Theoretical aspects about bright future of polymer nano-composites in mechanical engineering

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Abstract: In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles (e.g. minerals), sheets (e.g. exfoliated clay stacks) or fibres (e.g. carbon nanotubes or electrospun fibres). The area of the interface between the matrix and reinforcement phase(s) is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement.

Keywords: nanocomposites, nanotubes, fibres, polymers.

Introduction

Polymer nanocomposites are constructed by dispersing a filler material into nanoparticles that form flat platelets. These platelets are then distributed into a polymer matrix creating multiple parallel layers which force gases to flow through the polymer in a “tortuous path”, forming complex barriers to gases and water vapor. Nanoparticles allow for much lower loading levels than traditional fillers to achieve optimum performance. Usually addition levels of nanofillers are less than 5%, which significantly impact weight reduction of nanocomposite films. This dispersion process results in high aspect ratio and surface area causing higher performance plastics than with utilized, the most common is a nanoclay material called montmorillonite-a layered smectite clay. Different types of fillers are Clays, in a natural state, are hydrophilic while polymers are hydrophobic. To make the two compatible, the clay’s polarity must be modified to be more “organic” to interact successfully with polymers. Additional nanofillers include carbon nanotubes, graphite platelets, carbon nanofibers, as well as other fillers being investigated such as synthetic clays, natural fibers (hemp or flax), and POSS (polyhedral oligomeric silsesquioxane). Carbon nanotubes, a more expensive material than nanoclay fillers which are more readily available, offer superb electrical and thermal conductivity properties.

Nanocomposites from other Polymers and Fillers

Nanocomposites from bioactive molecules and clays have also been reported. One such example is smectite nanocomposites that use the ability of smectites to induce specific cointercalation of purines and pyrimidines. Thus, thymine and uracil in nanocomposites are absorbed on MMT appreciably if solutions also contain coabsorbed adenine. Layered double hydroxides (LDHs) present a layered structure comprised of di- and trivalent metal cations [M(II) and M(III)] coordinated by six oxygen anions. The substitution of M(III) cations induces an overall positive charge that is counterbalanced by exchangeable interlayer anions. Thus, LDHs can serve as hosts for polymeric intercalation. An attractive, potential application of LDHs is controlled drug release carriers. Several bioactive compounds like DNA and pharmaceuticals have been incorporated within LDH hosts.

Types of Nano-Composites

Ceramic-matrix nanocomposites

In this group of nanocomposites the main part of the volume is occupied by a ceramic, i.e. a chemical compound from the group of oxides, nitrides, borides, silicides etc.. In most cases, ceramic-matrix nanocomposites encompass a metal as the second component. Ideally both components, the metallic one and the ceramic one, are finely dispersed in each other in order to elicit the particular nanoscopic properties. Nanocomposite from these combinations were demonstrated in improving their optical, electrical and magnetic properties as well as tribological, corrosion-resistance and other protective properties. The binary phase diagram of the mixture should be considered in designing ceramic-metal nanocomposites and measures have to be taken to avoid a chemical reaction between both components. The last point mainly is of importance for the metallic component that may easily react with the ceramic and thereby loose its metallic character. This is not an easily obeyed constraint, because the preparation of the ceramic component generally requires high process temperatures. The most safe measure thus is to carefully choose immiscible metal and ceramic phases.
A good example for such a combination is represented by the ceramic-metal composite of TiO₂ and Cu, the mixtures of which were found immiscible over large areas in the Gibbs’ triangle of Cu-O-Ti.

The concept of ceramic-matrix nanocomposites was also applied to thin films that are solid layers of a few nm to some tens of µm thickness deposited upon an underlyng substrate and that play an important role in the functionalization of technical surfaces. Gas flow sputtering by the hollow cathode technique turned out as a rather effective technique for the preparation of nanocomposite layers. The process operates as a vacuum-based deposition technique and is associated with high deposition rates up to some µm/s and the growth of nanoparticles in the gas phase. Nanocomposite layers in the ceramics range of composition were prepared from TiO₂ and Cu by the hollow cathode technique that showed a high mechanical hardness, small coefficients of friction and a high resistance to corrosion.

Metal-matrix nanocomposites

Metal matrix nanocomposites can also define as reinforced metal matrix composites. This kind of composites can be classify as continuous and non continuous reinforced materials. One of the important nanocomposites is Carbon nanotube metal matrix composites which is emerging new materials that are being developed to take advantage of the high tensile strength and electrical conductivity of carbon nanotube materials. Critical to the realization of CNT-MMC possessing optimal properties in these areas are the development of synthetic techniques that are (a) economically producible, (b) provide for a homogeneous dispersion of nanotubes in the metallic matrix, and (c) lead to strong interfacial adhesion between the metallic matrix and the carbon nanotubes. In addition to carbon nanotube metal matrix composites, boron nitride reinforced metal matrix composites and carbon nitride metal matrix composites are the new research areas on metal matrix nanocomposites.

Another kind of nanocomposite is the energetic nanocomposite, generally as a hybrid sol–gel with a silica base, which, when combined with metal oxides and nano–scale aluminium powder, can form superthermite materials

Polymer-matrix nanocomposites

In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often in very dramatic degree, by simply capitalizing on the nature and properties of the nanoscale filler (these materials are better described by the term nanofilled polymer composites). This strategy is particularly effective in yielding high performance composites, when good dispersion of the filler is achieved and the properties of the nanoscale filler are substantially different or better than those of the matrix, for example, reinforcing a polymer matrix by much stiffer nanoparticles of ceramics, clays, or carbon nanotubes. It should be noted that the improvement in mechanical properties may not be limited to stiffness or strength. Time-dependent properties could be improved by addition of the nanofillers. Alternatively, the enhanced crystallization behaviour and other physical properties of high performance nanocomposites may be mainly due to the high aspect ratio and/or the high surface area of the fillers, since nanoparticulates have extremely high surface area to volume ratios when good dispersion is achieved.

Nanoscale dispersion of filler or controlled nanostructures in the composite can introduce new physical properties and novel behaviours that are absent in the unfilled matrices, effectively changing the nature of the original matrix (such composite materials can be better described by the term genuine nanocomposites or hybrids). Some examples of such new properties are fire resistance or flame retardancy and accelerated biodegradability.

In a recent study, polymeric nanocomposites were fabricated using various one-dimensional carbon nanostructures such as single- and multi- walled carbon nanotubes and two-dimensional carbon and inorganic nanomaterials such as single- and multi- walled graphene oxide nanoribbons, graphene oxide nanoplatelets and molybdenum disulfide nanoplatelets as reinforcing agents to improve the mechanical properties of poly(propylene fumarate) nanocomposites, for bone tissue engineering applications. Significant mechanical reinforcement (i.e. increases in the Young's modulus, compressive yield strength, flexural modulus and flexural yield strength) were observed at low loading concentrations (0.01-0.2 wt%) of nanomaterials. Results suggested that mechanical reinforcement is dependent on the nanostructure morphology, defects, dispersion of nanomaterials in the polymer matrix, and the cross-linking density of the polymer. In general, two-dimensional nanostructures can reinforce the polymer better than one-dimensional nanostructures and inorganic nanomaterials are better reinforcing agents compared to carbon based nanomaterials.

Scope of new hybrid material

Hybrid materials are composites consisting of two constituents at the nanometer or molecular level. Commonly one of these compounds is inorganic and the other one organic in nature. Thus, they differ from traditional composites where the constituents are at the macroscopic (micrometer to millimeter) level. Mixing at the microscopic scale leads to a more homogeneous material that either show characteristics in between the two original phases or even new properties.
Many natural materials consist of inorganic and organic building blocks distributed on the nanoscale. In most cases the inorganic part provides mechanical strength and an overall structure to the natural objects while the organic part delivers bonding between the inorganic building blocks and/or the soft tissue. Typical examples of such materials are bone, or nacre.

**Development of hybrid materials**

The first hybrid materials were the paints made from inorganic and organic components that were used thousands of years ago. Rubber is an example of the use of inorganic materials as fillers for organic polymers. The sol–gel process developed in the 1930s was one of the major driving forces what has become the broad field of inorganic–organic hybrid materials.

**Classification**

Hybrid materials can be classified based on the possible interactions connecting the inorganic and organic species. Class I hybrid materials are those that show weak interactions between the two phases, such as van der Waals, hydrogen bonding or weak electrostatic interactions. Class II hybrid materials are those that show strong chemical interactions between the components such as covalent bonds.

Structural properties can also be used to distinguish between various hybrid materials. An organic moiety containing a functional group that allows the attachment to an inorganic network, e.g. a trialkoxysilane group, can act as a network modifier because in the final structure the inorganic network is only modified by the organic group. Phenyltrialkoxysilanes are an example for such compounds; they modify the silica network in the sol–gel process via the reaction of the trialkoxysilane group without supplying additional functional groups intended to undergo further chemical reactions to the material formed. If a reactive functional group is incorporated the system is called a network functionalizer. The situation is different if two or three of such anchor groups modify an organic segment; this leads to materials in which the inorganic group is afterwards an integral part of the hybrid network. The latter type of system is known as network builder.

Blends are formed if no strong chemical interactions exist between the inorganic and organic building blocks. One example for such a material is the combination of inorganic clusters or particles with organic polymers lacking a strong (e.g. covalent) interaction between the components. In this case a material is formed that consists for example of an organic polymer with entrapped discrete inorganic moieties in which, depending on the functionalities of the components, for example weak crosslinking occurs by the entrapped inorganic units through physical interactions or the inorganic components are entrapped in a crosslinked polymer matrix. If an inorganic and an organic network interpenetrate each other without strong chemical interactions, so called interpenetrating networks (IPNs) are formed, which is for example the case if a sol–gel material is formed in presence of an organic polymer or vice versa. Both materials described belong to class I hybrids. Class II hybrids are formed when the discrete inorganic building blocks, e.g. clusters, are covalently bonded to the organic polymers or inorganic and organic polymers are covalently connected with each other.

**Distinction between nanocomposites and hybrid materials**

The term nanocomposite is used if one of the structural units, either the organic or the inorganic, is in a defined size range of 1–100 nm. Large molecular building blocks for hybrid materials, such as large inorganic clusters, may be of the nanometer length scale. The term nanocomposites is generally used if discrete structural units in the respective size regime are used and the term hybrid materials is more often used if the inorganic units are formed in situ by molecular precursors, for example applying sol–gel reactions. Examples of discrete inorganic units for nanocomposites are nanoparticles, nanorods and carbon nanotubes.

Advantages of hybrid materials over traditional composites:

- Inorganic clusters or nanoparticles with specific optical, electronic or magnetic properties can be incorporated in organic polymer matrices.
- Contrary to pure solid state inorganic materials that often require a high temperature treatment for their processing, hybrid materials show a more polymer-like handling, either because of their large organic content or because of the formation of crosslinked inorganic networks from small molecular precursors just like in polymerization reactions.
- Light scattering in homogeneous hybrid material can be avoided and therefore optical transparency of the resulting hybrid materials and nanocomposites can be achieved.

**Future of Nanocomposites**

By 2009, it is estimated that the flexible and rigid packaging industry will use five million pounds of nanocomposites materials in the beverage and food industry. By 2011, consumption is estimated to be 100 million pounds. Beer is expected
to be the biggest consumer by 2006 with 3 million pounds of nanocomposites until carbonated soft drinks bottles are projected to surpass that to use 50 million pounds of nanocomposites by 2011. Polymer nanocomposites are the future for the global packaging industry. Once production and materials cost are less, companies will be using this technology to increase their product’s stability and survivability through the supply chain to deliver higher quality to their customers while saving money. The advantages that nanocomposites offer far outweigh the costs and concerns and with time the technology will be further refined and processes more developed. Research continues into other types of nanofillers (i.e., carbon nanotubes), allowing new nanocomposite structures with different improved properties that will further advance nanocomposite use in many diverse packaging applications.

References

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