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A REVIEW ARTICLE ON NANO-COMPOSITES

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ABSTRACT: Nanocomposite is a multiphase solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm) or structures having nano-scale repeat distances between the different phases that make up the material.^{[1][2]}

The idea behind Nanocomposites is to use building blocks with dimensions in nanometre range to design and create new materials with unprecedented flexibility and improvement in their physical properties.

In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nano-dimensional phase(s) differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Size limits for these effects have been proposed.^[3]

KEYWORDS-nanocomposite, nanometer, porous, copolymers, physical, catalytic

I. INTRODUCTION

1. <5 nm for catalytic activity
2. <20 nm for making a hard magnetic material soft
3. <50 nm for refractive index changes
4. <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement

Nanocomposites are found in nature, for example in the structure of the abalone shell and bone. The use of nanoparticle-rich materials long predates the understanding of the physical and chemical nature of these materials. Jose-Yacaman et al.^[4] investigated the origin of the depth of colour and the resistance to acids and bio-corrosion of Maya blue paint, attributing it to a nanoparticle mechanism. From the mid-1950s nanoscale organo-clays have been used to control flow of polymer solutions (e.g. as paint viscosifiers) or the constitution of gels (e.g. as a thickening substance in cosmetics, keeping the preparations in homogeneous form). By the 1970s polymer/clay composites were the topic of textbooks,^{[5][6]} although the term "nanocomposites" was not in common use.

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).^[7] 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. Ajayan et al.^[8] note that with polymer nanocomposites, properties related to local chemistry, degree of thermoset cure, polymer chain mobility, polymer chain conformation, degree of polymer chain ordering or crystallinity can all vary significantly and continuously from the interface with the reinforcement into the bulk of the matrix.

This large amount of reinforcement surface area means that a relatively small amount of nanoscale reinforcement can have an observable effect on the macroscale properties of the composite. For example, adding carbon nanotubes improves the electrical and thermal conductivity. Other kinds of nanoparticulates may result in enhanced optical properties, dielectric properties, heat resistance or mechanical properties such as stiffness, strength and resistance to wear and damage. In general, the nano reinforcement is dispersed into the matrix during processing. The percentage by weight (called mass fraction) of the nanoparticulates introduced can remain very low (on the order of 0.5% to 5%) due to the low filler percolation threshold, especially for the most commonly used non-spherical, high aspect ratio fillers (e.g. nanometer-thin platelets, such as clays, or nanometer-diameter cylinders,

such as carbon nanotubes). The orientation and arrangement of asymmetric nanoparticles, thermal property mismatch at the interface, interface density per unit volume of nanocomposite, and polydispersity of nanoparticles significantly affect the effective thermal conductivity of nanocomposites.^[9]

Ceramic-matrix nanocomposites

Ceramic matrix composites (CMCs) consist of ceramic fibers embedded in a ceramic matrix. The matrix and fibers can consist of any ceramic material, including carbon and carbon fibers. The ceramic occupying most of the volume is often from the group of oxides, such as nitrides, borides, silicides, whereas the second component is often a metal. Ideally both components are finely dispersed in each other in order to elicit particular optical, electrical and magnetic properties^[10] as well as tribological, corrosion-resistance and other protective properties.^[11]

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 lose its metallic character. This is not an easily obeyed constraint because the preparation of the ceramic component generally requires high process temperatures. The safest measure thus is to carefully choose immiscible metal and ceramic phases. A good example of 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'.^[12]

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 underlying 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^[13] that showed a high mechanical hardness, small coefficients of friction and a high resistance to corrosion.

Metal-matrix nanocomposites

Metal matrix nanocomposites can also be defined as reinforced metal matrix composites. This type of composites can be classified as continuous and non-continuous reinforced materials. One of the more important nanocomposites is Carbon nanotube metal matrix composites, which is an emerging new material that is being developed to take advantage of the high tensile strength and electrical conductivity of carbon nanotube materials.^[14] 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.^[15]

A recent study, comparing the mechanical properties (Young's modulus, compressive yield strength, flexural modulus and flexural yield strength) of single- and multi-walled reinforced polymeric (polypropylene fumarate—PPF) nanocomposites to tungsten disulfide nanotubes reinforced PPF nanocomposites suggest that tungsten disulfide nanotubes reinforced PPF nanocomposites possess significantly higher mechanical properties and tungsten disulfide nanotubes are better reinforcing agents than carbon nanotubes.^[16] Increases in the mechanical properties can be attributed to a uniform dispersion of inorganic nanotubes in the polymer matrix (compared to carbon nanotubes that exist as micron sized aggregates) and increased crosslinking density of the polymer in the presence of tungsten disulfide nanotubes (increase in crosslinking density leads to an increase in the mechanical properties). These results suggest that inorganic nanomaterials, in general, may be better reinforcing agents compared to carbon nanotubes.

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 aluminum powder, can form superthermite materials.^{[17][18][19][20]}

Polymer-matrix nanocomposites

In the simplest case, appropriately adding nanoparticulates to a polymer matrix can enhance its performance, often dramatically, by simply capitalizing on the nature and properties of the nanoscale filler^[21] (these materials are better described by the term nanofilled polymer composites^[21]). This strategy is particularly effective in yielding high performance composites, when uniform dispersion of the filler is achieved and the properties of the nanoscale filler are

substantially different or better than those of the matrix. The uniformity of the dispersion in all nanocomposites is counteracted by thermodynamically driven phase separation. Clustering of nanoscale fillers produces aggregates that serve as structural defects and result in failure. Layer-by-layer (LbL) assembly when nanometer scale layers of nanoparticulates and a polymers are added one by one. LbL composites display performance parameters 10-1000 times better than the traditional nanocomposites made by extrusion or batch-mixing.

Nanoparticles such as graphene,^[22] carbon nanotubes,^[23] molybdenum disulfide and tungsten disulfide are being used as reinforcing agents to fabricate mechanically strong biodegradable polymeric nanocomposites for bone tissue engineering applications. The addition of these nanoparticles in the polymer matrix at low concentrations (~0.2 weight %) cause significant improvements in the compressive and flexural mechanical properties of polymeric nanocomposites.^{[24][25][26]} Potentially, these nanocomposites may be used as a novel, mechanically strong, light weight composite as bone implants. The results suggest 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 than carbon based nanomaterials. In addition to mechanical properties, polymer nanocomposites based on carbon nanotubes or graphene have been used to enhance a wide range of properties, giving rise to functional materials for a wide range of high added value applications in fields such as energy conversion and storage, sensing and biomedical tissue engineering.^[27] For example, multi-walled carbon nanotubes based polymer nanocomposites have been used for the enhancement of the electrical conductivity.^[28]

Nanoscale dispersion of filler or controlled nanostructures in the composite can introduce new physical properties and novel behaviors that are absent in the unfilled matrices. This effectively changes the nature of the original matrix^[21] (such composite materials can be better described by the term genuine nanocomposites or hybrids^[21]). Some examples of such new properties are fire resistance or flame retardancy,^[29] and accelerated biodegradability.

A range of polymeric nanocomposites are used for biomedical applications such as tissue engineering, drug delivery, cellular therapies.^{[30][31]} Due to unique interactions between polymer and nanoparticles, a range of property combinations can be engineered to mimic native tissue structure and properties. A range of natural and synthetic polymers are used to design polymeric nanocomposites for biomedical applications including starch, cellulose, alginate, chitosan, collagen, gelatin, and fibrin, poly(vinyl alcohol) (PVA), poly(ethylene glycol) (PEG), poly(caprolactone) (PCL), poly(lactic-co-glycolic acid) (PLGA), and poly(glycerol sebacate) (PGS). A range of nanoparticles including ceramic, polymeric, metal oxide and carbon-based nanomaterials are incorporated within polymeric network to obtain desired property combinations.^[32]

II. DISCUSSION

Magnetic nanocomposites

Nanocomposites that can respond to an external stimulus are of increased interest due to the fact that, because of the large amount of interaction between the phase interfaces, the stimulus response can have a larger effect on the composite as a whole. The external stimulus can take many forms, such as a magnetic, electrical, or mechanical field. Specifically, magnetic nanocomposites are useful for use in these applications due to the nature of magnetic material's ability to respond both to electrical and magnetic stimuli. The penetration depth of a magnetic field is also high, leading to an increased area that the nanocomposite is affected by and therefore an increased response. In order to respond to a magnetic field, a matrix can be easily loaded with nanoparticles or nanorods. The different morphologies for magnetic nanocomposite materials are vast, including matrix dispersed nanoparticles, core-shell nanoparticles, colloidal crystals, macroscale spheres, or Janus-type nanostructures.^{[33][34]}

Magnetic nanocomposites can be utilized in a vast number of applications, including catalytic, medical, and technical. For example, palladium is a common transition metal used in catalysis reactions. Magnetic nanoparticle-supported palladium complexes can be used in catalysis to increase the efficiency of the palladium in the reaction.^[35]

Magnetic nanocomposites can also be utilized in the medical field, with magnetic nanorods embedded in a polymer matrix can aid in more precise drug delivery and release. Finally, magnetic nanocomposites can be used in high frequency/high-temperature applications. For example, multi-layer structures can be fabricated for use in electronic applications. An electrodeposited Fe/Fe oxide multi-layered sample can be an example of this application of magnetic nanocomposites.^[36]

In applications such as power micro-inductors where high magnetic permeability is desired at high operating frequencies.^[37] The traditional micro-fabricated magnetic core materials see both decrease in permeability and high

losses at high operating frequency.^[38] In this case, magnetic nano composites have great potential for improving the efficiency of power electronic devices by providing relatively high permeability and low losses. For example, As Iron oxide nano particles embedded in Ni matrix enables us to mitigate those losses at high frequency.^[39] The high resistive iron oxide nanoparticles helps to reduce the eddy current losses where as the Ni metal helps in attaining high permeability. DC magnetic properties such as Saturation magnetization lies between each of its constituent parts indicating that the physical properties of the materials can be altered by creating these nanocomposites.

Heat resistant nanocomposites

In the recent years nanocomposites have been designed to withstand high temperatures by the addition of Carbon Dots (CDs) in the polymer matrix. Such nanocomposites can be utilized in environments wherein high temperature resistance is a prime criterion.^[40]

III. RESULTS

Polymer nanocomposites (PNC) consist of a polymer or copolymer having nanoparticles or nanofillers dispersed in the polymer matrix. These may be of different shape (e.g., platelets, fibers, spheroids), but at least one dimension must be in the range of 1–50 nm.^[1] These PNC's belong to the category of multi-phase systems (MPS, viz. blends, composites, and foams) that consume nearly 95% of plastics production. These systems require controlled mixing/compounding, stabilization of the achieved dispersion, orientation of the dispersed phase, and the compounding strategies for all MPS, including PNC, are similar. Alternatively, polymer can be infiltrated into 1D, 2D, 3D preform creating high content polymer nanocomposites.^[2]

Polymer nanoscience is the study and application of nanoscience to polymer-nanoparticle matrices, where nanoparticles are those with at least one dimension of less than 100 nm.

The transition from micro- to nano-particles lead to change in its physical as well as chemical properties. Two of the major factors in this are the increase in the ratio of the surface area to volume, and the size of the particle. The increase in surface area-to-volume ratio, which increases as the particles get smaller, leads to an increasing dominance of the behavior of atoms on the surface area of particle over that of those interior of the particle. This affects the properties of the particles when they are reacting with other particles. Because of the higher surface area of the nano-particles, the interaction with the other particles within the mixture is more and this increases the strength, heat resistance, etc. and many factors do change for the mixture.

An example of a nanopolymer is silicon nanospheres which show quite different characteristics; their size is 40–100 nm and they are much harder than silicon, their hardness being between that of sapphire and diamond.

Bio-hybrid polymer nanofibers

Many technical applications of biological objects like proteins, viruses or bacteria such as chromatography, optical information technology, sensorics, catalysis and drug delivery require their immobilization. Carbon nanotubes, gold particles and synthetic polymers are used for this purpose. This immobilization has been achieved predominantly by adsorption or by chemical binding and to a lesser extent by incorporating these objects as guests in host matrices. In the guest host systems, an ideal method for the immobilization of biological objects and their integration into hierarchical architectures should be structured on a nanoscale to facilitate the interactions of biological nano-objects with their environment. Due to the large number of natural or synthetic polymers available and the advanced techniques developed to process such systems to nanofibres, rods, tubes etc. make polymers a good platform for the immobilization of biological objects.^[3]

Bio-hybrid nanofibres by electrospinning

Polymer fibers are, in general, produced on a technical scale by extrusion, i.e., a polymer melt or a polymer solution is pumped through cylindrical dies and spun/drawn by a take-up device. The resulting fibers have diameters typically on the 10- μ m scale or above. To come down in diameter into the range of several hundreds of nanometers or even down to a few nanometers, Electrospinning is today still the leading polymer processing technique available. A strong electric field of the order of 10³ V/cm is applied to the polymer solution droplets emerging from a cylindrical die. The electric charges, which are accumulated on the surface of the droplet, cause droplet deformation along the field direction, even though the surface tension counteracts droplet evolution. In supercritical electric fields, the field strength overbears the surface tension and a fluid jet emanates from the droplet tip. The jet is accelerated towards the counter electrode. During this transport phase, the jet is subjected to strong electrically driven circular bending motions that cause a strong

elongation and thinning of the jet, a solvent evaporation until, finally, the solid nanofibre is deposited on the counter electrode.

Bio-hybrid polymer nanotubes by wetting

Electro spinning, co-electrospinning, and the template methods based on nanofibres yield nano-objects which are, in principle, infinitively long. For a broad range of applications including catalysis, tissue engineering, and surface modification of implants this infinite length is an advantage. But in some applications like inhalation therapy or systemic drug delivery, a well-defined length is required. The template method to be described in the following has the advantage such that it allows the preparation of nanotubes and nanorods with very high precision. The method is based on the use of well defined porous templates, such as porous aluminum or silicon.

The basic concept of this method is to exploit wetting processes. A polymer melt or solution is brought into contact with the pores located in materials characterized by high energy surfaces such as aluminum or silicon. Wetting sets in and covers the walls of the pores with a thin film with a thickness of the order of a few tens of nanometers.

Gravity does not play a role, as it is obvious from the fact that wetting takes place independent of the orientation of the pores relative to the direction of gravity. The exact process is still not understood theoretically in detail but its known from experiments that low molar mass systems tend to fill the pores completely, whereas polymers of sufficient chain length just cover the walls. This process happens typically within a minute for temperatures about 50 K above the melting temperature or glass transition temperature, even for highly viscous polymers, such as, for instance, polytetrafluoroethylene, and this holds even for pores with an aspect ratio as large as 10,000. The complete filling, on the other hand, takes days. To obtain nanotubes, the polymer/template system is cooled down to room temperature or the solvent is evaporated, yielding pores covered with solid layers. The resulting tubes can be removed by mechanical forces for tubes up to 10 μm in length, i.e., by just drawing them out from the pores or by selectively dissolving the template. The diameter of the nanotubes, the distribution of the diameter, the homogeneity along the tubes, and the lengths can be controlled.

Applications

The nanofibres, nanocomposites, hollow nanofibres, core-shell nanofibres, and nanorods or nanotubes produced have a great potential for a broad range of applications including homogeneous and heterogeneous catalysis, dental restorative materials,^{[4][5]} sensorics, filter applications, and optoelectronics. Here we will just consider a limited set of applications related to life science.

Tissue engineering

This is mainly concerned with the replacement of tissues which have been destroyed by sickness or accidents or other artificial means. The examples are skin, bone, cartilage, blood vessels and may be even organs. This technique involves providing a scaffold on which cells are added and the scaffold should provide favorable conditions for the growth of the same. Nanofibres have been found to provide very good conditions for the growth of such cells, one of the reasons being that fibrillar structures can be found on many tissues which allow the cells to attach strongly to the fibers and grow along them as shown.

Nanoparticles such as graphene,^[6] carbon nanotubes, molybdenum disulfide and tungsten disulfide are being used as reinforcing agents to fabricate mechanically strong biodegradable polymeric nanocomposites for bone tissue engineering applications. The addition of these nanoparticles in the polymer matrix at low concentrations (~0.2 weight %) leads to significant improvements in the compressive and flexural mechanical properties of polymeric nanocomposites.^{[7][8]} Potentially, these nanocomposites may be used to create novel, mechanically strong, light weight composite bone implants. The results suggest 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 than carbon based nanomaterials.

Delivery from compartmented nanotubes

Nano tubes are also used for carrying drugs in general therapy and in tumor therapy in particular. The role of them is to protect the drugs from destruction in blood stream, to control the delivery with a well-defined release kinetics, and in ideal cases, to provide vector-targeting properties or release mechanism by external or internal stimuli.

Rod or tube-like, rather than nearly spherical, nanocarriers may offer additional advantages in terms of drug delivery systems. Such drug carrier particles possess additional choice of the axial ratio, the curvature, and the “all-sweeping”

hydrodynamic-related rotation, and they can be modified chemically at the inner surface, the outer surface, and at the end planes in a very selective way. Nanotubes prepared with a responsive polymer attached to the tube opening allow the control of access to and release from the tube. Furthermore, nanotubes can also be prepared showing a gradient in its chemical composition along the length of the tube.

Compartmented drug release systems were prepared based on nanotubes or nanofibres. Nanotubes and nanofibres, for instance, which contained fluorescent albumin with dog-fluorescein isothiocyanate were prepared as a model drug, as well as super paramagnetic nanoparticles composed of iron oxide or nickel ferrite. The presence of the magnetic nanoparticles allowed, first of all, the guiding of the nanotubes to specific locations in the body by external magnetic fields. Super paramagnetic particles are known to display strong interactions with external magnetic fields leading to large saturation magnetizations. In addition, by using periodically varying magnetic fields, the nanoparticles were heated up to provide, thus, a trigger for drug release. The presence of the model drug was established by fluorescence spectroscopy and the same holds for the analysis of the model drug released from the nanotubes.

Immobilization of proteins

Core shell fibers of nano particles with fluid cores and solid shells can be used to entrap biological objects such as proteins, viruses or bacteria in conditions which do not affect their functions. This effect can be used among others for biosensor applications. For example, Green Fluorescent Protein is immobilized in nanostructured fibres providing large surface areas and short distances for the analyte to approach the sensor protein.

With respect to using such fibers for sensor applications fluorescence of the core shell fibers was found to decay rapidly as the fibers were immersed into a solution containing urea: urea permeates through the wall into the core where it causes denaturation of the GFP. This simple experiment reveals that core-shell fibers are promising objects for preparing biosensors based on biological objects.

Polymer nanostructured fibers, core-shell fibers, hollow fibers, and nanorods and nanotubes provide a platform for a broad range of applications both in material science as well as in life science. Biological objects of different complexity and synthetic objects carrying specific functions can be incorporated into such nanostructured polymer systems while keeping their specific functions vital. Biosensors, tissue engineering, drug delivery, or enzymatic catalysis is just a few of the possible examples. The incorporation of viruses and bacteria all the way up to microorganism should not really pose a problem and the applications coming from such biohybrid systems should be tremendous.^[9]

Engineering applications

Polymer nanocomposites for automotive tire industry

Polymer nanocomposites are important for the automotive tire industry due to the possibility of achieving a higher fuel efficiency by designing polymer nanocomposites with suitable properties.^[10]

The most common type of filler particles utilized by the tire industry had traditionally been Carbon black (Cb), produced from the incomplete combustion of coal tar and ethylene.^[11] The main reason is that the addition of Cb to rubbers enables the manufacturing of tires of a smaller rolling resistance which accounts for about 4% of the worldwide CO₂ emissions from fossil fuels.^[12] A decrease in the rolling resistance of the car tires produced worldwide is anticipated to decrease the overall fuel consumption of cars due to the fact that a vehicle with tires of a smaller rolling resistance requires less energy to thrust forward. However, a smaller rolling resistance also leads to a lower wet grip performance, which poses concerns of the passenger's safety.

The problem can be partially solved by replacing Cb with silica, because it enables the production of "green" tires that display both improved wet grip properties as well as a smaller rolling resistance.^[13]

The main difference in the relevant properties of Cb and silica is that Cb is hydrophobic (as are the polymers used in the manufacturing of car ties) whereas silica is hydrophilic. So in order to increase the compatibility among the silica fillers and the polymer matrix, the silica is usually functionalized with coupling agents, which gives the possibility of tuning the filler-polymer interactions and thus producing nanocomposites of specific properties.^[14]

Overall, the main unresolved issue on the mechanical properties of filled rubbers is the elucidation of the exact mechanism of their mechanical reinforcement and of the so-called Payne effect; and owing to a lack of suitable theoretical and experimental approaches, both of them are still poorly understood.

Polymer nanocomposites for high temperature applications

Polymer nanocomposites aided with carbon quantum dots have been found to show remarkable heat resistance.^[15] These nanocomposites can be used in environments where heat resistance is a requirement.

Size and pressure effects on nanopolymers

The size- and pressure- dependent glass transition temperatures of free-standing films or supported films having weak interactions with substrates decreases with decreasing of pressure and size. However, the glass transition temperature of supported films having strong interaction with substrates increases of pressure and the decrease of size. Different models like two layer model, three layer model, $T_g(D, 0) \propto 1/D$ and some more models relating specific heat, density and thermal expansion are used to obtain the experimental results on nanopolymers and even some observations like freezing of films due to memory effects in the visco-elastic eigenmodels of the films, and finite effects of the small molecule glass are observed. To describe $T_g(D, 0)$ function of polymers more generally, a simple and unified model recently is provided based on the size-dependent melting temperature of crystals and Lindemann's criterion

$$T_g(D, 0) / T_g(\infty, 0) \propto \sigma_g^2(\infty, 0) / \sigma_g^2(D, 0)$$

where σ_g is the root of mean squared displacement of surface and interior molecules of glasses at $T_g(D, 0)$, $\alpha = \sigma_s^2(D, 0) / \sigma_v^2(D, 0)$ with subscripts s and v denoting surface and volume, respectively. For a nanoparticle, D has a usual meaning of diameter, for a nanowire, D is taken as its diameter, and for a thin film, D denotes its thickness. D_0 denotes a critical diameter at which all molecules of a low-dimensional glass are located on its surface.^[16]

Devices that use the properties of low-dimensional objects, such as nanoparticles, are promising due to the possibility of tailoring a number of mechanical, electrophysical, optical and magnetic properties granting some degree of control over the size of nanoparticles during synthesis. In the case of polymer nanocomposites we can use the properties of disordered systems.

Here recent developments in the field of polymer nano-composites and some of their applications have been reviewed. Though there is much use in this field, there are many limitations also. For example, in the release of drugs using nanofibres, cannot be controlled independently and a burst release is usually the case, whereas a more linear release is required. Let us now consider future aspects in this field.

There is a possibility of building ordered arrays of nanoparticles in the polymer matrix. A number of possibilities also exist to manufacture the nanocomposite circuit boards. An even more attractive method exists to use polymer nanocomposites for neural networks applications. Another promising area of development is optoelectronics and optical computing. The single domain nature and super paramagnetic behavior of nanoparticles containing ferromagnetic metals could be possibly used for magneto-optical storage media manufacturing.

IV. CONCLUSION

Nanocomposite hydrogels (NC gels) are nanomaterial-filled, hydrated, polymeric networks that exhibit higher elasticity and strength relative to traditionally made hydrogels. A range of natural and synthetic polymers are used to design nanocomposite network. By controlling the interactions between nanoparticles and polymer chains, a range of physical, chemical, and biological properties can be engineered.^[1] The combination of organic (polymer) and inorganic (clay) structure gives these hydrogels improved physical, chemical, electrical, biological, and swelling/de-swelling properties that cannot be achieved by either material alone.^[2] Inspired by flexible biological tissues, researchers incorporate carbon-based, polymeric, ceramic and/or metallic nanomaterials to give these hydrogels superior characteristics like optical properties and stimulus-sensitivity which can potentially be very helpful to medical (especially drug delivery and stem cell engineering) and mechanical fields.^[2]

Nanocomposite hydrogels are not to be confused with nanogel, a nanoparticle composed of a hydrogel.

Synthesis

The synthesis of nanocomposite hydrogels is a process that requires specific material and method. These polymers need to be made up of equally spaced out, 30 nm in diameter, clay platelets that can swell and exfoliate in the presence of water. The platelets act as cross-links to modify molecular functions to enable the hydrogels to have superior elasticity and toughness that resembles closely that of biological tissue.^[3] Using clay platelets that do not swell or exfoliate in water, using an organic cross-linker such as N,N-methylenebisacrylamide(BIS), mixing of clay and BIS, or preparing nanocomposite hydrogels in a method other than cross-link, will be unsuccessful.^[4]



Despite all the specifications, the process of synthesizing nanocomposite hydrogels is simple and because of the flexible nature of the material, these hydrogels can be easily made to come in different shapes such as huge blocks, sheets, thin films, rods, hollow tubes, spheres, bellows and uneven sheets.^[5]

Properties

Mechanical

Nanocomposite hydrogels are tough, and can withstand stretching, bending, knotting, crushing, and other modifications.

Tensile

Tensile testings were performed on nanocomposite hydrogels to measure the stress and strain it experiences when elongated under room temperature. The results show that this material can be stretched up to 1000% of its original length.^[6]

Compression

Hysteresis is used to measure the compression properties of nanocomposite hydrogels, which shows that this material can withstand around 90% compression. This data shows that nanocomposite hydrogels exhibit superior strength relative to conventionally-made hydrogels, which would have broken down under less compression.

Swelling and stimulus sensitivity

Swelling, de-swelling

The porous network of clay particles enable nanocomposite hydrogels to swell in the presence of water. Swelling (and de-swelling) distinguishes NC gels from conventionally-made hydrogels (OR gels) as it is a property that OR gels lack. The swelling property of NC gels allows them to collect the surrounding aqueous solution instead of being dissolved by it, which helps make them good candidates for drug delivery carriers.^[7]

Stimulus sensitivity

Nanocomposite hydrogels are observed to be temperature sensitive and will change temperature when their surrounding is altered.^[8] Inorganic salts, when absorbed, will result in changing the hydrogels to a lower temperature whereas cationic surfactant will shift the temperature the other way. The temperature of these hydrogels are around 40 degrees Celsius, making it a possible candidate for use as biomaterial.^[9] The stimulus-sensitivity of hydrogels allow for a responsive release system where the hydrogels can be designed to deliver the drug in response to changes in condition of the body.

Types

Via carbon-based nanomaterials

Nanocomposite hydrogels that are enforced with carbon-based nanomaterials are mechanically tough and electrically conductive, which make them suitable for use in biomedicine, tissue engineering, drug delivery, biosensing, etc. The electrical conducting property of these hydrogels allow them to mimic the characteristic of nerve, muscle, and cardiac tissues. However, even though these nanocomposite hydrogels demonstrate some functions of human tissue in lab environments, more research is needed to ensure their utility as tissue replacement.^[10]

Via polymeric nanoparticles

Nanocomposite hydrogels incorporated with polymeric nanoparticles are tailored for drug delivery and tissue engineering. The addition of polymeric nanoparticles gives these hydrogels a reinforced polymeric network that is more stiff and has the ability to enclose hydrophilic and hydrophobic drugs along with genes and proteins. The high stress-absorbing property makes them a potential candidate for cartilage tissue engineering.^[10]

Via inorganic nanoparticles

Most inorganic nanoparticles used for nanocomposite hydrogels are already present in and necessary for the body, and thus present no negative impacts on the body. Some of them, like calcium and silicon, help with preventing bone loss and skeletal development. Others, like nanoclays, improve the structural formation and characteristics of hydrogels where they acquire self-healing properties, flame retardant structures, elasticity, super gas-barrier membrane, oil-

repellence, etc. The unique properties obtained by incorporating nanocomposite hydrogels with inorganic nanoparticles will let researchers work on improving bone-related tissue engineering.^[10]

Via metal and metal-oxide nanoparticles

The electrical and thermal conductivity and magnetic property of metals enhance the electrical conductivity and antibacterial property of nanocomposite hydrogels when incorporated. The electrical conducting property is necessary for the hydrogels to start forming functional tissues and be used as imaging agents, drug delivery systems, conductive scaffolds, switchable electronics, actuators, and sensors.

Applications

Researchers have been looking for a material that can mimic tissue properties to make the tissue engineering process more effective and less invasive to the human body. The porous, interconnecting network of nanocomposite hydrogels, created through cross-link, enable wastes and nutrients to easily enter and exit the structure, and their elastomeric properties let them acquire the desired anatomical shape without needing prior molding. The porous structure of this material would also make the process of drug delivery easier where the pharmaceutical compounds present in the hydrogel can easily escape and be absorbed by the body. Aside from that, researchers are also looking into incorporating nanocomposite hydrogels with silver nanoparticles for antibacterial applications and microorganism elimination in medical and food packing and water treatment. Hydrogels infused with nanoparticles have a number of biological applications, including: tissue engineering, chemical and biological sensing and drug and gene delivery.

Tissue engineering

As tissue replacements, nanocomposite hydrogels need to interact with cells and form functional tissues. With the incorporated nanoparticles and nanomaterials, these hydrogels can mimic the physical, chemical, electrical, and biological properties of most native tissue. Each type of nanocomposite hydrogels has its own unique properties that let it mimic certain types of animal tissue.

Drug delivery

The emergence of nanocomposite hydrogels allow for more site-specific and time-controlled delivery of drugs of different sizes at improved safety and specificity. Depending on the method of inserting drugs into the material, for example, dissolved, encased, or attached, the drug carrier will be named differently: nanoparticles, nanospheres (where the drug is evenly dispersed throughout the polymeric network), or nanocapsules (where the drug is surrounded by a polymer shell structure).^[7] The elastomeric nature of this material allows the hydrogels to obtain the shape of the targeted site and thus the hydrogels can be manufactured identically and used on all patients.^[11]

Hydrogels are controlled drug delivery agents that can be engineered to have desired properties.^[12] Specifically, hydrogels can be designed to release drugs or other agents in response to physical characteristics of the environment like temperature and pH.^[12] The responsiveness of hydrogels is a result of their molecular structure and polymer networks.^[12]

Hydrogel nanoparticles have a promising future in the drug delivery field. Ideally, drug delivery systems should, "...maximize the efficacy and the safety of the therapeutic agent, delivering an appropriate amount at a suitable rate and to the most appropriate site in the body".^[13] Nanotechnology incorporated within hydrogels has the potential to meet all the requirements of an ideal drug delivery system. Hydrogels have been studied with a variety of nanocomposites including: clay, gold, silver, iron oxide, carbon nanotubes, hydroxyapatite, and tricalcium phosphate.^[13]

Nanoparticles, largely due to their size related physical properties, are highly useful as drug delivery agents. They can overcome physiological barriers and reach specific targets.^[14] Nanoparticles' size, surface charge and properties enable them to penetrate biological barriers that most other drug carriers cannot.^[14] To become even more specified, nanoparticles can be coated with targeting ligands.^[14] The ability of nanoparticles to deliver drugs to specific targets suggests the potential to limit systemic side-effects and immune responses.^[15]

The ability of nanoparticles to carry and release drugs is also largely dependent on characteristics which result from the small size and unique surface area to volume ratio of nanoparticles. Nanoparticles can generally carry drugs in two ways: drugs can either be bound to the outside of the nanoparticles or packed within the polymeric matrix of the nanoparticles.^[14] Smaller nanoparticles have higher surface area ratios and can thus bind a high quantity of drug, while larger nanoparticles can encapsulate more of the drug within its core.^[15] The best method of drug loading is dependent

on the structures of the drug to be bound. Also, drug loading can occur as the nanoparticles are produced, or the drugs can be added to pre-existing nanoparticles.^[14] The release of drugs, depends largely on the size of the nanoparticle carrying it. Because nanoparticles can be bound to the surface of nanoparticles, which is large relative to the volume of the particles, drugs can be released quickly. In contrast, drugs that are loaded within nanoparticles are released more slowly.^[14]

Antibacterial applications

Silver nanoparticles are inserted into the 3D polymeric networks of nanocomposite hydrogels for applications in antibacterial activity and improvement in electrical conductance. The presence of silver ions either stop the respiratory enzyme from transferring electrons to oxygen molecules during respiration or prevent proteins from reacting with thiol groups (-SH) on bacteria membrane, both result in the death of bacteria and microorganism without damaging mammal cells.^[16] The size of these silver nanoparticles need to be small enough to pass through the cell membrane and thus further research is required to manufacture them into appropriate sizes.

Concerns

Some concerns relating to hydrogels infused with nanoparticles are the chances of either bursting, or of incomplete release of drugs.^[13] Although hydrogels infused with nanoparticles are speculated to be quite promising methods of drug, protein, peptide, oligosaccharide, vaccine, and nucleic acid delivery, more studies regarding nanotoxicology and safety are required before clinical applications can be pursued.^[14] Further, to avoid accumulation, biodegradable gels and nanoparticles are highly desirable.^[14]

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