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Fillers Design and Best Use: Recent Trends and Basic Questions

Henri Van Damme, Alain Burr*

Ecole Supérieure de Physique et Chimie Industrielle (ESPCI-PCSM), 10 rue Vauquelin, 75231 Paris cedex 05, France

Summary : This paper is a discussion of a few selected topics or trends in recent research literature which raise fundamental issues in our understanding of the way fillers improve the properties of polymers. A first topic is the now well-established experimental and theoretical evidence that the T_g and the molecular mobility in free standing or supported films are modified over a much larger thickness than was previously thought. Considering their enormous interface area, this introduces a new look to the remarkable reinforcement effect obtained in delaminated clay nanocomposites. On the other hand, the reason why, in spite of their extraordinary mechanical properties and their very large surface area, carbon nanotubes, with their fibre-like morphology, are still far from giving the same reinforcement, is still an open question. A second topic to be mentionned is the development of hybrid materials and biomimetic approaches which, due to very small scale of the organic-inorganic heterogeneities which can be achieved, raises questions on the phase concept and points to the need for new theoretical approaches of the mechanical properties of these materials. Finally, a third topic is the control of the filler particles distribution in the matrix. The general theory of random diphasic media permits to define several types of "good" dispersions in terms of disordered distributions, according to the correlations of the particles positions in a matrix. This raises two problems, which are briefly discussed: (i) Are we able to define the type of dispersion we want? (ii) Is it relevant for modifying the properties?

Introduction

Several developments in recent literature show that the field of filler-polymer composites is undergoing an evolution in which the "bonded diphasic" description of these materials in terms of a filler phase, a matrix phase and surface chemistry-controlled interfacial bonds, is progressively replaced by a more integrated description in which the very concept of phase may loose its relevance and where, concomitantly, the patterning of space and the gradients of properties gain more importance. The purpose of this paper is to introduce and to discuss the questions raised by this evolution. The topics which will be chosen as basis for discussion are (i) the comparison between, on one hand, the recent physics of thin polymer films, with the

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clear evidence for surface-induced long range gradients of molecular mobility and, on the other hand, the fast growing field of nanocomposites with nanotubes and smectite clays, and the possible evidence for confinement effects; (ii) the development of hybrid materials and the limits of the phase concept; (iii) patterning, partitioning of space and the control of dispersion.

Thin films and nanocomposites: mesoscale gradients and confinement effects

It has now been verified by a number of different techniques including ellipsometry, x-ray reflectivity, Brillouin light scattering and positron annihilation spectroscopy, that the glass transition temperature of thin polymer films may be significantly modified with respect to that of the bulk material [1]. In the case of freely-standing films, a large reduction of T_g is observed, by as much as 80*K*. Remarkably, the film thickness over which these effects are observed is well beyond the nanometer scale and may be as large as 100 nm. In polymer films supported on a solid substrate, the effect may be either a decrease or an increase of T_g. However, it is clear that in cases where there are strong specific interactions between the polymer and the substrate, for instance poly(2-vinyl pyridine) [2] or PMMA [3,4] on silica, the glass transition temperature increases by as much as several tens of *K* with decreasing film thickness.

Although direct structural relaxation studies are still limited, the general interpretation of these changes is that the mobility of the polymer chains is either enhanced, close to a free surface or close to a non-wetting surface, or depressed, close to a strongly adsorbing surface. The theoretical explanation for this is still the matter of some debate. In general, explanations fall in either one of two categories : finite size effects on one hand, and surface or interface effects on the other hand. This is a general situation for nano- and mesomaterials. A finite size effect -a lower average density- was the first explanation to be proposed for the large decrease of T_g which may be observed in thin freely-standing films [5]. Indeed, starting from simple free volume calculations, it may be predicted that a decrease in the room temperature density of only ~1% should lead to an increase in free volume large enough to depress T_g by as much as 40K in polystyrene for instance. However, calculation of the disjoining pressure (drop of cohesive strength) due to van der Waals interactions in a thin polymer film shows that the values obtained are unable to lead to the necessary *permanent* density decrease [6].

What then could the origin of the observed strong effect ? Two other explanations have been proposed. The first, which is also a finite size effect, deals with the case of small polymers, with radius of gyration smaller than the thickness of the film. Its rationale is that the small size of the system (in one direction) allows for large density *fluctuations* which, as long as their amplitude is strong enough to bring *temporarily* the density of the film below the density of the glass, would prevent the film from being glassy [6]. The predicted decrease of T_g is of the right order of magnitude compared to the observed values. The second explanation, dealing with the case of long polymer chains with radius of gyration larger than the film thickness, is an interface effect. Its rationale is that this situations introduces new degrees of freedom related to the sliding motion of each chain along its own path [7]. In the bulk, this sliding is blocked at the end points, but in a thin film it would be allowed for chain arcs touching the surface.

On the other hand, in the case of strongly adsorbed polymer films, with a thickness smaller than the radius of gyration of the chain, the film behaves as a non homogeneous end-grafted molten polymer brush and its equilibrium density is modified by the stretching energy [6]. This results in an increase of the density, which leads to an increase of T_g for large molecular weight polymers [6].

Whatever the theoretical explanation for these meso- to long range modifications of molecular mobility indirectly revealed by a ΔT_g, they have far reaching consequences for our understanding of the action of fillers. With molecular properties modified over distances as large as, say, 50 nm away from the filler-matrix interface, the fraction of polymer matrix with modified properties would rapidly become the dominant fraction in the system. The filler particles surrounded by their wide interfacial sphere would represent a system of virtual or effective particles which, at usual filler loading, would be well beyond the percolation threshold and probably close to a jamming (disordered compact) situation. A similar situation arises in colloidal suspensions of charged particles. The charged particles surrounded by their ionic Debye sphere form a system of effective particles which may reach the random close packed limit and form a colloidal repulsive glass, even though the real particle volume fraction is still well below the percolation threshold. This concept of " effective jamming " may be particularly important for reinforcement of elastomers.

It is not obvious that the word "phase" can be used to described these wide mesoscale interfacial regions, due to the likely presence of property gradients (which have still to be quantitatively studied). This makes it particularly difficult, or at least tedious, to model the mechanical properties of the composites. Multiple shell models seem to be the best way to cope with the problem.

A class of polymer materials in which the mesoscale interfacial regions may definitely become dominant is that of clay-polymer nanocomposites [8-10]. This field has experienced an explosive development in recent years, due to the quasi-universal enhancement of mechanical, thermal and barrier properties which is obtained at small clay loading. The clays which are the most suitable for preparing nanocomposites are the smectites, also called swelling clays, the most widely used member of the family being montmorillonite. Like all clays, smectites are silicates with a layered crystal lattice [11]. Their elementary particles are negatively charged 0.96 nm thick single crystal silicate layers with an aspect ratio which may be as high as 2000 (2μm wide). The charge compensating cations are located in the interlayer space. The interest of smectite clays comes from the ease with which the surface properties of the elementary layers may be modified, primarily *via* cation exchange. This allows for preparing colloidal dispersions not only in water and aqueous solutions, but also in organic solvents and molten polymers. Provided these surface properties are properly tuned (hence, also the layer-layer interactions and the layer-dispersion medium interactions), the dispersion may reach a state where the individual layers are separated by large distances (swollen state). Due to the huge aspect ratio of the layers, this type of dispersion can only be obtained at very small clay volume fraction (typically of the order of 1%). When all the layers are in this situation, the system is said to be *delaminated.* In most situations, the dispersion is in a mixed state, with the layers being well-individualized in some regions and engaged in stacks on other places (Figure 1). In the stacked domains (called quasi-crystals [12]), the layers are separated by distances of the order of 1nm, corresponding typically to the diameter of one or a few solvent molecules, or to the thickness of a polymer segment in contact with the surface. In this stacked configuration, the system is said to be *intercalated.*

With an interface area of the order of 800 m^2/g, a flexible plate-like morphology, a huge aspect ratio and a tunable surface chemistry, smectite fillers are expected to modify the properties of the polymer matrix in which they are embedded. Simple geometrical arguments show that, with interfacial regions 50 nm wide, a volume fraction of 1% of delaminated clay in the nanocomposite would be enough to convert the total mass of polymer into interfacial polymer. No wonder that enhancements of the glassy and rubbery modulus as high as a factor of 2 or more can be obtained with clay volume fractions of the order of 1% in a large number of polymers, including epoxy polymers for instance [13,14].

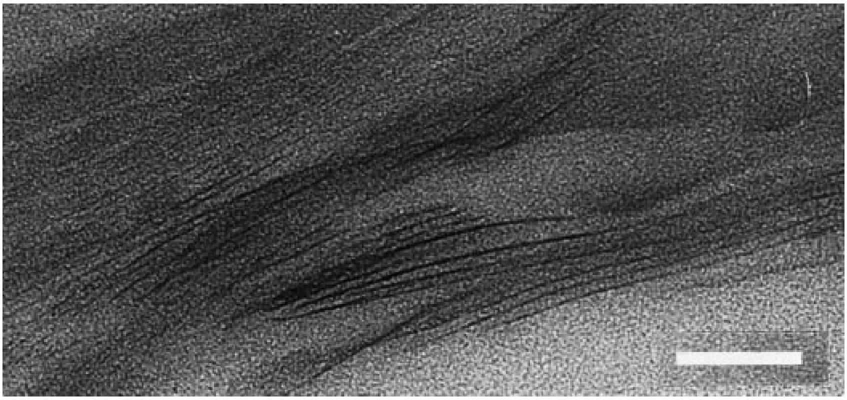

Figure 1. TEM micrograph of a thin section in a smectite clay dispersion in a polyurethane matrix. Several features are noticeable: the remarkable flexibility of the 1nm-thick iono-covalent layers; their tendency to be in the intercalated state, i.e. to form stacks (so-called "quasi-crystals") with small but regular interlayer distances in some regions, and to be in the swollen state, with large and distributed interlayer distances in other regions. In an ideally delaminated material, all the regions should be in the swollen state (scale bar: 50 nm).

It is of course very tempting to relate this remarkable enhancement to the change in glass transition temperature and molecular dynamics observed in thin polymer films, as summarized above. Although there is no doubt that the two classes of phenomena are indeed related, the relationship is less simple than one might think. Indeed, it seems than in strongly confining situations, the glass transition simply disappears. This has been observed for poly(ethylene oxide) - smectite intercalates (interlayer distance of the order of 1nm) [15].The most intriguing result is perhaps that simulation and experimental studies tend to show that molecular mobility is *higher* in a confined situation than in the bulk [16,17]. A closer look to molecular dynamic results on clay-polystyrene nanocomposites reveals that this is an average effect and that the very local behavior is more complex [17]. In fact, the segment density profile along the direction normal to the clay layers is found to be strongly inhomogeneous, with higher density regions where segment mobility is low alternating with lower density regions where mobility is high. What comes out from these studies, when compared with the existing results on thin films, is that spatial and/or temporal density fluctuations are indeed key factors. How they are related to the molecular properties of the polymer matrix, to the wall-polymer interaction and to the distance to the wall, or to the inter-wall distance, remains to be established.

In parallel to the explosive development of clay-polymer nanocomposites, several studies of polymer reinforcement with carbon nanotubes (NT) have been made on samples of macroscopic size and high filler loadings (up to more than 30%). Carbon nanotubes –in particular, single-wall nanotubes (SWNT)- have extraordinary mechanical properties. Direct measurements and simulations point to a Young modulus of the order of 1.2 Tpa [18,19]. At the same time, thanks to the easy changes in hybridization of the carbon atom, SWNT are remarkably flexible [20]. This unique combination of properties makes them ideal fibrous fillers. Surprisingly, current results are rather disappointing. Although the reinforcement effect was clearly evidenced, the modest amplitude of the effect shows that we are still far from taking full advantage of the extraordinary properties of carbon nanotubes. For instance, in a epoxy matrix, one has to go to a volume fraction of SWNT of more than 35% to increase the matrix modulus by a factor of 2 [19], which is way below the reinforcement obtained in clay nanocomposites. One possible reason for this is the fact that SWNT are forming bundles in which each SWNT can slide with respect to its neighbors. Another reason could be the poor quality of the SWNT-polymer interface. Finally, a fundamental reason could be the difference between fibers and platelets. Indeed, if confinement between (almost) flat walls turns out to be the reason for the excellent results obtained with delaminated smectite clays, then there is little hope to reach the same level of performance with fibers. This also has to be clarified.

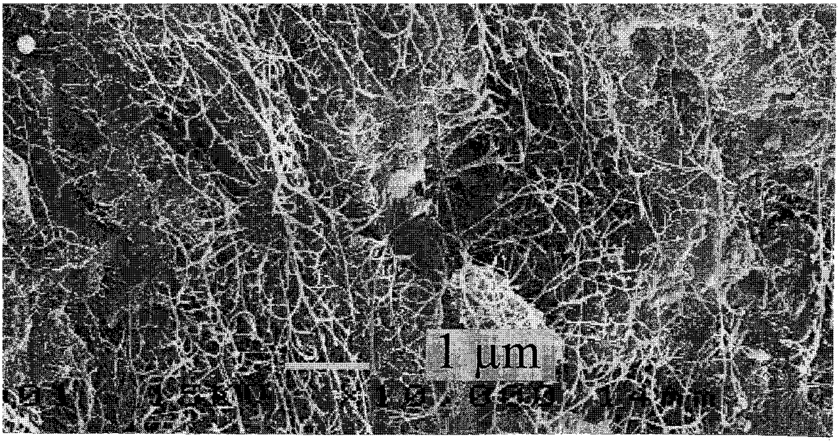

Figure 2. TEM micrograph of a thin section of a dispersion of single-wall carbon nanotubes in a PEEK matrix (from L. Vaccarini; adapted from ref. [19]). The fibers on the image are in fact bundles of several individual nanonubes.

From diphasic to hybrid

The general trend towards the control of the " microstructure " of composite materials at increasingly small length scales finds its ultimate point in hybrid materials, in which inorganic and organic molecular moieties are associated to each other at molecular scale by covalent bonds. Well-known examples are the siloxane-based materials prepared by hydrolysis and condensation of organo-substituted silicic acid esters of general formula $R'_nSi(OR)_{4-n}$, or their bridged versions, $X_3Si\text{-}R'\text{-}SiX_3$ (X = Cl, Br) or $(RO)_3Si\text{-}R'\text{-}Si(OR)_3$, with a central organic group bearing a trifunctional halosilyl or alkoxysilyl group at each end[21,22]. Hybrid materials are most often developed for optical applications, coatings, sensors or dielectrics. In polymer science and technology, their interest as filler-matrix coupling agents has been known for more than twenty years[23] but they can also be used as precursors for silica (or titania) cluster - reinforced polymers[24], provided the organic bridging group is chosen long and flexible enough, or provided the organo-substituted inorganic precursor is hydrolyzed in an hydroxylated polymer matrix. Clusters containing but a few siloxane units can be prepared in this way. At this point, we are probably out of the domain where the concept of filler as a separate phase, in Gibbs sense, applies. In addition to its practical interest, this *in situ* generation of filler clusters or particles offers a way to test the limits of mixture theories for properties.

Partitioning of space and the control of dispersion

What is a *good* dispersion? Behind this deceptively simple question is the recognition of our lack of fundamental understanding of the relationships between the properties of the composite material and the details of the distribution of filler particles in the matrix. The question itself may appear irrelevant since qualifying a dispersion as "good" implies that all the particles which we wanted to be dispersed are indeed separated from each other. What more could we ask for? Perhaps some homogeneity or, at least, the absence of clustering. If this is achieved, then we have every reason to be satisfied.

In fact, the recent progress in the structural analysis of diphasic media (porous media, composites) provide the tools to go beyond the two previous criteria (separation of particle, good homogeneity) and to define at least three different types of "good" dispersions, each with a characteristic signature. These tools are the chord distribution functions, which have been used to model various processes such X-ray scattering, molecular diffusion or energy transfer in porous media[25]. A chord is a line segment between two encounters with an interface. Thus, there are matrix chords and filler chords. A chord distribution function gives the distribution of chord lengths, obtained by tracing random straight lines through the medium. Of particular interest in polymer composites is the matrix chord distribution function, $f_m(r)$ which give information on the polymer layer thickness distribution between filler particles. It may be used to quantify the degree of confinement in polymer nanocomposites. The filler chord distribution function, $f_f(r)$, is also interesting since it allows to check whether the particles belong to the same family or, in other words, whether there are agglomerates or not. These distribution functions may be obtained from image analysis of electron micrographs or from scattering experiments.

The three types of disordered dispersions are as follows [25,26]:

- *Debye or Boolean disorder.* Debye disorder is probably what one spontaneously has in mind when thinking about the disorder he would like ideally to achieve. It corresponds to a situation where a walker who would cross the medium along a straight line would have a constant probability of hitting a filler-matrix interface. It is characterized by an exponential distribution of matrix chord lengths, $f_m(r) \propto \exp(r/\lambda)$. An example is given in Figure 3

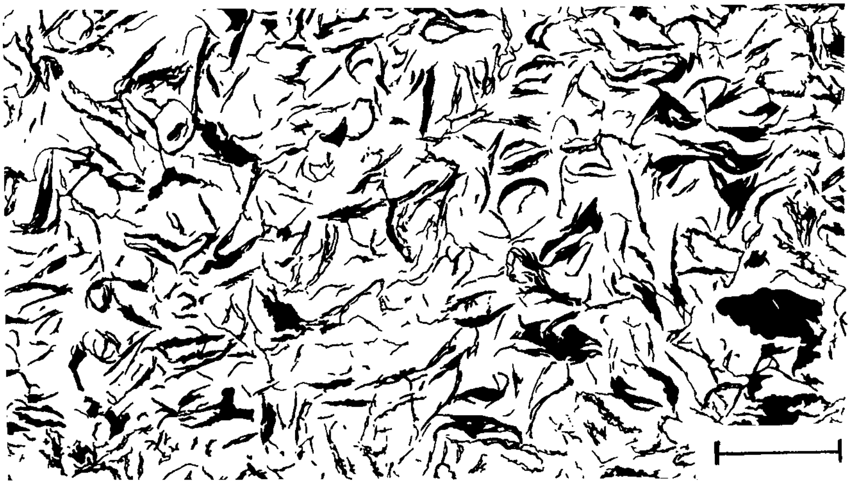

Figure 3. Digitized TEM micrograph at low resolution of a thin section in a smectite clay dispersion. This dispersion is an almost perfect example of Boolean or Debye disorder. A walker crossing this picture has a constant probability of hitting an interface. The matrix chord length distribution function is a decreasing exponential function. Note that this is not a delaminated dispersion. The particles visible on the picture are in fact complex assemblies of nanoplatelets, as in Figure 1. The scale bar is 2 μm.

A Boolean distribution corresponds to total randomness and is the type of situation expected for a population of particles undergoing Brownian motion, provided re-agglomeration may be prevented. Boolean disorder is the stationary state of this random dynamic process. Low viscosities are required for this mechanism to be effective.

- *Correlated disorder*. This is in fact quasi-order. It corresponds to a situation where, in spite of some apparent randomness in the texture, there is a well-defined maximum probability in the distribution function, corresponding to a quasi-periodicity. In its perfect version, it would be crystallographic order. In order to obtain this type of distribution, an interaction mechanism is needed which tries to impose a characteristic length scale. In colloidal dispersions, this can easily be achieved by long range repulsive forces (colloidal crystals or glasses). In polymers, selective affinity of the filler particles for a type of segment or for the interface in a patterned block polymer matrix could be a way to obtain it.
- *Hierarchical disorder*. This is a kind of disorder in which there is a power law (algebraic) distribution of interparticle chord lengths, $f_m(r) \propto r^{-\alpha}$. Many different interparticle distances may be observed, even very long ones. Visually, this texture looks like an inhomogeneous or lacunar dispersion, with some regions with a high density of filler particles and other regions which look almost empty (Figure 4).

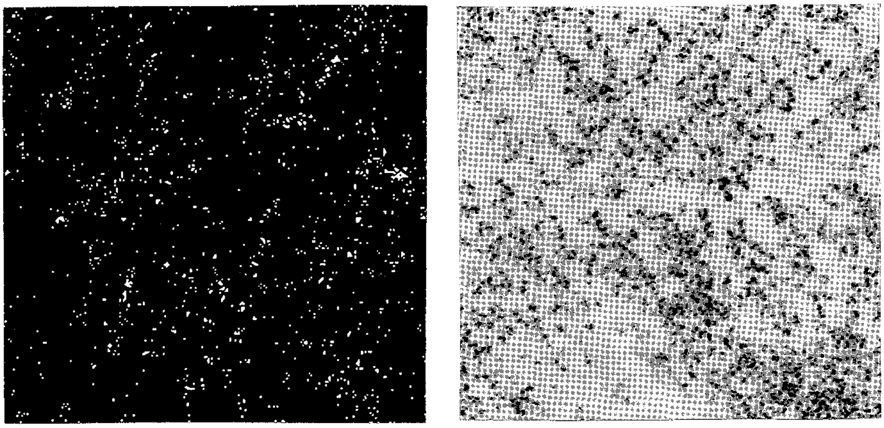

Figure 4. Left: a computer-generated hierarchical distribution of particles with a power law distribution function of matrix chord lengths (adapted from ref. [25]); Right: an AFM picture of an elastomer reinforced with silica partilces (adapted from ref. [28]; image size: 5 μm).

In fact, this is only a visual impression. There is a continuous distribution of local densities. Although there is no real proof for this, this might be the kind of disorder produced by a hydrodynamically-controlled dispersion mechanism, in which the fragments of the sheared agglomerates would follow the stream lines in the mixer. The hierarchical distribution of matrix chord lengths would be the frozen signature of the chaotic nature of the mixing process[27].

Being able to identify different types of dispersions leads directly to the important question: Are the different types of dispersions just described equivalent? Is there one which is better than the others for improving a given property? It is likely that there is no general answer to these questions. As long as the filler particles do not significantly modify the polymer matrix properties, a simple property like Young's modulus should not be sensitive to the type of dispersion. However, with long range interface-induced gradients of properties, everything changes. In general, non linear properties at large strain and hysteresis phenomena are expected to be much more sensitive to the type of dispersion than linear properties at small strain. As far as complex properties such as tear or wear resistance, or shock resistance are concerned, the answer is far from obvious.

Conclusion

This paper was a simple look to a few trends or results in recent literature which find their place in the general move towards nanotechnologies, biomimetic approaches and simulation studies in material science. One of these results was the evidence that the properties of a polymer near a wall may be modified over mesoscale distances (up to several 100 nm). A strong trend was the development of nanocomposites and the remarkable properties obtained with swelling clays. Another trend was the increasing place of hybrid materials and templating or patterning techniques. The final look was at the application of simple theoretical concepts on disorder to characterize and to model heterogeneous media. Remarkably, each of these results or trends raises questions which show that, in spite of remarkable achievements, even the simplest questions about the mechanism of polymer reinforcement are still, to a large extent, open questions. The simple mixture-type diphasic picture of filled polymers tend to be replaced by a more gradual or blurred picture in which the distribution of matrix chord lengths, the orientational correlations between interfaces and the mesoscale gradients of properties become the important parameters. Spatial (below T_g) or temporal (above T_g)

fluctuations of density seem to be of outermost importance, especially in nanocomposite materials.

As far as modeling is concerned, this does not simplify the problem. Homogenization techniques should be able to give an analytical answer. The Distributed Generalized Self-Consistent method has already been used to compute the stress, strain and energy density distribution in reinforced elastomer networks[29] at small strain and below the particle percolation threshold. The method takes into account the distribution of local filler particle concentration. Each local concentration is related to a composite sphere, with a core representing the local filler particle volume fraction. Any filler-reinforced composite material can thus be described by a gathering of composite spheres. Extending the method in order to take explicitely into account the distribution of particle-to-particle distances and the gradients of matrix properties in the gap is a considerable task.

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