

Clay/nanocomposite hydrogels: In review

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Abstract: The development of advanced materials those are stronger, more rigid, lighter, hotter and self-renewable than existing materials has been the rising point of many research studies conducted in recent years. Within this scope, the interest to production of nanostructured materials is received considerable attention worldwide due to their potential positive contribution to wide variety of technological areas such as electronics, catalysis, adsorbents, ceramics, magnetic data storage, structural components etc. In these efforts polymer nanocomposites as the form of hydrogels, reinforced with well-dispersed layered silicate, typically montmorillonite can be given as a one of the promising composite material. However, long-standing problems for polymer-clay nanocomposites include actual exfoliation of clay particles in discrete layers, uniform distribution of clay layers throughout the polymer, and randomness of clay sequences. For the exfoliation of clay particles, although the chemical modification of clay minerals in aqueous media is the well-known and more general way applied by researchers, the physical pathway method performed by high-energy ball mills is also gaining increasing attention as an alternative pretreatment way. Grinding of crushed materials is one of the key processes in the mineral and cement industry, but the increased concern on the preparation of fine-grained powders (nano powders) or the manufacture of composites with desirable properties, especially performed with use of high-energy ball mills, has led to significantly widen the usage field of grinding. Undoubtedly, the main reason for these efforts is to improve the performance of existing materials. In this paper the fundamental concepts, classification, physical and chemical characteristics and the production methods of clay/polymer nanocomposites was briefly reviewed base on the composite hydrogel. Particular attention was paid to the pre-treatment (exfoliation) of clays with high-energy ball mills, which is increasingly being accepted as an alternative method to eliminate the negative effects of chemical treatment in some composite forms.

Keywords: hydrogel, clay, composite hydrogel, exfoliation, high energy ball mills

1. Introduction

In last decades polymeric materials have recognized as one of the engineering materials with the greatest increase in applications due to their high strength/density ratio, low weight, anti-corrosion properties, ease of processing and relatively low energy consumption required in manufacturing. Especially than after the introduction of synthetic polymers, these materials have gradually started to replace with traditional raw materials in every aspect of human life. On the other hand, some non-rewarding properties such as lack of adequate mechanical strength and low thermal stability of pristine forms greatly restrict their use in applications. One methodology to overcome these limitation is modify polymer properties by impregnating and dispersing inorganic fillers, such as carbon black, metallic or silicate (clays) particles, wood flour and calcium carbonate throughout the polymer host via blending or compounding to yield a polymer composite. Today, approximately, more than 95% of polymers are compounded with organic/inorganic additives in manufacturing to create composites (Alam et al., 2018; Kuśtrowski et al., 2018; Bee et al., 2018). However, these attempts are only partially successful, because of the composites have micron-size dispersion phases have lower mechanical properties

sometimes fall significantly short of the needs of many applications that require a nano-size dispersion phase.

In composite polymer synthesis, the type of the polymer influences the efficiency of the product, nevertheless, the nature, properties, dimensions, content and the uniform dispersion of the reinforcement components within the polymer matrix are also main features that determine the final properties of modified polymers (composites). The efficiency of improvements strongly depends on the interfacial interactions between matrix and dispersed phase, the properties of the filler/additives, and the adhesion between matrix and additives. Within these, the aspect ratio of the filler is important and crucial for developing of many properties in composite such as electrical, mechanical and thermal. The incorporation of carbon nanotubes and nanofibers can be given as efficient additives, but platelet clays have also gained high acceptance as low-cost candidate materials. Compared with micro-size, the combination of nanoscale size and high aspect ratio with adequate dispersion of the additives in the polymer matrix leads to significant improvements in polymer properties at very low filler /additive amounts/volume fractions (Table 1). As a result of this lower usage, the macroscopic homogeneity and low density of the primary polymer maintains as well as its opacity in the final nanocomposite form.

Table 1. Comparison of composite and nanocomposite materials

Composites	Nano composites
Stiffness and strength	Mechanical properties (strength, bulk modulus, withstands limit, etc.)
Low coefficient of expansion	Hinders flame and reduce smoke generations
Resistance against fatigue	Permeability of gases, water, and solvents are reduced
Ease in manufacturing complex shapes	More surface appearance
Simple repair of damaged structures	Improved electrical conductivity
Resistance to corrosion	Increased chemical resistance
	Enhanced optical clarity as compared to conventionally filled polymers

One of the applications that have attracted attention in polymer composite structures consist of high aspect ratio reinforcement additives is the synthesis of inorganic clay incorporated hydrogels. It has been found as a preferred way to achieve the best mechanical structures, excellent optics, along with swelling and stimulus sensitive properties, simplicity and self-healability (Haraguchi, 2007, 2011; Chirani et al., 2016; Warren et al., 2017). However, long-standing problems for polymer-clay nanocomposites include actual exfoliation of clay particles in discrete layers, uniform distribution of clay layers throughout the polymer, and randomness of clay sequences. It is important to know that the physical mixture of polymer and layered silicate may not always form nanocomposites with desired properties. In this article, the basic concepts, classification, physical and chemical properties, production methods and exfoliation of clay additives before use are reviewed based on clay composite hydrogel. A special emphasis is also paid use of high energy ball milling to exfoliation of clay particles or intercalation of polymer during synthesis process as an effective alternative.

2. Hydrogel

Hydrogel can simply be described as a three-dimensional hydrophilic polymer material. As can be seen at Fig. 1, these can be classified under many consideration factors (Vasile et al, 2020) such as natural, synthetic or hybrid, depending on the source of the constituting polymers, preparation methods; network structure (as permanent (chemically crosslinked or irreversible), and non-permanent (physically crosslinked or reversible, hydrogen-bonded hydrogels); dimensions (macrogels, microgels, nanogels); sensitivity to stimuli (such as physical, chemical, and biochemical stimuli); charge of polymer network (nonionic, ionic, zwitterion, and amphoteric); physical aspect (micro-/nanoparticle, film, matrix, gel, etc.); configuration (amorphous and semicrystalline); composition (homopolymeric, multipolymeric or heteropolymeric, copolymeric, and interpenetrating polymer networks, hybrids, composites).

Around 1900, the term 'hydrogel' first appeared in the scientific literature when it was used to describe a colloidal gel of inorganic salts (Buwalda et al., 2014). Hydrogels as we know them today were

first reported in 1960 by Wichterle and Lim, cross-linked macromolecular networks swollen with water. In the two decades following this discovery, hydrogel researches have been focused mainly on relatively simple, chemically crosslinked synthetic polymer networks. In this period, polyacrylamide (PAM) was used as one of the most used hydrogel-forming polymers. Although it was initially used in industrial applications such as agricultural gels, has been involved in extensive research as a potential candidate in later years for early biomedical applications, particularly for the physical retention of cells and enzymes.

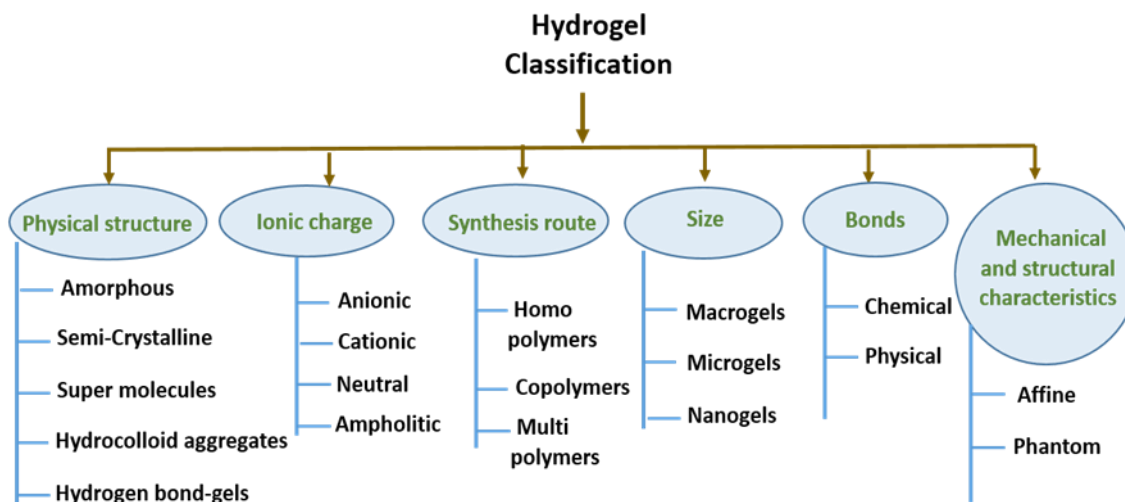


Fig. 1. Classification of hydrogels

Table 2. Polymers used for hydrogel preparations

Polymer Type	Hydrophilic	Hydrophobic
	Poly(ethylene glycol), PEG Poly(vinyl alcohol), PVA Poly(glutamic acid), PGA Poly(vinylpyrrolidone), PVP Polyacrilamide, PAM Polyethyleneimine, PEI	Poly(ϵ -caprolactone), PCL Poly(lactic acid), PLA Poly(lactic co-glycolic acid), PLGA Poly(propylene oxide), PPO Poly(sebacic acid), PSA Poly(aspartic acid), PASP

Today many different hydrophobic and hydrophilic polymers are formed in single and co-polymer forms are used for hydrogel preparation (Table 2), however, PAM gels still retain their importance as basic starting material. They have recently found widespread biomedical application as soft tissue fillers, augmentation materials and absorbent/adsorbent for environmental applications. Then, starting in the seventies, a different concept of hydrogels gained prominence: second-generation materials that can respond to specific stimuli, such as changes in temperature, pH, or the concentration of certain molecules in solution. These specific stimuli can be used to trigger similar specific events such as polymerization of the material, a drug delivery, or the formation of an in situ pore. Finally, third-generation hydrogels focused on the research and development of stereo complex materials. A detail of the progress of the hydrogels and applications can be found in the recent review papers released by (Buwalda et al., 2014; Bahram et al., 2016; Sharma et al., 2018; Bustamante-Torres et al., 2021).

As briefly summarized above, hydrogels are chains of natural/synthetic polymers linked together by cross-linkers to produce a hydrophilic material with the macromolecular structure of a gel. Hydrophilic groups in the structure, such as hydroxyl, carboxyl, and amide, allow it to swell in water and retain large amounts of water. They can swell to several times their dry weight and contain up to 99% water or biological fluid (Hernández et al, 2016). This is especially important for hydrogel absorption/adsorption applications. Moreover, chemical and physical cross-linking of individual polymer chains ensures that the hydrogel remains stable to a certain degree. The cross-linked polymer network is highly sensitive to stimuli such as solvent composition, solutes, pH, temperature, electric

field, and light. These properties have made hydrogels an attractive material in different fields ranging from environmental to biomedical applications in recent years. Desired crosslinking is accomplished primarily by covalent bonds (chemically) or non-covalent interactions such as ionizing radiation, entanglement, electrostatic and crystallite formation (physically). Among the various types of polymer hydrogels, although chemically crosslinking is widely used way for practical applications, such as soft contact lenses and superabsorbent due to the easy controllable of their network composition and the degree of crosslinking, they have several serious limitations because of their network structure, which consists of a random arrangement of a large number of chemical crosslinks. To overcome these limitations recently, remarkable improvements have been made to synthesis of the hydrogels by creating new types of network structures such as networks with sliding crosslinks, organic/inorganic networks created with nanoparticles (NC gels), interpenetrating networks (double-network gels), self-assembled networks (macromolecular microsphere composite gels), and networks with the same Mc (tetra-poly(ethylene glycol) (PEG) gels).

3. Nanoparticles and fabrication of nanocomposites hydrogel

3.1. Nano particles

Nanoparticles are of scientific interest as they act, as bridges between bulk materials and atomic or molecular structures. A bulk material has constant physical properties regardless of its size, but at the nanoscale, size-dependent properties are getting important. The interesting and unexpected properties of nanoparticles can be attributed to the large surface area, and this dominates the contributions made by the small bulk of the materials. For example, titanium dioxide impart a self-cleaning effect when it is nano sized, nanoparticles of zinc oxide have superior ultraviolet blocking properties compared to their bulk substitute is therefore they are often used in the preparation of sunscreen lotions. The usage of nanoparticles dates back to the Roman time, in the fourth century the famous Lycurgus cup (Figure 2) made of dichroic glass, as well as in the 9th century in Mesopotamia for creating a glittering effect on the surface of pots.



Fig. 2. The famous "Lycurgus Cup" is one of the earliest known uses of nanotechnology in human history

Pottery from the middle Ages and Renaissance often retains a distinct gold or copper colored metallic glitter. This luster is caused by a metallic film that was applied to the transparent surface of a glazing (Harris and McNeil, 2020). Nanocomposite materials are polyphaser materials in which at least one of the phases is in nanospace. In general, nanomaterials provide reinforcement efficiency due to their high aspect ratios. The Reinforcement material is usually organic or inorganic nanoparticles such as glass fiber, organic fiber, etc. as a dispersed phase. Fibrous materials such as matrix material are a continuous phase and include metallic, inorganic non-metallic and polymer matrix materials. Therefore, they are basically divided into three classes; metal matrix, ceramic matrix and polymer matrix nanocomposites. Within these groups, polymer nanocomposites are the most researched materials for applications.

3.2. Nano composite hydrogels

The interesting and unexpected properties of nanoparticles with large surface area compared to bulk materials and their dominance in bulk material properties with the addition of small amounts have led

to the development of nanoparticle-containing composite materials. Over the last years, nanotechnology has been implemented in almost all branches of human life. The combination of nanotechnology with other fields of science has attracted increasing attention during the past decades. There have been numerous approaches to incorporate nano-scale methods with conventional methods toward manufacturing improved materials. Nanocomposite hydrogels are one example of such a combination between nanotechnology and biomaterial science.

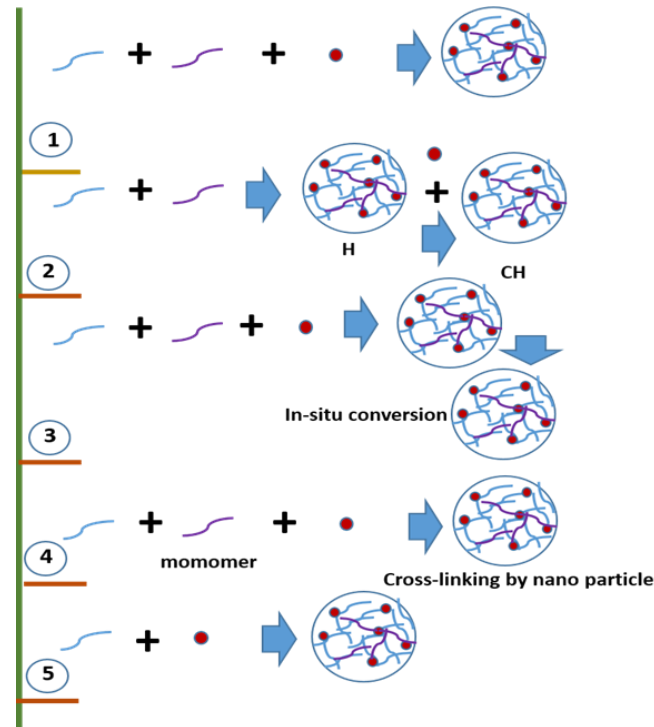


Fig. 3. Five main approaches used to obtain hydrogel-nanoparticle

According to final application area, five main approaches are concerned for the production of NCHs as reported by Thoniyot et al., 2015. These are hydrogel formation in a nanoparticle suspension, physically embedding the nanoparticles into hydrogel matrix after gelation, reactive nanoparticle formation within a preformed gel, cross-linking using nanoparticles to form hydrogels, and finally gel formation using nanoparticles, polymers, and distinct gelator molecules (Fig. 3). Within these approach, the first method is the simplest and widely employed approach to forming a nanoparticle-hydrogel composite, however, it should be noted that the success of the method closely related to cross linking density, due to the possibility of leaching of nanoparticles out of the hydrogel matrix, the cross linking density should be maintained as high as possible. Over the last decade, it is seen that, various types of nanofillers have been considered for the production of polymer-based composite materials in industrial applications and research studies. However, clay-based polymer nanocomposites are still keeping their great interest in today's materials research, as it is possible to achieve impressive property improvements compared to pure polymers or traditional filled composites. These improvements include higher modulus, increased strength and heat resistance, reduced gas permeability and flammability, and increased degradability of biodegradable polymers (Ray, 2013). The most generally used clays for the preparation of polymer nanocomposites belong to the family of phyllosilicates, that is, layered or sheet like structures more commonly referred to as layered silicates. Montmorillonite, hectorite, illite, and chlorite can be given as mostly used examples of this 2:1 phyllosilicates groups. Their crystal structures typically consist of two silica tetrahedral sheets with central Al octahedral sheets. Neighboring layers are held together primarily by van der Waals force and electrostatic force and occurred negative charge due to the isomorphs substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer, are balanced by the presence of exchangeable cations (Na^+ ,

Ca²⁺, etc.) in the lattice structure. This makes them differ from other silicates on the basis of their high dispersity, hydrophilicity, sorption ability, and ion exchange (Zhumagaliyeva et al. 2017).

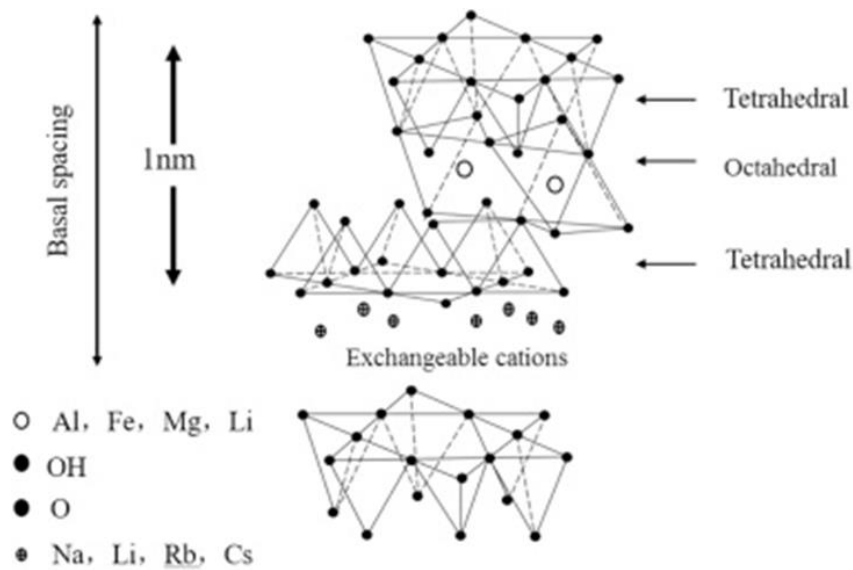


Fig. 4. Structure of commonly used 2:1 phyllosilicates (Fu et al. 2019)

As can be seen at Fig. 4 these minerals are composed of nanoplatelets with a length of about 0.5–1 μm and a thickness around 1 nm, leading to a large aspect ratio (500–1000). However, processing of nanocomposites is a real challenge because the elementary nanolayers or tactoids of a few platelets need to be uniformly dispersed and not be aggregated to develop the highest amount of interfacial zone. Although there are many explanations such as Ribbon or band-like structures related to the distribution of montmorillonite particles in their structures, the preliminary explanation of the nanoplatelet association released by Van Olphen, 1963, is considered one of the first and common approach (Fig.5).

In this model aggregation were described by the (FF) association, whereas the continuous gel-like structure was a consequence of (EF) and (EE) associations.

As a result, the relations between rheological behavior of particle suspensions and their distribution of nanoclay platelet associations is an important feature of such suspensions that should be considered for composite material synthesis (Burgentzlé et al., 2004). Furthermore, due to the layered silicate clays are hydrophilic; they are not suitable for mixing and interacting with most polymers. This situation is analogous to that of immiscible polymer blends, and in most cases, separation into discrete phases takes

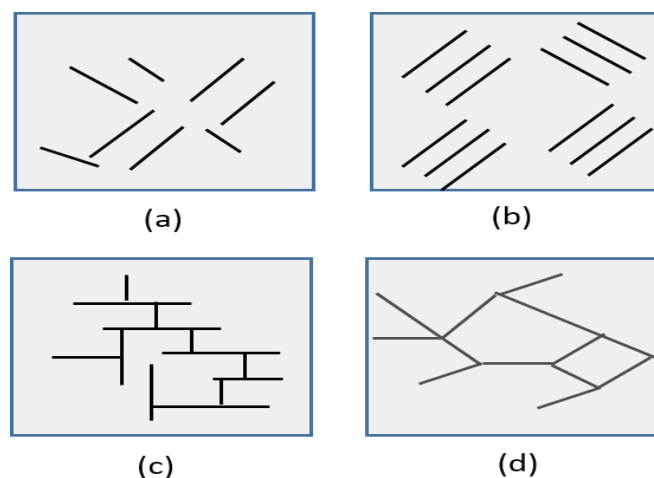


Fig. 5. (a) dispersed; (b) face-to-face (FF); (c) edge-to-face (EF); (d) edge-to-edge (EE) aggregation. (FF) association leads to thicker and larger tactoids, whereas (EF) and (EE) lead to three-dimensional "house of cards" structures

place. In immiscible systems, which typically correspond to more conventionally filled polymers the poor physical interaction between the organic and the inorganic components leads to poor mechanical and thermal properties. In contrast, the strong interactions between polymer and clay in polymer NC lead to nanometer dispersion of organic and inorganic phases. As a result, NC exhibit unique properties not shared by their micro equivalents or conventionally filled polymers. On the other hand, although it is considered positive in terms of mechanical resistance due to tight stacking of lamellar clay platelets by electrostatic forces, counter ions are attracted by the net negative charge inside the clay platelets, and sharing of them by two neighboring platelets, resulting in a tightly held platelet and stacking of them inside make unable to interact with polymer matrices. Therefore, using untreated clay to make polymer nanocomposites is not effective, clay have to modified / treated before being used to prepare polymer nanocomposites (Fu et al., 2019).

The first report on polymer-based nanocomposites can be found back in the early 1960s on methyl methacrylate-based polymer chains adsorbed on the surface of montmorillonite (MMT) clay by A. Blumstein, thereafter, studies were conducted on amalgamation of clays in various types of polymeric matrix such as thermoplastics, thermosets and elastomers. The aforementioned different clays are derived from either solid rocks or they are synthesized. Among those clays, MMT clay has been used in both laboratory researches as well as in industry for manufacturing commercial products due to cost effectiveness as well as good compatibility with most polymers. The basic route of preparation of polymer/clay nanocomposites is either placing the polymer chains in-between (intercalation) or to polymerize the desired monomers/precursors in-between clay layers (exfoliation) (Murugesan and Scheibel, 2020). The schematic representation of these process is given at Fig. 6 an example of this is the morphology of polymer composites assembled by the Toyota research group with chains of macromolecules arranged in silicate layer galleries with a distance of several nanometers between the basal planes of the crystal.

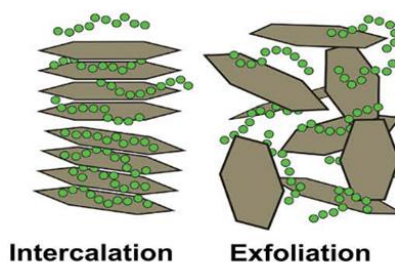


Fig. 6. A schematic representation of Intercalation and exfoliation process

In exfoliation, full or partial delamination of the clay layers in the polymer matrix is performed with extensive diffusion of the polymer chains into the interlayer space (Fig. 7). The average distance of the delaminated layers depends on many factors such as amount of clay loading in a polymer matrix, clay functionalities, and the interface interaction between the matrix and clay. However, the clay platelets have some difficulties to maintain uniform layer spacing's since no sufficient attractions exist between the silicates layers. Therefore in literature, it has been proposed that the physico-mechanical properties of exfoliated polymer/clay morphologies are more dominant than that of intercalated ones.

Clays are often hydrophilic, so the complete exfoliation of nanoclays is fairly difficult to accomplish as repulsion forces exist between clay and polymer matrix. Therefore, surface modification of clays is important for improving the compatibility with hydrophobic polymers. Quaternary ammonium salts (QAS) are commonly used as surface active agents due to their versatile functionalization, easy mode of modification and cost effectiveness. This modification is help to expand the interlayer space, thereby activating the polymer clay combination.

3.3. Exfoliations performed on nano composite hydrogels

As briefly discussed above, the preparation of polymer/clay nanocomposites are generally performed by intercalation or exfoliation methods. Both of these methods it is clear that the pretreatment of clay minerals plays an important stage for successful synthesis of the composite material with desired

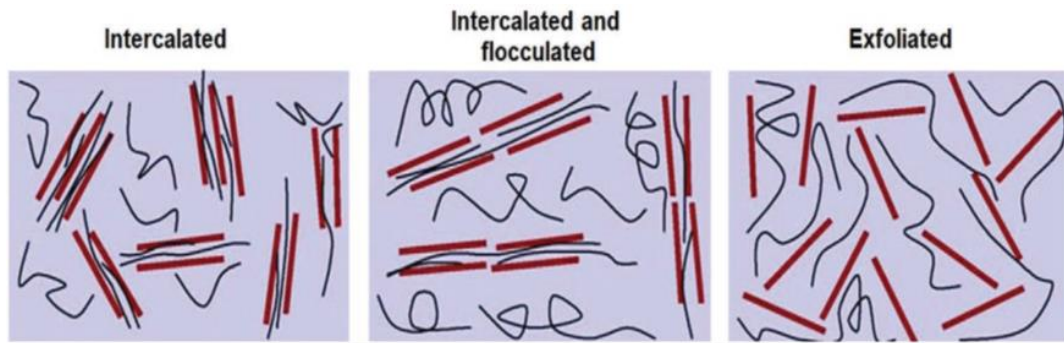


Fig. 7. Intercalation and exfoliation process of clay lamellar with monomers

properties. The common practices for successful preparation of clay surface before subjecting to in situ polymerization for nanocomposite production are;

- Chemical route mainly performed by cation exchange
- Physical route e.g. by using ultrasonicator or homogenizer, high shear mixing using twin screw extruder or by using high energy ball milling etc. (Mechanical stirring and ultrasonication)

In aqueous environments, due to the hydrophilic nature of clays, water molecules are attracted to the interlayer space by exchangeable cations, thereby expanding of the interlayer space can be performed. In a dilute aqueous dispersion, the aggregates can spontaneously separate into particles and the particles can be partially or even completely exfoliated to form nanoplates. Because nano layers are loaded, they function as polyelectrolytes. Therefore it is clear that such decomposition and exfoliation depends on the suspension concentration, type of clay minerals and the exchange cations in the interlayer area. For example, as reported by Zhu et al., 2019, when Na^+ - montmorillonite (Mt) powder is added into water, Na^+ ions tend to hydrated to form hydrated Na^+ ions. As a result, a large number of water molecules enter the interlayer space, causing the crystalline structure of Mt to expand in the direction perpendicular to the layers. Moreover, an electric double layer can be formed on the surface of charged Mt layers. As such, Na^+ - Mt particles delaminate to be nanolayers. However, high stacking of platelet especially at nanosize should be considered as pointed out above. For achieving the nanolayers expansion rather than the polar solution, the clay surface needed to be organically modified to form organo-clay (OC). In practice, tetramethylammonium chloride (TMA), tetradecyltrimethylammonium bromide (TDMA), hexadecyltrimethylammonium bromide (HDTMA, and benzyldimethylhexadecylammonium chloride (BDHDMA) are the most employed surfactants to convert clays from organophobic to organophilic. The more detail on exfoliation or intercalation performed by organic surfactants especially for clay-nanocomposites can be found in recent paper published by Yıldız and Kurama, 2021.

In these methods, although the chemical route for the delamination of clay minerals in aqueous media is well known and is a more general way applied by many researchers, the physical pathway method is also gaining increasing attention with its application in high-energy ball mills with various surfactants. Quaternary ammonium salts (QAS) are commonly used as surface active agents due to their versatile functionalization, easy mode of modification and cost effectiveness.

3.3.1. Mechanical activation

Particle size reduction is an important step in many industrial applications. The process can be defined as the mechanical breakdown of solids into smaller particles without changing their state of aggregation. Mechanical milling may be used to create particles of a certain size and shape (including nanosize), to increase the surface area and induce defects in solids which is needed for subsequent operations such as chemical reactions, sorption, etc. Milling not only increases the surface area of solids. It is likely to increase the proportion of regions of high activity in the surface, therefore it also called mechanochemical activation (MA). MA is a process able to induce structural disorder, amorphisation and increased chemical reactivity in the material treated by intensive grinding (Baláz. 2008). MA is a simple method to apply, especially when done by high energy ball milling. The entire process is

characterized by small energy requirements, low processing temperatures, and thus reduced costs, and increased environmental friendliness.

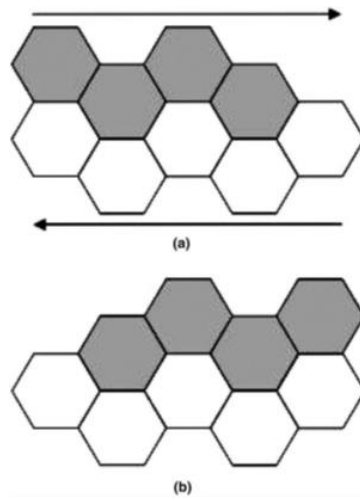


Fig. 8 Grain boundary sliding model: (a) initial position of grains and (b) position after top layer has slid to right (Meyers et al., 2006)

In nano powder synthesise, or working with nano powders to produce composites the synthesis process are generally performed in a non-equilibrium state by "energizing and quenching". The energization involves bringing the material into a highly non-equilibrium (metastable) state by some external dynamical forcing, e.g., through melting, evaporation, irradiation, application of pressure, or storing of mechanical energy by plastic deformation. For the mechanical milling, several mechanisms were proposed. Detail of these processes can be find at released report by Suryanarayana, 2001. The schematic illustration of grain boundary observed during the deformation is given in Fig. 8. It is generally agreed that once the nanocrystalline structure is wholly achieved no further reduction in grain size is possible due to the extremely high stress that is required to deform the small nanometer sized grains. The formation and movement of dislocations in such conditions is difficult, and hence, grain boundary sliding becomes the governing deformation mechanism. The layer of grains slides with respect to the other, producing a shear strain in the process. Plastic deformation has taken place by virtue of the top layer of grains translating to the right with respect to the bottom layer of grains. This requires grain-boundary sliding and is the principal mechanism in super plasticity. For nanocrystalline materials, this has been proposed to be the dominant deformation mechanism at grain sizes <50 nm. Different types of high-energy milling equipment can be used In MA, however in which planetary ball mill, attritor mill and the Spex mill are high lightened as mainly preferred mills that used in MA. They differ in their capacity, efficiency of milling and additional arrangements for cooling, heating, etc. The applied main stress types in milling can be classified as compression, shear (attrition), impact (stroke) and impact (collision), as given in Fig. 9.

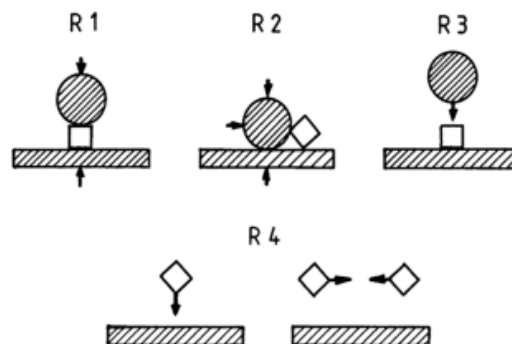


Fig. 9. Main stress types in mills, R1 - compression, R2 - shear (attrition), R3 - impact (stroke), R4 - impact (collision), circle - mass of milling media, square - mass of material charge, rectangle - mass of mill wall

In dry or wet milling, surfactants are mostly used to prevent aggregation and stabilize the separated nanoparticles. This is performed by electrostatic or steric ("organic") stabilization by adsorbing surfactant on the solid interfaces (Fig. 10).

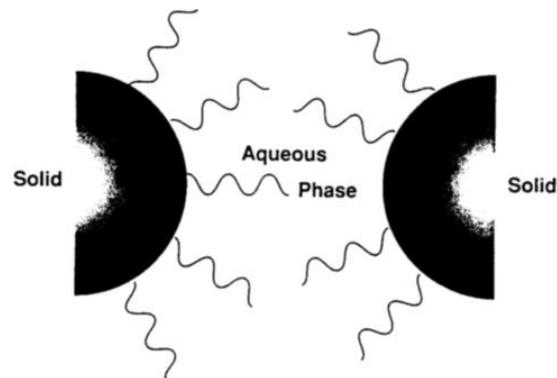


Fig. 10. Steric stabilization of nanoparticles by polymeric surfactants

In literature, a number of researchers have studied the structural changes of various clay minerals by high energy ball milling, for example Frost et al., 2001 reported that delaminated kaolinite particles could be achieved with mechanical milling. Later the group was also reported that the prolonging the milling time positively affected the intercalation. A study performed by Mani et al., 2003 can also be given as a good example for the physical path. In this study, combined ball milling of organo-montmorillonite produced nano-sized clay mineral particles was carried out by ultrasonication. The author noted that no significant increase in specific surface area was observed after milling, however, the desired result was achieved after sonication. Later in another study, Lee et al. (2007) used stirred ball milling, with water and kerosene as solvents to intercalate various alkylammonium ions. This technique was found to be effective on increasing the basal spacing by intercalated alkylammonium ions. In the study performed by Perrin-Sarazin et al., 2009 can be given another example for the beneficial effect of ball milling on montmorillonite structure and whole process. In this study, ball milling was investigated as an alternative way (dry and with coupling agent) to achieve final clay exfoliation in PP/montmorillonite polymer nanocomposite, by creating preliminary mechanical clay delamination prior to melt-compounding.

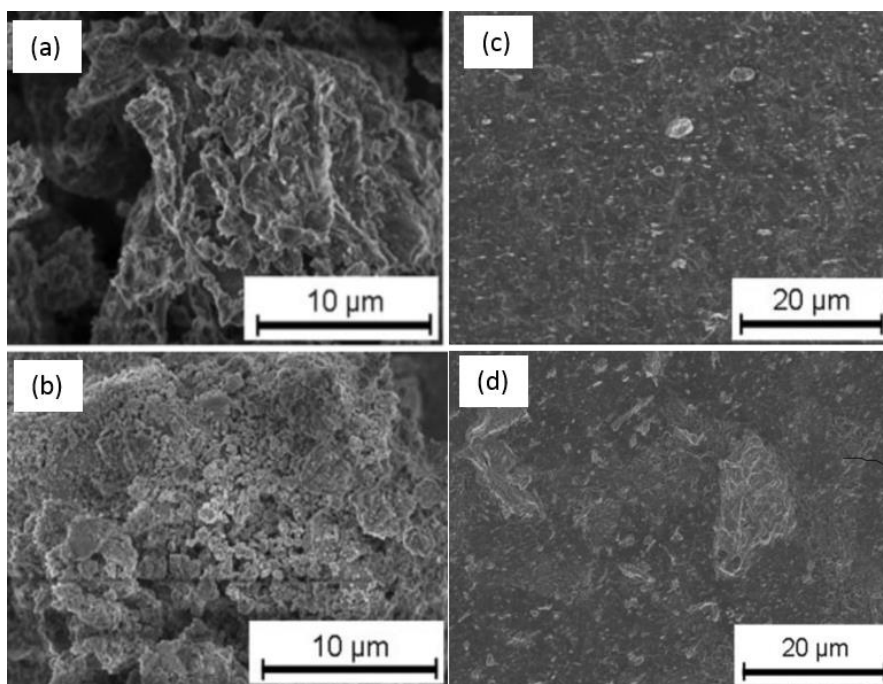


Fig. 11. SEM micrographs of CNa⁺ after: (a) 0, (b) 60 min of ball milling, at magnifications of 35000, Can⁺-based compounds: at 32000 magnification

Ball milling was done using a SPEX mill. The author stated that according to morphological analysis, the clay particles are agglomerated without grinding. It is difficult to characterize the level of platelet delamination and breakage. However, as the grinding time increased, the clay pellets showed smaller particles with a rounder texture (Fig 11 a and b). On the otherhand as can be seen at Fig.11-c and d the clay micro and nanodispersion in the CNa^+ -based compounds show significantly finer and more homogeneous dispersion especially at lowered milling time by the help of coupling agent (Fig. 11-d). Ramadan et al., 2010 conducted a comparative study to observe the effect of high energy ball milling on Na^+ - MMT) and organo-montmorillonite (Cloisite 30B) structure under different conditions. The samples were dry milled in a planetary ball mill (Retch PM 400 MA) with different milling times, milling speeds and ball to powder ratios. It was reported that both processed and pre-treated samples were mostly composed of separate layers, especially for increased grinding speed and time. The authors also noted that ball milling did not significantly degrade the crystal structure, and the intercalated alkylammoniums in Cloisite 30B played a role in stabilizing the structure compared to the Na^+ - MMT sample. More recently high energy ball milling was investigated as an easy technique to achieve maximum exfoliation of OMt (Cloisite 30B) by Chatterjee et al., 2017. In this study Powdered OMt (Cloisite 30B) was put into stainless steel jar together with stainless steel balls (10 mm in diameter) keeping ball-to-powder mass ratio of 5 to 1 and were dry-milled in a planetary ball mill (Retsch PM-100, Germany) under milling speeds of 200 rpm and 400 rpm separately. The results indicated that separation of the clay mineral layers could not be achieved even after 4 h of milling under 200 rpm but was attained after 2 h of milling under 400 rpm. Another application of ball milling to increase the adsorption performance of local clay for Ni(II) removal was recently performed by Malaki and Karimi-Jashni, 2017. In this study, the effect of ball milling process on the properties of the natural local clay, which was mainly composed of montmorillonite and quartz, including structural changes and adsorption capacity for the removal of Ni (II) ions from aqueous solutions, was investigated. Mechanical milling of clay minerals was carried out using planetary ball mill at the balls to powder ratio of 10:1 and 20:1, milling speed was 500 rpm, and the grinding time was applied 5 to 20 h. The results showed that the layer structure of montmorillonite has been broken by increasing the time and intensity of milling, and the only existing crystalline phase in the final ground product was quartz. The milling of clay samples occurred in two steps, which included particle size reduction at the beginning of the grinding and aggregation of particles for prolonged milling that led to increasing particle size. It was reported that ball milling of the local clay for 10 h with 10:1 weight ratio of ball to powder enhanced the adsorption capacity of Ni(II) ions by 71.7% compared to the initial un-milled clay.

3.4. Enrichment and characterization tools of clay and clay based nano composite hydrogels

Clay is a versatile industrial mineral. Although the oldest uses was mainly limited as a ceramic raw material, presently the usage areas of clays are widened coating and filler pigment for paper, filler or reinforcement material for paint, rubber, composites, cosmetics, medicines. They can also be used as an effective sorbent for the treatment of industrial waste discharges. Although more efforts are made to use clays more efficiently and to discover new areas of use with the development of science and technology, clays are natural minerals and therefore, depending on their origin and precipitation environment, they often contain various impurities that degrade the properties of the clay and affect its use for certain purposes (Jayasree and Prabhakaran, 2021). There are two main techniques used in industrial production for the enrichment of clays: dry process and wet process. In the dry process, the raw material is crushed to the desired size, classified, and enriched by gravity separation methods, magnetic separation or air flotation. The dry process is simpler but produces a lower quality product than the wet process. In wet processing, clay is processed by separating it into coarse and fine fractions using centrifuges, hydrocyclones or hydro separators. The size reduction of clays is mainly accomplished by grinding (high energy ball mills or stirrer mills) with the aid of process control agents. Surface area measurement, porosity, solubility, particle size distribution, aggregation, shape, size, direction, intercalation and distribution of nanoparticles, surface potential and stability in solution are the main parameters that need to be determined in nanoclay applications. Some other techniques such as Fourier Transfer Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) are also more commonly used for characterization and morphological analysis.. Except than the raw materials, polymer layered silicate nanocomposites as

briefly discussed above, especially in the form of composite hydrogels, are received interest as relatively new class of nanoscale materials due to the providing an opportunity to explore new behaviors and functions compared to traditional materials. In the last two decades, great progress has been made in both the modification of nanomaterial surfaces and the development of synthesis techniques of correct composite structures that can respond to desired properties. However, it is clear that such advances need to be supported by good/sufficient characterization to gain insight into the morphology of the composite structure and the various factors affecting its properties so that the fabrication can be properly designed. Characterization of the nanocomposite materials would be help to understanding of the parameters such as quality of surface modification of the reinforcement materials, dispersion of them in the polymer matrix, interactions of the additives with the polymer chains, their effect on the resulting morphology and composite properties. Furthermore it can also help to analysis of a wide spectrum of properties to ascertain the application potential of the nanocomposites. A number of different nanocomposite characterization methods are available which include X-ray Diffraction (XRD), Thermogravimetric Analysis (TGA), Differential Scanning Calorimetry (DSC), FTIR spectroscopy, contact angle measurement, elemental analysis (XRF), Brunauer–Emmett–Teller (BET) analysis, SEM or TEM. etc. More information about characterization can found in some selected articles (Mittal, 2009 and 2012; He et al., 2014; Zhuang et al., 2015; Bee et al., 2018).

4. Conclusions

Hydrogels are soft materials that typically consist of water-swollen cross-linked polymer chains. While absorbing a large amount of solvent in the three-dimensional network with the contribution of osmotic pressure, they maintain their solid state with certain levels of mechanical performance. Hydrogels have many desirable properties such as swelling, mechanical strength and biocompatible nature that make them important candidates in various fields. Some of the most important applications of hydrogels are in food, agriculture, industry, cosmetics, pharmaceuticals and medical treatments. The stiffness of swollen polymer webs is often controlled by the addition of crosslinkers, however, these polymers are still brittle materials. The swelling and flexibility of hydrogels are directly related to the crosslink density of the network, the polymer to volume ratio, and the interactions between the solvent and the polymer. For these reasons, the majority of hydrogel structures today are produced as composite structures synthesized in the form of stimuli-sensitive entities (i.e. nanoparticles, nanoclay, nanocrystalline cellulose and functional polymer chains. One of the most popular applications among these composite structures is undoubtedly the synthesis of nanoclay-based hydrogels. However, in the literature, many studies have been reported on this subject, it still maintains its importance as a subject open to progress.

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