to the value for the corresponding continuous fiber within a length termed $L_c/2$. Then, L (: the full length of the short fiber) can be viewed as consisting of two $L_c/2$ end parts and a central $L-L_c$ part (if $L > L_c$). As a result of the reduced load bearing capacity, the short fibers will also act as if characterized by a reduced modulus of elasticity and this will be so for both unidirectional and random composites. Some semiempirical approaches and experimental data, especially for $\phi_f = 0.3$ and $f =$ glass or carbon [15], suggest that in the expressions for the modulus of an unidirectional composite the term $E_f \phi_f$ of Eq.1 should be multiplied by a factor of the order of ca. 0.2 for an aspect ratio of ca. 5 to 6 and by a factor of the order of 0.9 for an aspect ratio of ca. 50 to 60. It is also suggested that the same multiplication factor can be applied to the first term of the right sides of the equations Eq.4 and Eq.5, which assume randomization of fiber orientations. For example, for an aspect ratio of ca. 50 and the aforementioned systems:

$$E_{2-D,random} \approx 0.9 (3/8) E_{//} + (5/8) E_{\perp} \text{ (Eq.4b)}$$

More generally the appropriate multiplication factors as a function of aspect ratio are often highly case-specific, i.e. they depend on the matrix and fiber materials and the quality of the interface.

5.2.4. Effect of 1-D orientational deviations.

An 1-D composite can present orientational deviation if (a) there is some distribution of fiber orientation with respect to the target axis as a result of either imperfect processing of bundles of continuous fibers or crude 1-D alignment of chopped fibers or (b) the fibers are well aligned but the load is applied at an angle to the direction of fibers.

For small θ deviations one might apply Krenchel's equation (Eq. 6); a proper extension with an inclusion of a second, correction, term might be necessary for more accurate results in the case of larger θ values. As an example, we note that for $\theta = 10^\circ$, $\cos^4 \theta = 0.94$; however more involved approaches predict larger drops as a result of misalignment, e.g. a drop somewhat in excess of 10 % for $\theta = 10^\circ$.

A, related though not equivalent to (a) and (b), orientational deviation is also a built-in characteristic of highly anisotropic fibers (e.g. C and BN in the case of ceramics). In the case of highly anisotropic fibers, the fibers might consist of elongated sub-domains belonging to the same phase but exhibiting some misalignment of the strong bond elements (e.g. graphitic planes in the case of carbon fibers) from the fiber axis; the misalignment in consideration will be described by a θ angle of the maximum stiffness axis with respect to the fiber axis. All subdomains should exhibit comparable degrees of misalignment; otherwise the equation might, occasionally, fail. For reasonably well oriented carbon fibers, hence also for the similarly structured BN fibers, Northolt & Baltussen [49] have suggested:

$$1/E \approx 1/E_c + [\langle \sin\theta \rangle / g] \Rightarrow E_c/E = 1 + [E_c/g] [\langle \sin\theta \rangle] \text{ (Eq.7)}$$

Here $E < E_c$ (= axial fiber modulus for full alignment), g : shear modulus (ranging from 5 to 35 GPa for carbon fibers), while θ is the deviation. It should be noted that Northolt & Baltussen have suggested a somewhat different equation ($1/E \approx 1/E_c + [\langle \sin\theta \rangle / 2G_c]$) for highly oriented polymeric fibers (such as Kevlar, Spectra etc). Regardless of the differences of the two classes considered by Northolt & Baltussen, it is obvious that in both cases small deviations and high shear moduli (more accurately, high g/E_c) are needed in order to avoid large deviations from the theoretical E_c . For isotropic and near isotropic materials the shear modulus is comparable to $0.4E$, while for strongly anisotropic fibers it varies from ca. $E/10$ to ca. $E/200$; during axial tension a low g can allow tilted, at a θ angle, domains to slide easily against each other during uniaxial extension and thus lead to a drastic reduction of the modulus of elasticity.

5.3. Composites with Platelets.

Reinforcement with platelets is in principle the most attractive pertinent option because platelets are capable of in-plane instead of unidirectional (as in the case of fibers) reinforcement. Nature often takes advantage of this option while processing problems usually undermine corresponding synthetic efforts.

5.3.1. Modulus of Composites with Platelets.

The key expectations as regards modulus of composites with dispersions of platelets can be synopsized as follows:

(a) For parallel plates the theoretical predictions for the modulus parallel to the platelets and the modulus perpendicular to the plane of the platelets) are the same as the two modulus prediction for 1-D fiber composites (i.e. if we disregard Poisson ratio effects). However it is often nearly impossible to approach the theoretical in-plane value with synthetic composites for reasons that are explained below.

(b) For [quasi] 3-D random distributions, which however are usually difficult to achieve in practice, Christensen [50] is a good source of pertinent theoretical results. We will consider briefly simplifications of two of the latter results:

(i) For a dilute dispersion (low volume fraction of platelets: $\phi_{pl} \ll 1$), $\phi_{pl} E_p \ll E_m$ and $v_m = v_{pl} = 0.25$:

$$E \approx E_m + 7.5 \phi_{pl} E_{pl} \text{ (Eq.8)}$$

(ii) For a dilute dispersion (low volume fraction of platelets: $\phi_{pl} \ll 1$), $\phi_{pl} E_p \gg E_m$, $\phi_{pl} E_p \gg B_m$ (bulk modulus) and common values of v_m and v_{pl} (including the $v_m = v_{pl} = 0.25$ case):

$$E_{3-D,random} \approx E_m + 0.5 \phi_{pl} E_{pl} \text{ (Eq.9)}$$

Case (ii) is of more interest than case (i) as it is pertinent to much higher $\phi_{pl} E_p$ values. The second term of the right side of (Eq. 9), i.e. $0.5\phi_{pl} E_{pl}$, can be compared to the corresponding, $0.2\phi_f E_f$ term for a 3-D random distribution of fibers; see Krenchel's approach in 5.2.1. The latter comparison allows for the claim [36] that the platelet version (*if* possible to fabricate) can be substantially more reinforced (in terms of E) than the corresponding short fiber version. However, while it is possible to satisfy the $\phi_{pl} E_p \gg E_m$ condition with appropriate ceramics and polymers (e.g. $\phi_{pl} = 0.05$, $E_p = 250$ GPa, $E_m = 1$ GPa) the currently achievable maximum load of effectively dispersed platelets in synthetic composites often does not exceed the $1/5^{\text{th}}$ or $1/10^{\text{th}}$ of

that achievable through short fibers. With the main partial exception of the composites with organo-clays, and the possible success of current attempts with forms of graphene, too much has been expected and little has been achieved so far as regards *mechanical* properties of corresponding composites. On the other hand, in the case of *conductive* (e.g. graphene) platelets one can still achieve attractive conductivity levels (e.g. ca. 0.1 S/cm) with low particle loads (e.g. 1 to 1.5 vol. %) in view of the low, often 0.1 to 1 vol. %, percolation threshold of conductivity for platelet dispersions. The latter is just one example of the often overlooked fact that the rules for transport properties of composites are very different from those for mechanical properties of composites.

5.3.2. Packing issues.

Properly shaped (e.g. regular hexagonal) same platelets are space-filling objects and hence they can form, e.g. a composite with a high in-plane modulus upon incorporation of a minimal amount of polymer 'glue' ($< 10\%$ to $\ll 10\%$) and this for example is the case of nacre, where Nature deposits calcium carbonate (aragonite) in layers consisting of space filling hexagonal platelets of submicron thickness, while 2-10 vol. % protein serves as glue located between layers.

We have already seen that liquid crystallinity type of effects constitute a nuisance in the case of chopped fibers when enhanced randomization is desirable. However in the latter case, and at least for low to moderate chopped-fiber volume fractions (a) wetting (with a prepolymer etc) problems can be bypassed by taking advantage of directions perpendicular etc to the long dimension of the fiber, (b) short fibers normally do not group into low aspect ratio pockets surrounded by fiber-free shells of matrix. The situation is usually different as regards both (a) and (b) in the case of the platelets which also exhibit liquid crystallinity packing trends. In the case of platelets and synthetic composites, both (a) and (b) problems are often severe and hard to bypass and, hence, limit the possibility to take advantage of the theoretical capacity of platelets for substantial reinforcement.

In particular, if one attempts to disperse platelets by simple component-mixing, the geometric outcome is often a dispersion of low aspect ratio agglomerates with little or no-polymer between the platelets of the same agglomerate; aspects of the platelet part of the latter structure (/mode of stacking) can be seen in some sizable haphazardly-filled 'jars of pennies'. The material will be a composite with mechanical properties possibly inferior to those of the same polymer with inorganic symmetric-particle filler occupying the same volume fraction; in terms of modulus of elasticity, something like $E \approx 2 E_m$ is a reasonable expectation. Even if some polymer manages to be inserted between all platelets it is still possible that the areas where polymer alternates with ceramic platelets will have the form of pockets surrounded by thick shells of pure polymer. In the latter case while some of the mechanical properties (e.g. toughness) will improve, the modulus will remain a, largely matrix-controlled, low one. As a result, while there is no difficulty to built (through a brick (plate) and mortar process) a *macroscopic* analogue of the structure in discussion it is a rarity to encounter *synthetic* microcomposites or nanocomposites having a 'reasonable' ceramic load ($\gg 5$ vol. %) and exhibiting mechanical properties close to the theoretical

expectations, either for parallel or for quasi-random platelet arrangements. Overall, it is a frequent disappointing outcome of polymer/ceramic-platelet composites research, the preparation of composites with a modulus differing little from that of the polymer, despite initial hopes for ‘ceramic dispersion E’ + ‘ceramic volume fraction’ control for the modulus of elasticity of the composite. Hence, while theoretically platelets (each capable of in-plane reinforcement) are better reinforcing agents than fibers (each capable of single-direction reinforcement) the latter prevail in synthetic composites practice. It is possible that *ribbons* deserve more attention as reinforcements of synthetic composites; this is because ribbons have a reinforcement capacity intermediate of those of fibers and platelets while liquid crystallinity arrangements of platelets will probably not undermine the modulus of corresponding composites.

It should be noted that because of platelet dispersion problems one usually aims at a strong *attractive* interaction between the platelet surface and the polymer and, hence, in almost all cases of interesting pertinent materials with nanoplatelets the polymer T_g is raised (at least locally) and the same is expected for the local stiffness of the matrix.

A potential new way to bypass the aforementioned packing-related limitations in the case of HAP platelets will be presented below (: synthesis of appropriate sturdy spherical platelet assemblies).

5.3.3. Special examples: Dentin and Bone.

Dentins and bones are often subjects of the same discussion as they both contain some form of HAP nanoplatelets, collagen (with a hierarchical organization exhibiting triple helices at the bottom level) and other biopolymers (corresponding to ca. 10 % of the total organics; there is also a small amount of lipids), water and porosity. Some differences do exist but it should also be noted that bone studies encompassing a wide range of compositions usually include various other ‘bone-like’ tissues ranging from mineralized turkey gastrocnemius tendon ($\phi_{HAP} \approx 0.15$) and deer antler tendon ($\phi_{HAP} \approx 0.38$) to whale bulla ($\phi_{HAP} \approx 0.72$). Overall, the terms ‘bone’ and ‘bone-like’ encompass a wide variety of tissues; some of the latter tissues, or parts of them, are more porous and some are less porous, some include high and some include low to medium HAP loads and so forth.

Still, the similarities (rather than the differences) between bones and dentins are considered as somewhat puzzling as, for example, the structures of the bones are renewed while those of the dentins are not (except to a limited extent under special conditions). Examples of some pertinent data are as follows: (a) bones often contain HAP nanoplatelets with large dimensions such as 30 to 60 nm (some up to 100 nm) and a thickness on the order of 2 nm (some up to 5 nm); the *large* platelet dimensions for the corresponding case of human dentin are comparable while in the case of thickness there is some substantial variation, with most of the reported values belonging to the range of 2-5 nm (intertubular dentin) to 9-10 nm (peritubular dentin), (b) human dentin contains ca. 4/3/2 : HAP/biopolymers/water on a relative volume basis. As regards (a) it might be noted that if indeed there is a substantial difference as regards the thickness of the HAP nanoplatelets this might turn out to be an important point as it suggests, at least for

some dentins, HAP particles having aspect ratios somewhat too low for (what is usually viewed as) ‘*platelet-type* reinforcement’. Currey [21] is a good starting point for the mechanics and many other features of the bones. Discussions of the modulus of elasticity of the bones in the latter work focus on (a) the qualitative success of a model of Katz that extends Krenchel’s description, (b) the supposed insights gained from the application of Halpin-Tsai models and (c) the attempt of Jäger & Fratzl (see below). Parts of a book edited by Fratzl [51], with contributions from Currey and others, update some parts of the aforementioned review by Currey [21].

Versions of the Jäger & Fratzl bone model [28, 51-53] continue to enjoy substantial popularity and, hence, we will describe it briefly. This model assumes that the nanoplatelets partially overlap instead of being arranged end-to-end as it was usually assumed in earlier models. For the modulus of the bone in a long platelet direction, which is also the axis of the collagen triple helix direction, and a 2-D version of the bone it is predicted that [39]:

$$E_{bone} \approx \phi_{HAP}^2 / [(\phi_{HAP}/E_{HAP}) + 4(1-\phi_{HAP})/(G_p\alpha^2)] + [(1-\phi_{HAP})E_p] \quad (\text{Eq.10})$$

Here G_p is the shear modulus of the ensemble of collagen chains and α is the aspect ratio of the particles, with suggested α values: 10 ± 5 . G_p is taken equal to $0.4 E_p$, while it is suggested that $E_p = 6.7$ GPa; it is also assumed that $E_{HAP} \approx 100$ GPa. There is substantial uncertainty as regards the appropriate mechanical characteristics of collagen and the actual characteristics might also vary with bone composition (/domain scale) and zone; see below. It is also noted that the assumed composite geometry can accommodate $\phi_{HAP} \leq 0.56$. A version of Eq.1, which corresponds to a plain ‘parallel’, upper bound model, is useful for an appreciation, through comparison, of some of the implications of Eq.10:

$$E_{com, //} = [\phi_{HAP}E_{HAP}] + [(1-\phi_{HAP})E_p] \quad (\text{Eq.1b})$$

The main idea of the ‘staggered’ Jäger & Fratzl model is that the lack of *continuous* ceramic material in the axial direction is partly compensated by the platelet overlap and the load communicates between platelets through shearing of the intervening collagen matrix. The right sides of Eq.1b and Eq.10 contain a similar second term but it is the first term of the right sides the one that can enhance substantially the bone modulus (for moderate ceramic loads), as it is the one that involves the modulus of the ceramic component. Large values of parameters G_p , which allows for effective load transfer, and α , which enhances overlap, are expected to favor a large (\gg lower bound) axial E_{bone} value. Indeed, according to Eq.10, for $\phi_{HAP}^2 / [(\phi_{HAP}/E_{HAP}) + 4(1-\phi_{HAP})/(G_p\alpha^2)] \rightarrow \phi_{HAP}E_{HAP}$ (: upper bound) a very small $4(1-\phi_{HAP})/(G_p\alpha^2)$ is needed; the latter is favored by increasing ϕ_{HAP} values (i.e. when the collagen is more mineralized), while larger G_p and larger α^2 favor enhanced modulus values for a given ϕ_{HAP} . Many of the, aiming at the calculation of E etc, models for the microstructure of the bones do not take into account (sufficiently or at all) the *hierarchical* structure of actual bones. In addition, possibly other critical, for the understanding of the mechanical responses, physical chemical and geometrical aspects of the bones

remain incompletely understood. An example of an overlooked physical chemical possibility is that, because of change of the mobility of chains located between platelets and found at the nanoscale, the modulus of the matrix varies with the fraction of the ceramic, even when the ceramic particles exhibit fixed particle dimensions.

Consequently, for moderate ceramic loads the modulus of the matrix (or the ‘effective modulus’ of the matrix) might differ substantially from what can be estimated via modulus data extrapolation to zero ceramic fraction. In addition, the modulus of collagen in the axial direction and in the high slope stress-strain part can be substantial even in the absence of ‘nanoeffects’ as the chains are found in a quasi-extended conformation; hence, the generic value of $E_{\text{collagen}} = 6.7$ GPa assumed by Gupta et al [53] and Jäger & Fratzl [28] need not be viewed as an excessive one, when applied to cases of bones and related tissues that included at least a moderate HAP fraction.

Also for models such as that of Jäger & Fratzl the portion of the hierarchical collagen structure between plates might vary as regards geometry and, hence, as regards its G_p value etc, when its width varies as a result of ϕ_{HAP} variation; the latter will be in addition to the aforementioned ϕ_{HAP} -dependent effect from collagen–nanoceramic interaction. Finally, for a given bone structure the actual axial collagen modulus might even vary from zone to zone, along the direction of extension, given that there might be an alternation of structural features in this direction.

An example of a geometrical possibility is that there is some connectivity between nanoplatelets, at least if it is true that a bone with an $E = 17$ GPa and a strength of 130 MPa shows the same modulus and a (low yet non-zero) strength of 6 MPa upon having its organic phase removed, as Vincent [10] states. Another geometrical possibility is that the arrangement of structural elements does not remain one of a fixed type when the volume fraction of the HAP ceramic changes. In the latter case an equation based on assumptions different from those considered for models available so far will be necessary for the proper, non-empirical, description of the modulus as a function of composition; it is even possible that the same composition can be found in very different bone geometries. Hence, despite advances such as those from Jäger & Fratzl and co-workers [28, 51-53], it might be wise to continue to adopt an older statement of Vincent as regards the microstructural interpretation of bone’s modulus: ‘*we are still confused, albeit on a somewhat higher plane*’ [24].

What appears to be reasonably safe to state is that bones with an E of order 10^1 GPa correspond to a combination of moderate stiffness and high toughness; Porter [54] has even argued, though not safely enough, that the *maximum* of toughness is for a composition close to that of a standard bone. It is also true that usually the toughness of a bone (typically: 1 to 10 kJm^{-2}) exceeds the toughness of a dentin (typically: 0.25 -1 KJ/m^2). The enamel, which can be up to 80-90 % as stiff as apatite, is much stiffer than dentin but a less tough material (enamel toughness = 0.06-0.3 KJ/m^2). However as regards toughness we should keep in mind that enamel does not operate as a separate material but as a composite surface component of an elaborate composite tissue (= tooth).

5.4. Spherical and other low aspect ratio particles.

As we have already noted (1) and (2) constitute, respectively (and at least approximately), upper and lower bounds. For statistically isotropic particulate composites certain more narrow bounds, those of Hashin & Shtrikman [41], are sometimes considered; nevertheless, these H-S bounds have been derived for composite geometries exhibiting uncommon features, especially as regards particle-particle contacts. The H-S treatment [55] does not allow for particle-particle contacts despite the fact that in the case of random dispersions the particle-particle contacts are extensive, already somewhat below the percolation threshold (theoretically at $\phi_p \approx 0.16$). The material geometries assumed by H-S are an extension of these of the periodic composites that J.C. Maxwell assumed in 1873 [56] in order to successfully describe ‘Conduction through heterogeneous media’. Nevertheless, contacts of the dispersed particles do not render automatically useless the H-S approach since in the case of modulus there are no percolation-type phenomena as a result of plain particle-particle contacts; there is only a so-called rigidity percolation [57] for the modulus networks of *robustly* connected sticks etc but this is not an issue of direct interest here. Thus the problem with the H-S geometrical assumptions is not the issue of particle-particle per se but the unaccounted-for asymmetries in the, resulting from randomness, stress fields around particles. In addition there is a potential scale (nanoscale) effect (already discussed in 5.1.6) and, overall, the methods of bounds usually offer limited insights at the cost (or benefit?) of a lot of discussion.

5.4.1. Modulus of Particulate Composites with Thermoplastic or Thermoset Matrices.

The reinforcement achieved in the case of spherical and other low aspect ratio ceramic particles (at a fraction of ϕ_p) dispersed in either thermoset or thermoplastic (hence, non-elastomeric) polymeric matrices ($E_m \ll E_{\text{particle}}$) tends to be somewhat better than that suggested by Eq. 2. Pictorially the connection with Eq.2 is understood (and somewhat overemphasized) upon noting that a, perpendicular to the fiber axis, cross-section of an 1-D composite with regularly arranged fibers is indistinguishable from an appropriate cross-section of a composite bearing spherical particles in a simple regular arrangement. In practise, (Eq.2) tends to underestimate the modulus which for example for a $\phi_p = 0.50$ is kE_m , where k is usually between 2.5 and 4; matrices of elastomeric character (see below) favor somewhat higher k values, while according to (Eq.2): $k \approx 2$. In the case of low aspect ratio particles the nanoscale contributions to the modulus can be significant; also, at least in principle, the details of particle arrangement might also have a moderate effect on the modulus of composites. Literature includes a, neither necessary nor useless, wealth of quasi-theoretical and empirical equations that tend to predict values somewhat higher than those predicted by Eq.2. For example, Ishai & Cohen [58] have suggested:

$$E_{\text{com}} \approx E_m + (E_m \phi_p) / [n/(n-1) - \phi_p^{1/3}] \quad (\text{Eq.11}),$$

where $n = E_p/E_m (>>1)$, for $\phi_p < 0.3$ to 0.5.

For ‘very’ large n :

$$E_{\text{com}} \approx E_m (1 + (\phi_p / (1 - \phi_p^{1/3}))) \quad (\text{Eq.11a})$$

For comparison purposes, we note that the Ishai & Cohen equation suggests $E_{\text{com}} \approx 3.4 E_m$, for $\phi_p = 0.5$; a mild underestimation is considered possible for such a high volume fraction.

It is of practical importance that neither the bulk of alternative equations nor the bulk of experimental data suggest that very stiff spherical (or quasi-spherical) ceramic particles enhance strikingly the modulus of the soft polymeric matrix more than does an equal volume of moderately stiff ceramic particles; if there is an additional mildly important factor, this might be the Poisson ratio of the matrix, which, for example, appears, in an involved way, in the Lewis & Nielsen modification [59] of the so-called Kerner equation [60].

Overall, on the basis of the above it appears that there is no strong reason to employ low aspect ratio particles of ceramics having a *very* high E (possibly accompanied by a high cost) as low cost, moderate E ceramic particles constitute a nearly as good option; e.g. chalk and other calcium carbonate powders (with an E of ca 35 to 70 GPa) are not strikingly inferior even to diamond powder (with an E of ca 1100 ± 100 GPa), at least as far as E of the composite is concerned; our selection should be guided e.g. by low cost, low density (for the purpose of higher specific modulus etc) and the consequences as regards *other* mechanical properties of interest (e.g. strength of composite). Actually, the dominant technical term ‘filler’ (supposedly something that just occupies space and/or enhances volume at low cost) is a reflection of a low expectations view; e.g. in terms of (*nearly any* type of) significance the adopted technical language suggests: filler [$<$ extender] $<$ matrix material $<$ reinforcement material. However, there is a host of other composite properties, starting with strength and toughness, that suggest a need for substantial attention to the ‘filler’ characteristics such as surface chemistry, precise particle shape and size distribution, mode of dispersion etc. In addition, even the modulus of the composite ceases to be insensitive to the details of the filler at the nanoscale (5.1.6; see also 5.4.5). Hence the days that low aspect ratio inorganics were fillers chosen mainly on the basis of minimum-cost criteria should be over.

5.4.2. Packing issues.

The so called rcp (random close packing) model of J.D. Bernal [61] suggests that randomly packed same spheres occupy a ca. 0.637 fraction of the space; in addition there are three other, ‘metastable’, more loose non-ordered packings corresponding to occupation of ca. 0.56, 0.61 and 0.625 fraction of space. Next we will assume that the maximum is ca. 0.6 for spherical and quasi-spherical particles as well; we will include even cuboidal randomly packed particles, despite the fact that cube is a space-filling shape. If we consider that robustness will be enhanced if the ceramic spheres do not touch each other we will have to reduce the ceramic content to one at the level of ca 0.47-0.50 and thus we encounter again a modulus equal to 2 to 4 times that of the matrix. However in principle we are allowed to apply the same concept at different scales, i.e. the space between the large spheres can be occupied in part by much smaller nearly close packed spheres and so forth. This ‘fractal’-type of loading and structure can lead to a total ceramic fraction of ca. $0.5 + 0.5 \times 0.5 + 0.5 \times 0.5 \times 0.5 [+ \dots] > 0.80$; actually, it is intuitively obvious that given a sufficient

number of scales this amounts to a space filling process and this is nothing but a geometrical representation of the familiar series sum $\Sigma (1/2)^n = 1$. For a composite with small particles it is realistic to limit the scales to three; e.g. we might attempt to load a polymer with 50 % spheres with a diameter of 50 microns, then occupy half of the remaining volume with 1 micron spheres and, finally, do the same at a lower scale with 200 Å spheres; the achievable load should suffice for a composite modulus much higher than 2 to 4 times that of the matrix.

At the micron and submicron/nano scale the described approaches poses a substantial challenge as regards realization; on the other hand something very similar is done routinely on a larger scale with gravel and sand etc.

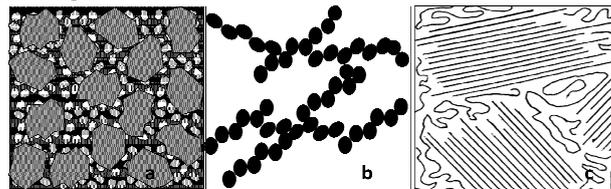


Figure 1. (a) Low aspect ratio grains at various scales (fine white dots, white pockets with wavy pattern, large pockets with parallel-line pattern) allow for an enhanced occupation of the material volume by dispersed particles. (b) High aspect ratio arrangements of low aspect ratio particles (as observed e.g. in the case of certain carbon particles in NR). (c) A common and undesirable arrangement of ceramic platelets in a polymer matrix; this material performs no better than one with a simple dispersion of low aspect ratio ceramic particles in the same matrix.

One might also note that there are regular packings that are more dense than rcp; e.g. fcc and hcp packings of same spheres occupy ca. 0.7405 of space. However while 2-D ordering of same spheres or discs can be often induced by properly manipulating the periphery of an ensemble (and by extension the same is true for an ensemble of parallel cylindrical rods), usually this is not so for 3-D packing of same spheres. Unless special favorable interactions (due to charges, stresses etc) prevail, the 3-D same sphere arrangement will be a, more or less, random one. On the other hand, Nature has found ways to produce 3-D ordering of nanospheres as in the case of opal (regular (cubic or hexagonal) close packing of 150 to 300 nm silica nanospheres). Nature also involves low aspect ratio particles in certain biocomposites; this tends to be viewed (though not necessarily correctly) as a practice of lesser significance.

For the effect of the nanoscale on the value of E for dispersions of ceramic nanospheres in polymers see section 5.1.6. For properties other than E and spherical ceramic particles, the LDPE/CaCO₃ report of Fu & Wang [62] is an example of a good source of pertinent information.

5.4.3. Modulus of Particulate Composites with Elastomeric Matrices.

Neat elastomers exhibit a modulus that it ca. 3 orders of magnitude lower than that of other polymers. For elastomeric matrices that bear a dispersion of ‘hard’/non-deformable particles the Smallwood-Guth (S-G) [63,64] equation is applicable:

$$E_{\text{com}} \approx E_m (1 + 2.5\phi_p + 14.1 \phi_p^2) \quad (\text{Eq.12})$$

The original derivation of the S-G equation derivation is a thinly disguised duplication of Einstein’s derivation of the viscosity of a low volume fraction dispersion of spherical particles

in a liquid, supplemented by an obscure extension leading to the 14.1 coefficient for the ϕ_p^2 term. We note the following:

(a) The continuous medium in Einstein's (1906/1911) derivation is a liquid (Poisson ratio, $\nu = 0.50$), while for S-G the continuous medium is a rubber; yet a rubber is microscopically and mobility-wise (except for around the crosslinks) liquid-like, as verified macroscopically by Poisson ratios imperceptibly-only deviating from 0.50 (e.g. for lightly vulcanized NR samples the Poisson ratio is ca. 0.495 to 0.499). Rubber is microscopically something close to a liquid because of the ' $T_g + 50\text{ }^\circ\text{C} < T_{use}$ ' usual condition and the low density of crosslinks (typically 1/50 monomers thus even allowing for random walk conformation of chain segments between crosslinks). It follows that it is rather unsafe to apply (as it is sometimes done) the S-G equation in the case of non-elastomeric polymeric matrices e.g. for polymers with an $\nu \approx 0.35$; highly deformable polymers with an ν approaching 0.50 might be better candidates; yet further a systematic study of this point is necessary LDPE with $\nu \approx 0.47$ at RT appears to be a reasonable candidate; yet because of the lamellar polymeric crystals that occupying ca. 50 % of the LDPE volume the material is not *microscopically* isotropic.

(b) The coefficient 14.1 is known to be inaccurately large (the correct value for the ϕ_p^2 coefficient is 5.6 ± 0.06); yet for a host of reasons (including the omission of contributions from higher order terms), (Eq.12) is frequently found to be nearly correct in practice. There are also various alternative equations some of which, sometimes associated with the name of Landel, can be simplified as follows:

$$E/E_m \approx (1-1.56\phi_p)^{-1.6} \text{ (Eq.13)}$$

Examination of the equation of Landel shows that it is compatible with the corrected form of S-G equation under the [unwarranted] assumption that we are dealing with a simple Taylor expansion. Further, (Eq.13) embodies the rcp limit of Bernal [46] in the following sense: for $\phi_p \rightarrow 0.64$ (Eq.13) predicts that $E/E_m \rightarrow \infty$, that is an elastomer with a dispersion of non-deformable spherical particles becomes 'ultrastiff' (in practice $E/E_m \geq 10^2$); also according to the viscosity version of (Eq.13), for $\phi_p \approx 0.64$ the dispersion of particles in a liquid becomes immobile. Similar results yields, despite its somewhat different form, an equation by Chong et al [65], while numerous other equations have also been suggested.

(c) Certain types of carbon black in natural rubber (NR) and certain types of nanosilica in silicone are known to lead to modulus values substantially higher than that predicted by S-G and related equations (e.g. the latter equations underestimate values by a factor of 2 to 5 for particle volume fractions of 0.25 to 0.50). Possible explanations for this 'super-reinforcement' effect for particular pairs of elastomers and particles are as follows: (a) formation of elongated (necklace type) particle clusters (Fig. 1(b)) and (b) physical chemical particle-matrix interactions leading to equivalent E-raising physical-chemical crosslinks and/or to the enhancement of the equivalent volume of precipitates.

(d) Overall, equations (such as those of S-G, Landel etc) for the reinforcement of elastomers suggest (if we ignore cases of 'super-reinforcement' effect) an E/E_m of ca. 5 for ϕ_p levels such as 0.4 to

0.5; this is comparable but higher (e.g. by a factor on the order of 2) than that predicted for non-elastomeric matrices.

It might be noted that the equations for stiff spherical particles and elastomeric matrices (Eq. 12 and 13), the equations for stiff spherical particles and [much softer but] non-elastomeric matrices (e.g. Eq.11a) and the equations for transversely tensioned stiff cylindrical fibers (versions of Eq. 2) in much softer matrices all suggest that, for low to medium loads, the modulus depends on that of the matrix and the volume fraction of the stiff particles and not on the modulus of the particles. The dependence on the latter volume fraction is nearly linear with a coefficient of ca. 1 to 2.5 for low particle volume fractions (e.g. for fractions up to 0.1 or somewhat higher) and the result reaches the level of kE_m , where $k = 2$ to 5, for particle volume fractions of 0.4 to 0.5; the higher of the k values correspond to spherical particles and elastomeric matrices. Given the moderate compatibility of all latter results (pertaining to a rather diverse spectrum of cases) it is hardly surprising that numerous works claiming wider applicability of new equations and others advertising case-specific accuracy coexist in the literature.

5.4.4. Modulus for composites with dispersed spherical particles vs. modulus for composites with 3-D random dispersed needles.

We will assume that (a) the matrix is a thermoplastic or a thermoset polymer, (b) the chopped fibers are isotropic (or statistically isotropic or nearly isotropic and having a length longer than the critical one), (c) no nanoscale effects are important, (d) deviations from randomness in the case of chopped fibers do not lead to substantial deviations from the predicted E_{3-D} , random modulus.

We have seen that $E_{3-D,random} \approx (1/5) E_{//} + (4/5) E_{\perp}$. We will now consider a reasonably (for synthetic composites) 'high' load of 50 vol. % (ϕ_p or $\phi_f = 0.50$):

For the fiber case the result is:

$$E_{3-D,random} \approx E_f/10 + E_m/10 + 8/5 E_m = 0.1 E_f + 1.7 E_m \text{ (Eq.14)}$$

For the spherical particle case a typical example is: $E_{particle} \approx 4 E_m$ (Eq.15)

We will now insert some characteristic modulus values for the two components:

(i) For $E_m = 3$ GPa and $E_{ceramic} = 70$ GPa (e.g. glass), the result will be ca.12.1 GPa in the first case and ca. 12 GPa in the second case.

(ii) For $E_m = 1.5$ GPa and $E_{ceramic} = 100$ GPa (e.g. apatite) the result in the first case will be ca. 12.6 GPa and in the second case ca. 6 GPa.

(iii) For $E_m = 3$ GPa and $E_{ceramic} = 400$ GPa (e.g. alumina or boron) the result in the first case will be ca. 45.1 GPa and in the second case ca. 12 GPa.

Hence:

(a) For moderate modulus ceramics the results for spheres and chopped fibers can be comparable (as in example (i)); this explains why some short glass fibers employed as 3-D (pseudo-) random dispersions are occasionally described as fillers. Still, chopped fibers are better (as in example (ii)) in the case of very soft polymers (e.g. polyethylene or polypropylene),

(b) For certain high modulus ceramics the chopped fibers lead to a moderate density, moderate E quasi-isotropic composites, while in the case of particles the product will remain a plain 'filled-polymer'.

On the basis of Eq.14 and Eq.15 and for ϕ_p or $\phi_f = 0.50$, we conclude that in order for 3-D random dispersions of long needles (/chopped fibers) to offer much more reinforcement than spherical particles in the same polymer matrix the condition is:

$$0.1 E_f + 1.7 E_m \gg 4 E_m \Rightarrow E_f/E_m \gg 23 \text{ (Eq.16)}$$

For a relatively soft polymeric matrix (e.g. $0.2 \text{ GPa} \leq E_m \leq 1.5 \text{ GPa}$) glass is already a good fiber choice according to Eq.16 and apatite is an even better one. However for relatively hard polymeric matrices (e.g. $2.5 \text{ GPa} < E_m < 4 \text{ GPa}$) glass and apatite are borderline fiber choices (apatite remains somewhat better than glass). For relatively hard polymer matrices one should employ much stiffer ceramic needles or chopped fibers (e.g., possibly costly ones, with a modulus of 300-400 GPa) in order to achieve an $E_{3-D,random}$ value that is remarkably better than the modulus achievable upon incorporation of moderate E ceramic powders (or even chopped glass fibers). The situation becomes more favorable for apatite and glass fibers when reinforcement is limited to a plane, as instead of (16) we obtain:

$$E_f/E_m \gg 13.7, \text{ for 2-D randomness (Eq.17)}$$

Finally in the same manner and for a single direction we obtain:

$$E_f/E_m \gg 7, \text{ for the 1-D case (Eq.18)}$$

5.4.5. Nanoscale effects for polymer/spherical ceramic nanoparticles.

Here we briefly extend our 5.1.6 discussion. In 1989 Vollenberg and coworkers [39,40] reported that the modulus of elasticity of composites with various polymer matrices and dispersed spherical ceramic particles was often enhanced substantially upon reduction of the particle size from ca. 100 microns to ca. 35 nm. For example a-PS with $E = 3.45 \text{ GPa}$ and a load of 15 vol. % led to a composite with $E = 4.15 \text{ GPa}$ for 100 micron particles and to a composite with $E = 6.90 \text{ GPa}$ for 35 nm particles.

In the more recent years it became clear that both local increases and local decrease of E_{matrix} (and matrix T_g) are possible [43,45,66,67,68]; while the case of E enhancement is already intuitively attractive, the opposite case when considered from the point of view of enhanced local matrix mobility is also of interest in special cases. For example, A.M. Mayes [67] had noted that a polymer polyelectrolyte with a locally (around weakly wetting nanoparticles) reduced T_g can allow for a substantially enhanced ionic conductivity. We might also note that the percolation of enhanced mobility zones (found around T_g -reducing ceramic nanoparticles) might allow for interesting features in the toughness vs. ceramic nanoparticle load function.

5.4.6. A special example: Spherical assemblies of asymmetric nanoparticles.

Recently [69] we have reported ways to generate sturdy spherical assemblies of asymmetric HAP nanoparticles (needles or platelets) arranged isotropically or quasi-isotropically by modifying, through gelatin addition, a known solution route for the preparation of loose HAP needles. We have also employed solution routes modified by gelatin addition for the precipitation of

other ceramics of biological significance (calcium carbonate, calcium silicates, silica) [70]; the morphological outcomes were equally interesting yet geometrically different from those for HAP. In the case of HAP the sheet/layer-like features of precursor phases (as, for example, OCP structure can be thought of as special alternation of apatite-type and hydrated layers) probably remain the source of asymmetry of individual particles, while gelatin allows for the formation of organized assemblies and its level affects asymmetric particle geometry (e.g. needles vs. platelets).

Fig.2a captures the initial stage of evolution of a HAP assembly resulting from the gelatin modification of a solution precipitation route that leads to the formation of isolated needles. At the end of the conversion the ensemble of parallel needles undergoes an impressive 'ecdysis' step; overall, we refer to a mesoscopic 'chrysalis transformation' [69] leading to needle assemblies such as those pictured in Fig.2b,c (needle aspect ratio is on the order of 200). A doubling of the gelatin concentration leads to platelet assemblies of the type shown in Fig.2d (platelet aspect ratio is on the order of 40).

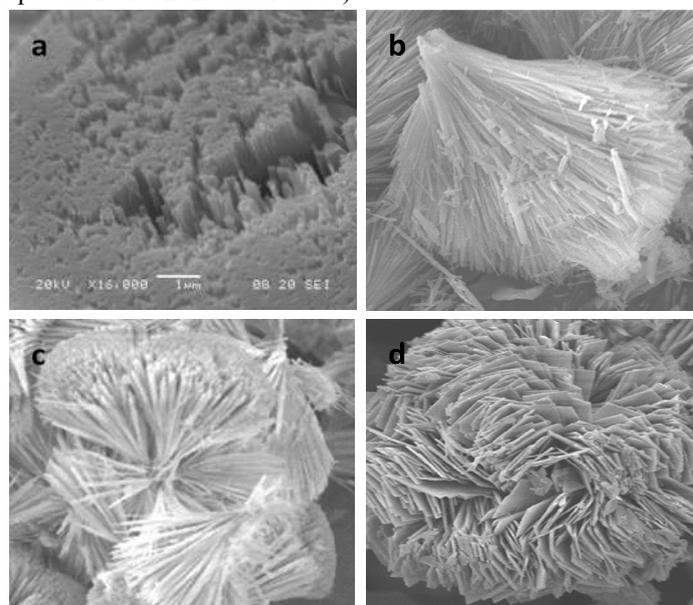


Figure 2. (a) a tablet-shaped precursor having a thickness in excess of 1 micron begins to transform (starting at a lateral face of the tablet) into a dense set of parallel HAP needles, (b) a sturdy needle assembly can be thought of as the eighth or so of a full spherical 'urchin' (diameter of the hypothetical spherical 'urchin': 45-50 microns), (c) a cluster of needle assemblies, (d) a near spherical assembly of HAP platelets; assembly diameter: 35 to 40 microns.

The following features of our assemblies should be noted:

- (i) The spherical aggregates are a few tens of microns wide and hence, despite the fact that the individual particles are of nanoscale thickness the sturdiness of the assembly guarantees that there is no health danger associated with the size of free nanoparticles.
- (ii) The needles form radiating assemblies; while the needles are non-randomly arranged they exhibit arrangements that are, at a local scale, more isotropic than the liquid crystal like domains of distinct needles; somewhat similar comments are applicable to the case of our the platelet assemblies.
- (iii) The minimum viscosity for dispersions is that for dispersed *spheres*. Because of lower viscosity and also a reduced chance for

particle fracture, it is possible that processing will be easier than that for separate particles of the same aspect ratio and at the same volume fraction.

According to (Eq. 14) and if we overlook possible nanoscale effects, a load of $\phi_f = 0.50$ apatite needles in a 3-D quasi-random arrangement cannot lead to a composite with an E exceeding 10-12 GPa for a soft polymer matrix or exceeding 15-16 GPa for an ordinary hard polymer matrix. If one employs spherical needle agglomerates and forms a mildly interpenetrating packing of them while the interagglomerate space (occupying ca. 50 % of the volume of the composite) is occupied by a largely particle-free polymer then one finds a lower bound of ca. 3 GPa in the case of a composite with a soft polymer and one of ca. 4 GPa in the case of a composite with a harder polymer. The lower limits are estimated by assuming that the inter-agglomerate space contribute as much as porosity of the same volume fraction (i.e. the original modulus should be multiplied by a factor of ca. $(0.50)^2 = 0.25$). The case of spherical aggregates of platelets (Fig. 2 d) appears to offer a more attractive option. We will now limit our attention to the Fig. 2b & c structures. While the assumption that the HAP-free part of the matrix contributes in the manner of pores undoubtedly leads to an underestimation of the lower bounds one cannot easily envision composites (with HAP of the Fig. 2c type) that exhibit modulus values in clear excess of those achievable with comparable loads of low aspect ratio HAP particles; here we

4. CONCLUSIONS

Polymer matrix/ceramic dispersion composites are structural materials that usually bear low to moderately high (up to 50 to 65 vol. %) ceramic loads in the case of synthetic versions and medium (e.g. 30 to 40 vol. %) to high (e.g. 70 to over 90 vol. %) ceramic loads in the case of natural versions.

‘Liquid crystallinity’ effects while often overlooked during the processing of composites with asymmetric particles: (i) can undermine quasi- isotropy at small to medium size scales in the case of chopped fibers and (ii) can be fully disastrous, as regards properties such as the E of the composite, in the case of platelets.

According to detailed considerations presented herein one can distinguish:

- (i) cases that the modulus of the polymer/ceramic composites is controlled by ‘polymer matrix E’ + ‘ceramic volume fraction’; here the exact ceramic is almost immaterial, at least if we disregard nanoeffects and also limit our focus to modulus,
- (ii) cases that the modulus of the composites is controlled by ‘ceramic dispersion E’ + ‘ceramic volume fraction’; here the exact ceramic is obviously important,
- (iii) intermediate cases.

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can add the condition of comparable particle diameters in order to take into account, at least approximately, contributions from possible nanoscale effects. The latter situation is hardly surprising in view of the related discussion of equation (16): the moderate modulus of HAP limits substantially the modulus achievable with 3-D quasi-isotropic needle-type reinforcements. Yet, one might use agglomerates of the Fig. 2(b) & (c) type:

(i) as templates for the effective dispersion of a stiffer second phase and aim, ultimately, at hybrid composites; we have already grown successfully carbon nanotubes on such aggregates [71] while conceivably it is also possible to infiltrate the system of spherical aggregates with polymers (or pre-polymers) bearing low aspect ratio nanoparticles (e.g. ceramic nanospheres with a $d = 200 \text{ \AA}$),

(ii) in case enhanced local scale isotropy, which is uncommon in usual chopped-fiber synthetic composites, turns out to have a positive impact on certain mechanical properties (e.g. toughness) of the ‘[quasi] 3-D random’ composites; also in the case of a medical applications it might be of interest that the mode of biodegradation will be different from that of a composite with low aspect ratio HAP particles.

(iii) as models for the development of other similarly shaped clusters of asymmetric particles of stiffer ceramics (e.g. Al_2O_3 etc).

HAP is a key natural ceramic of biocomposites while it constitutes a reasonable, though not striking, option for synthetic structural composites

With a characteristic exception that of enamel, HAP based natural composites tend to combine medium to low modulus with medium to high toughness.

Modeling of the mechanical properties of the composites remains a challenge and overlooked scale related issues might be part of the problem.

In terms of modulus, structural composites with needle/fiber HAP reinforcement appear more attractive when reinforcement is desired in certain directions; this is not unlike the corresponding case of glass composites.

In the area of composites, there is a near uniqueness when HAP (or some HAP precursor phase) is involved in synthetic materials for medical and related applications.

Newly fabricated spherical assemblies of asymmetric HAP nanoparticles offer safe handling of a nanopowder component, reduced viscosity during composite processing and model materials for similar pursues with other ceramics.

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