We are IntechOpen,
the world's leading publisher of
Open Access books
Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

154
Countries delivered to

Our authors are among the

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS
BOOK CITATION INDEX
INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Clay Hybrid Materials

Tanushree Choudhury

Abstract

The modern trend is to prepare hybrid material using nano clay. Formation of nano clay, an exfoliated clay, and proper dispersion in a polymer matrix remains a challenge. The green composite so formed by clay polymer mixing has many improved properties such as high Tg (glass transition temperature), high flame resistance, high tensile strength, and improved barrier properties, which may find application in textile industry, automobile industry, environmental and polymer engineering field.

Keywords: nano clay, dispersion, CTAB, organic modifier, properties

1. Introduction

Hybrid Materials, in general, have enhanced properties to their components alone. Some of the properties of these hybrid materials, which have been studied in depth, are moduli, thermal expansion coefficients, gas permeability, ionic conductivity, etc. These hybrid materials are classified based on their interaction between host and guest phases. Depending on the type of matrix and guest phase, hybrid materials have been classified into three groups: (i) "OI" organic-inorganic or molecular hybrids, "IO" inorganic-organic intercalation compounds, nanocomposite materials, and solid-state hybrids exhibited by clay-calixarene derivatives [1].

One of such hybrid materials is clay-based hybrid material. Clay minerals are aluminosilicates. Though different types of clay have been used, for making hybrid materials, one of the most commonly used clay is montmorillonite. It belongs to 2:1 type of clay, two silicate layers and one octahedral brucite type of layer containing a mostly aluminum-oxygen hydroxyl group. Isomorphous substitution of trivalent Al^{3+} ion by divalent/monovalent or tetrahedral Si with trivalent Al^{3+} ion leads to charge imbalance in the crystal. This imbalance is compensated by the presence of counter ions present at the surface of the sheet layer. The edge of each platelet has a hydroxide group allowing it to form water gels.

Clay particles are small in size <2 μm, have a large surface area-to-mass ratio. The counter ions (at the exchangeable sites on clay) along with water molecules also serve a bridge between the two layers keeping them inbound.

Exchangeable cations adsorbed on the surface layer can be replaced by other materials. Inherently clay surfaces are hydrophilic attracting polar groups. However, they can be made oleophilic by exchanging the cations with organic ions like cetyl trimethyl ammonium bromide ions or cetyl trimethyl ammonium pyridinium ions etc., producing organoclay composites or polymer clay nanocomposites (PCNs). These composites are extremely investigated in material science and find widespread applications as adsorbents for heavy metal ions [2–4], ceramics and thin films [5], building materials [6], photocatalysts for wastewater treatment [7, 8],

drug delivery vehicle [9], bio-inspired materials [10], optoelectronic devices [11], ferrofluids [12], and hydrogel clay hybrids for pesticide and nutrient retention [13].

This review focuses on the properties of the different types of clay hybrid materials that can be prepared by intercalation chemistry, in situ polymerization and sol-gel techniques. It would also provide an insight into the application of these hybrids for a sustainable environment.

2. Clay-based hybrid materials

2.1 How clay can be used in a hybrid material

2.1.1 Structure of clay

Clay minerals belong to phyllosilicates. The principal building elements of the clay minerals are two-dimensional arrays of Si-O- tetrahedral and 2-D arrays of Al or Mg-O-OH octahedral as shown in **Figure 1**. In most clay minerals, such sheets of tetrahedral and octahedral are superimposed in different fashions [14].

a. **Structure of tetrahedral sheet:** In the Si-O sheets, the Si atoms are coordinated with four oxygen atoms. The O atoms are located on the four corners of a regular tetrahedron with the Si atom in the center. In the sheet, three of the four oxygen atoms of each tetrahedron are shared by three neighboring tetrahedral. The fourth oxygen atom of each tetrahedron is pointed downward. This Si-O sheet is called a tetrahedral sheet or silica sheet.

b. **Structure of octahedral sheet:** In the Al, Mg-O-OH sheets, the Al or Mg atoms are coordinated with six oxygen atoms or –OH groups, which are located around the Al or Mg atom, with their centers on the corners of a regular octahedron resulting in hexagonal close packing. This sheet is called alumina or magnesia sheet. The fourth oxygen atom protruding from the tetrahedral sheet is shared by the octahedral sheet. This sharing of atoms may occur between one silica and one alumina sheet as 1:1 layer minerals.

In 2:1 layer minerals, one alumina or magnesia sheet shares oxygen atoms with two silica sheets, one on each side. These layers in clay minerals are stacked parallel to each other.

2.2 Origin of surface charge and modification of clay surface

In the tetrahedral sheet, tetravalent Si is sometimes partly replaced by trivalent Al. In the octahedral sheet, there may be replacement of trivalent Al by divalent Mg without complete filling of the third vacant octahedral position. Al atoms may also be replaced by Fe, Cr, Zn, Li, and other atoms. The small size of these atoms permits them to take the place of small Si and Al atoms; therefore, the replacement is often referred to as isomorphous substitution. When an atom of lower positive charge replaces one of higher valence, a deficit of positive charge takes place or in other words, excess of negative charge. This excess of negative charge is compensated by the adsorption on the layer surfaces of cation, which are too large to be accommodated in the interior of the crystal. In the presence of water, the compensating cations on the layer surfaces may be easily exchanged by other cations when available in solution, hence they are called exchangeable cations. Thus clay minerals bear the potential of forming hybrid materials.
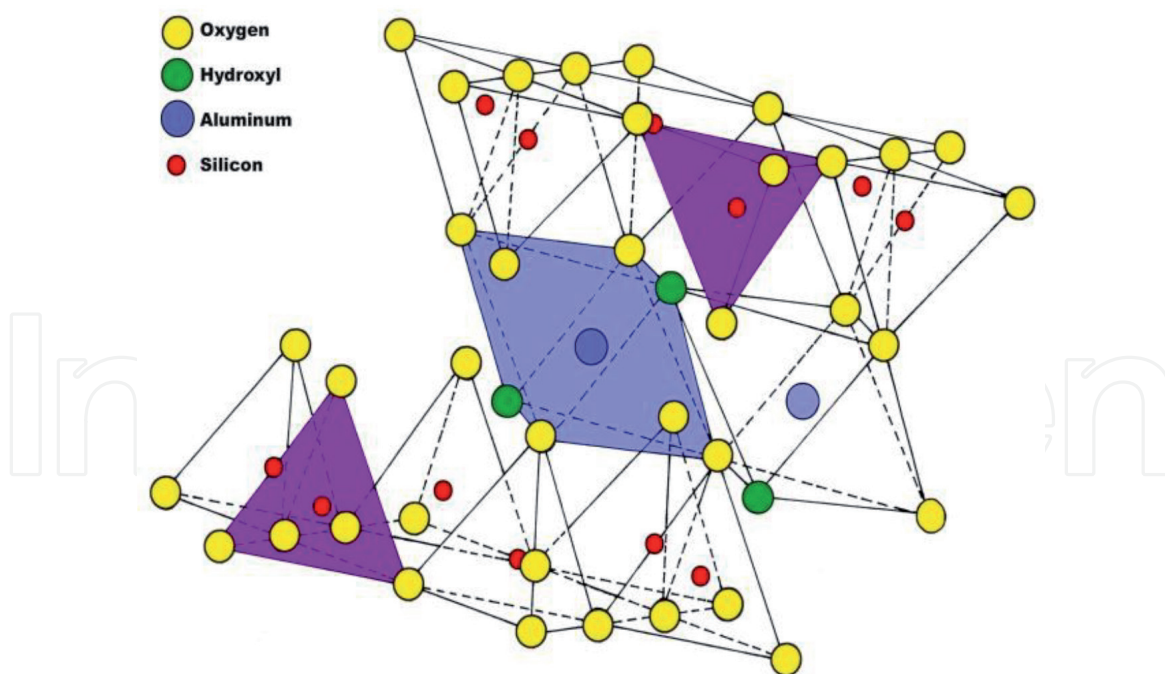
Figure 1.
Structure of clay mineral.

Natural clay is hydrophilic. The surface of the clay needs to be modified so that it can interact with hydrophobic polymers. The modification of clay surface is generally done by the cation exchange process. The ability of clays to exchange cations between each of their layers and retain them is a unique characteristic. The intercalated cations can be exchanged by other cations by treatment of other cations in solution. This cation exchange capacity can be defined as the maximum amount of cations that a given amount of clay can take up and this is constant. The ability to cation exchange in the interlayer space determines the adsorption ability of montmorillonite [15]. The most exchangeable cations that can be adsorbed on the clay surface by the cation-exchange process are inorganic ions (mostly Na^+, Ca^{2+}, Mg^{2+}, K^+), amines, amino acids, cationic surfactants, and non-ionic surfactants. The surface of the clay can also be rendered organophilic by the reaction of hybrid monolayers of clay mineral and amphiphilic alkyl amino cation using Langmuir-Blodget method [16]. When a solution of an amphiphilic alkyl ammonium cation is spread onto clay suspension, negatively charged clay platelets in the suspension are adsorbed onto a floating monolayer of the alkylammonium cation at an air-clay suspension interface. The hybrid monolayers of clay platelets and alkylammonium cations formed at the interface can be transferred onto a solid surface to fabricate a hybrid multilayer.

2.3 Types of clay hybrid materials

The common types of clay hybrid materials are:

1. Intercalation compounds

2. Exfoliated/delaminated compounds

3. Sol-gel hybrid materials

Intercalation compounds: These compounds result from the intracrystalline insertion of organic compounds inside the layers of certain lamellar solids as shown in **Figure 2**.

i. Intercalation of ionic species: Clay minerals exhibit isomorphous substitution as a result of which Si is replaced by Al in a tetrahedral layer or Al by Mg in octahedral layer leading to charge deficiency, which in turn is compensated by exchangeable cations. Exchangeable metal ions located in the inter-lamellar space of MMT may be replaced by different organic cations such as alkylammonium ions in solution. Alkylammonium cations thus incorporated in organosilicates lower the surface energy of inorganic hosts and improve the wetting characteristic with polymer [17]. It provides a functional group that can react with polymer or initiate polymerization of monomers to improve interfacial strength between inorganic host and polymer. Layered double hydroxides (LDH), for example, $Mg_6Al_2(OH)_{16}CO_3. 4H_2O$, have a positive charge on the Mg $(OH)_2$ layers. They provide an opportunity for intercalation with organic anions [18].

ii. Intercalation of neutral species: Formation of organic-inorganic compounds by intercalation of neutral molecules in 2D solids, generally phyllosilicates of clay minerals family and it is also observed for other inorganic layered materials, for example, 2D transition metal halides, oxyhalides, dichalco-genides, graphite, and graphite oxide, layered phosphates, phosphorous trichalcogenides. Different mechanisms are proposed that come into play during host-guest interactions in these intercalated materials. Van der Waals forces mainly occur when long-chain alkylammonium ions are inserted in the clay layers. When interlayer cations preserve the hydration shell, an association of molecules takes place with water molecule acting as H bond bridges, which on heating, eliminates water and produces direct coordination between guest species and involved transition metal [19]. Macrocyclic compounds such as crown ether and cryptands penetrate the interlayer space of phyllosilicates and other layered solids giving stable intracrystalline complexes [20]. The interlayer environment of certain layered solids exhibits acid character, which is typical of clay minerals group. Interaction with basic species produces a proton transfer between the inorganic host and organic guest molecule. The organic molecules being protonated gives rise to organic cations balancing the electrical charge of the silicate [21]. Many redox reactions occur during intercalation of organic and organometallic species into various 2D solids. Clays containing interlayer cations like Cu (II) can interact with aromatic compounds such as benzene giving intercalation compounds characterized by the existence of σ or π bonds between the host solid and guest molecule [22].

Exfoliated or delaminated compounds: These compounds are formed when the layers of clay are delaminated and the resulting platelets are homogeneously dispersed throughout the polymer matrix as shown in **Figure 3**. The resulting materials
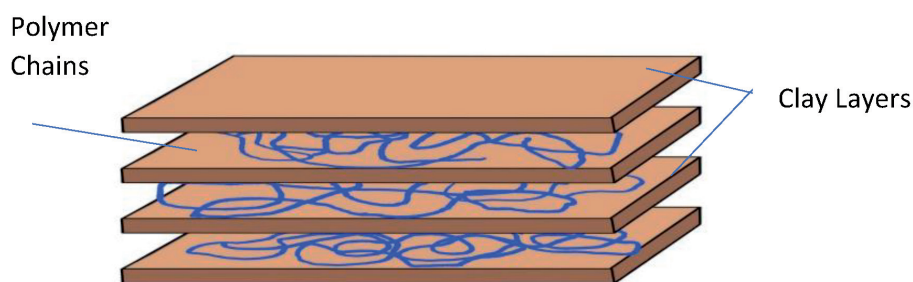

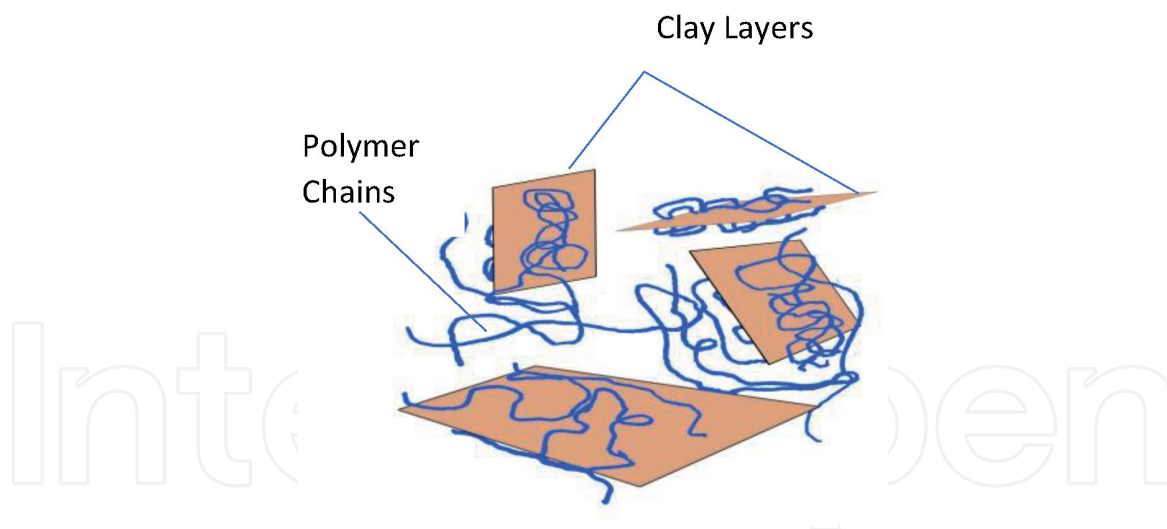**Figure 2.**
Intercalated clay.

4

Figure 3.
Exfoliated clay.

are considered as nanocomposites as the interaction takes place at the atomic level between inorganic hosts and organic guest molecules.

Clay mineral is a potential candidate for the filler of these hybrid materials since it is composed of layered silicates, 1 nm thick, which can undergo intercalation with organic molecules [23]. The mechanism of interaction of clay with different polymers is discussed below.

  i. Vinyl polymers: These include vinyl addition polymers derived from monomers like methyl methacrylate [24–30], acrylic acid [31], vinyl ester [32], vinyl polymer [33, 34], styrene [35–38], allyl ester resin [39], and acrylates [40].

Studying the mechanism of interaction of ethylene-vinyl acetate with clay, it has been found that as VA (vinyl acetate) content increases, copolymer presents increasing polarity but lower crystallinity with different mechanical behavior. Increasing polarity with increasing VA content is useful in imparting a high degree of polymer-clay surface interaction. Structure and mobility properties of EVA polymer are influenced by VA content and this chain mobility in and around clay galleries tend to modify the level of interaction in clay hybrid materials [41]. Polymer chains of PVA get adsorbed on individual inorganic lamellae in stages after the exfoliation of the clay mineral leading to the formation of intercalated nanocomposites [42]. PVA forms a composite structure with sodium montmorillonite and studies reveal the existence of both exfoliated and intercalated MMT layers for low and moderate silicate loadings. Exfoliation of layers has been attributed to water casting method used since the water suspended layers become kinetically trapped by the polymer and cannot reaggregate [43]. Syndiotactic PS (thermoplastic polymer) differs from other PS (such as a-PS) in that phenyl rings regularly alternate from side to side concerning polymer chain backbone. Two important factors responsible for homogenous dispersion of clay layers in s-PS hybrids are: (a) surfactant should be intercalated between silicate layers of clay by ionic bonding and (b) the hydrophobic tail of the surfactant molecule should be partially compatible or interacted with s-PS molecules [44].

Organophilic modification of clay and amine-terminated PS employing anionic polymerization yielded completely exfoliated hybrids with aspect ratio exceeding 600 when such organoclays were melt compounded with PS. In contrast to this, small molecular weight modifiers only promoted intercalation and failed to exfoliate silicate particles during melt compounding. ABS (thermoplastic polymer) forms

an intercalated-exfoliated composite with clay. HENA (hydroxyethyl isonicotin-amide) is used as an anchor monomer for homogeneous dispersion of clay minerals in PET (polyethene terephthalate) matrix [45].

Acrylonitrile co-monomer incorporated into poly (styrene-co-acrylonitrile) copolymer accelerates intercalation of copolymers into the galleries of silicate layers modified with an organic intercalant. The faster intercalation of a matrix polymer leads to the better dispersion of silicate layers in the matrix polymer [46]. In the hybrids of SAN, clay particles or nanoscale building blocks are distributed uniformly and their sizes are strongly dependent on co-monomer content. Acrylonitrile co-monomer incorporated into SAN facilitates the intercalation of copolymers into the galleries of silicate layers modified with an intercalant. H-bonding interaction between the nitrile groups of SAN and –OH groups on silicate layer makes a negative contribution to exchange energy of mixing so that the intercalation of copolymers into the galleries of the silicate layer is accelerated. It is also expected that the enhanced polarity of SAN due to incorporated acrylonitrile co-monomer can destroy H-bondings of intercalant in the galleries. This might also increase the rate of intercalation of SAN into the galleries of silicate layers modified with intercalants. Synthesis of hybrid materials using natural clay and modified PVC resulted in the removal of heavy metals (Fe, Cu, Pb, Zn, Cd, Co, and Mn) from aqueous solution and also exhibited good adsorption capacity for Fe (III) [47].

ii. Condensation step polymers: Several important polycondensates have been used in nanocomposites preparation with layered silicates. They are poly-amides [48], polyimides [49], polyurethane urea [50], polyurethane [51], poly (butylene terephthalate) [52], poly (ethylene terephthalate co-ethylene naphthalate) [53], epoxy [54, 55], amino, sulfonic acid, and silyl functional-ized groups [56–59], and surface-modified groups [60].

Polyamides and polyimides are polymers containing polar functional groups and form homogenous and exfoliated dispersion of silicate layers as silicate layers of clay have polar functional groups and are compatible only with polymers containing polar functional groups. Polyamide-6 (PA6), Polyamide 66 (PA-66), and Nylon form majority of commercial polyamides. PA-66 contains a mixture of chains (only amines, acid groups, or a mixture of two). Differences in end group configuration can lead to significant differences in morphology and properties of blends with functionalized polymers. A lower degree of exfoliation in PA-66 nanocomposites, the affinity of PA-66 for organoclay is less than PA-6 nanocomposites forming the basic aspect of difference in the chemical structure of two polyamides [61]. Nylon-6-clay hybrids (NCHs) have been prepared by using $10A^0$ silicate layers of clay minerals, which are dispersed homogeneously in the polymer matrices resulting in a drastic change in properties (high strength, high modulus, high heat and distortion temperature) and this has been achieved with only a few % of clay [62]. The compatibility of forming hybrids with clay and polymers containing amide and imide groups increases as both contain polar functional groups. PBI (polybenzimidazole) is a thermally stable thermoplastic polymer, contains 1,3-dinitrogen heterocycle. When PBI is added to clay suspensions in a polar environment, the mineral layers will first adsorb the bulky macromolecule and the intercalation proceeds to comple-tion via exchanged sites of the organically modified clay [63]. Polyurethane (PU) elastomers are segmented polymers with soft segments derived from polyols and hard segments from isocyanates and chain extenders. Linear PU is obtained by poly condensate technique using a mixture of diols and diisocyanate. MMT nanolay-ers are dispersed in PU matrix replacing hydrophilic organic exchange cations of native mineral with more organophilic diethanolamine/triethanolamine. Presence

of these groups in galleries of MMT renders them organophilic and promotes the absorption of diol into the interlayer of MMT and improves the particle-matrix interactions since di and triethanolamine contain functional groups, which react with diisocyanate [64].

Pure PU exhibits an amorphous halo at 20° in 2θ. The gallery spacing of the layered clay is 1.1 nm. The gallery spacing of the layered clay in the composites increases to 1.6 nm for the PU/layered nanocomposites. This indicates that PU chains were intercalated between the layers of clay [65]. A multilayered structure consisting of alternate PU chains stacked with the layers of the silicate layers in the microstructure of PU/OMT nanocomposites has been confirmed in literature [66].

With increasing and urgent market demand to produce higher performance electronic devices with a smaller size, lighter weight, and better quality, developing PI films with low coefficient of thermal expansion (CTE) has increasingly become one of the most important issues. The best way to lower the CTE of PI is to introduce low CTE inorganic materials such as clay into PI matrix, yielding PI/clay hybrid composites [67]. Polar aprotic solvents are used for the synthesis of these hybrids, but due to solvent-solute interaction, are not easily removed from the PAA film at temperatures used during thermal curing for PI. The residual solvent causes the PAA (polyamic acid)/clay films to be plasticized during thermal imidization and thus leads to PI/Clay hybrid films with relatively higher values in CTE, but lower than pure film. To eliminate such negative effects of the aprotic solvents on CTE, PAA solutions not containing them should be prepared. A novel PI/clay hybrid film prepared from PAA salt of triethylamine and organoclay in a mixed solvent of THF/MeOH is described in the literature. It is expected that the hybrid will have a much lower CTE than those obtained from PAA in an aprotic solvent.

Full separation of clay layers in the polymer matrix is also achieved by using epoxy resin, which has high polarity and curing property [68]. The presence of polar –OH groups in clay layers impede nonpolar species from entering the galleries and exfoliating the clay layers. The mechanism of clay exfoliation in epoxy clay systems have been studied and reported in the literature. According to it, the acidity of alkylammonium ions catalyze homopolymerization of diglycidyl ether of bisphenol A (DGEBA) molecules inside the clay galleries. CEC of clays determines the number of alkylammonium ions present between clay layers and therefore controls the space available for the diffusion of DGEBA molecules during mixing of organoclay with epoxy resin.

   iii. Polyolefins: These include polypropylene [69–74], polyethylene [75–77], ethylene propylene diene methylene linkage rubber [78].

These polymers do not contain any polar groups and homogenous dispersion in the silicate matrix is difficult. Homogenous dispersion of silicate layers in PP is not realized even by using an MMT intercalated with di-stearyl ammonium ion (DSDM-MT) in which polar surfaces of clay are covered with nonpolar long alkyl groups. A novel method of preparing PP-clay hybrid has been developed. PP is mixed with DSDM-MT and polyolefin oligomer with polar telechelic –OH groups (PO-OH) as a compatibilizer. In this process, PO-OH oligomer intercalates between the layers of clay through the strong H-bonding between –OH groups of PO-OH and oxygen groups of silicates. Interlayer spacing increases thus resulting in weakening of interaction between layers.

Another method of preparing PP/clay nanocomposites is by improving the compatibility of PP with organoclay by functionalizing the backbones of PP with polar monomers such as epoxy and maleic anhydride (MA) [79]. Compatibilizers promote compatibility of clay and polymer for good nano dispersion. Polyolefin-graft

MA as compatibilizer is used to enhance the possibility of intercalation of polymer between clay layers. The presence of MA increases the possibility of nanocomposite formation for PS, but this does not appear to help PP. PP/clay nanocomposites modified with the optimum level of compatibilizer yielded the greatest improvement of composite properties [80].

PE (polyethene) is another widely used polyolefin polymers. Alkylammonium ion facilitates interaction with polymer because it renders hydrophilic clay surface organophilic. Organically modified clay is not well dispersed in nonpolar PE as the nonpolar groups are too hydrophobic. Exfoliation and interaction behaviors depended on the hydrophilicity of PE grafted with MA and chain length of the organic modifier in the clay. When the number of methylene groups in alkyl amine (organic modifier) was larger than 16, exfoliated nanocomposites were obtained and the MA grafting levels was higher than about 0.1 wt% for the exfoliated nanocomposite with modified clay [81].

Rubber is another such polymer. Carbon blacks are excellent reinforcers due to their strong interaction with rubbers, but they often decrease the processability of rubber compounds because of high viscosity at high volume loading. MMT exchanged with a liquid rubber (LR) is termed as LR-MMT for utilization of its favorable shape. Co-vulcanization of nitrile rubber was done with LR-MMT for the formation of the molecular composite. It has been studied that there exist strong rubber-filler interactions as (comparable to those in carbon black filled system) in LR MMT, in which negatively charged silicate layers are bonded to LR molecules with positively charged terminal sites forming "bound rubber."

Polymers grafted on silicate surfaces also helps in delamination of its layers. It has been reported in the literature that PDMS (polydimethylsiloxane) grafted onto MMT layer surface via condensation of hydroxyl groups of PDMS and those hydroxyl groups on MMT layers prevents the nanolayers of MMT from reaggregating.

Intercalation of EPDM chains into OMMT galleries provided a strong interaction between EPDM and OMMT sheets in exfoliated composites.

It has been observed that the photoluminescence quantum efficiency of conjugated polymer PE improves manifold in the presence of the inorganic phase like montmorillonite clay [82]. Incorporation of montmorillonite clays into conjugate polymers like PAni gives rise to hybrid/inorganic composites with special properties for application in organic light-emitting diodes (OLEDs), organic field-effect (OFETs), organic solar cells (OSCs), and electrochromic devices (ECDs) [83].

 iv. Fiber-reinforced polymers: Many fibers have been added as reinforcements to the polymer matrix. They are PS-Sisal fiber composites [84]. Bamboo polymer composites [85], short oxide fiber reinforced in kaolin [86], bamboo glass-reinforced in PP [87], thermoplastic starch [88], switchgrass.

 v. Biodegradable-polymers: These include biodegradable resin clay composites [89].

Metal incorporated clay composites such as phosphorous clay composites show improved fire performance [90].

Starch modified by grafting with vinyl monomers (e.g., methyl acrylate) onto the starch backbone yielded thermoplastic materials. Kaolin, a natural mineral, hydrated aluminosilicate, with high surface and presence of polar groups showed very good compatibility with thermoplasticized starch.

Aliphatic polyesters, polylactide (PLA) comes under the area of environmentally degradable polymer materials. These are well suited for the preparation of disposable devices because of their biodegradability. The main characteristics of the PLA

matrix are its easiness to degrade by the enzymatic or hydrolytic way. Hydrolytic degradation of PLA is a well-known process. Hydrolytic chains cleavage proceeds preferentially in amorphous regions, leading therefore to an increase of polymer global crystallinity. The formation of lactic acid oligomers, which directly follows from this chain scission, increases the –COOH end groups concentration in the medium. These carboxylic functions are known to catalyze the degradation reaction. Relative hydrophilicity of clay plays determining roles in the hydrolytic degradation process. More hydrophilic the filler, more pronounced is the degradation. Thermoplastic corn starch (TPS) clay hybrids showed enhanced biodegradation as compared to TPS alone [91].

vi. Hyperbranched polymers: These polymers have a tree-like structure with a large number of branch points radiating from a multifunctional core molecule and hence a potentially high degree of end-group functionality per molecule. The –OH end groups are assumed to be concentrated in the periphery of the molecules in a hydrophilic environment. Polyester HBPs also show excellent processing char and shrinkage control. Dispersion of HBPs with various types of organically modified MMT in THF led to intercalation over the whole range of MMT contents and the layer expansion correlated with the polarity of organic modifier rather than the size of HBPs [91].

HBPs with highly branched, 3D structure and high concentration of end groups have the promise of good internal bonding rubber phase due to the presence of surface functional groups, in addition to low initial viscosity [92].

Sol-gel hybrid materials: This class of hybrids has received different names such as ORMOSILS and ORMOCERS, referring to organically modified silicates or ceramics, respectively.

The technological importance of the sol-gel process is due to the simplicity in its preparation. Silicon alkoxides are the main precursors used in the synthesis of glasses and ceramics and they are also being used in the preparation of new organic-inorganic hybrid materials [93].

A solution of the molecular precursor is transformed into a sol or a gel by a chemical reaction, resulting in a solid material upon evaporation. This transformation allows the production of materials with different possible compositions, intercalated microstructures, and chemical homogeneity at temperatures less than those used for fusion.

Typical sol-gel processing variables leading to different morphologies of the materials are water to alkoxy and catalyst to alkoxy ratios and the type of solvent and catalyst used [94].

3. Conclusion and outlook

Clay mineral poses a host of technical issues, such as dispersion of the inorganic filler in the polymer/base matrix. Better is the dispersion, better is the hybrid. Clay dispersed in natural dispersant renders the most thermally stable organoclay.

Functionalization of clay surface for better compatibility with polymers is needed for the development of new synthetic layered materials with a wide range of properties. PAni/clay hybrids have been widely studied due to many advantages such as high optical contrast (%T), environmental stability, as well as comparatively low cost. However, the difficulties in processing PAni into films due to its very low solubility in most of the available solvents and the relatively poor mechanical properties decrease its performances and abilities in such applications. Green

hybrids reinforced with natural fibers and macromolecules have pronounced biodegradable and recyclable properties and thus emerge as better packaging materials.

Current research focuses on the use of advanced nanotech catalysts and materials for the purification/remediation of contaminated surface or groundwater and municipal water or industrial wastewater. Though clay hybrids have been extensively used as nano adsorbents for the removal of heavy metals, As, and dyes from wastewater, its fabrication as inorganic membranes have received limited attention in the literature. Titania pillared clay, an important class of layered materials, exhibits unique surface charge characteristics that make them a good candidate for removal of organics from wastewater by just adjusting the pH of the solution. Development of such membrane reactors integrating the separation process with photocatalysis would lead to an important new technological application that would add economic value to the vast natural deposits of clay minerals located worldwide. However, membrane fouling is still a critical problem that results in flux decline with time, needs to be addressed. In a nutshell, the outlook is bright and sustainable for clay hybrid materials.

Abbreviations

MMT	montmorillonite
VA	vinyl acetate
EVA	ethyl vinyl acetate
PVA	polyvinyl alcohol
ABS	acrylonitrile butadiene styrene
PET	poly (ethyl terephthalate)
HENA	hydroxyethyl iso-nicotinamide
SAN	styrene-co-acrylonitrile
PA	polyamide
PU	polyurethane
OMT	organic montmorillonite
PI	polyimide
CTE	co-efficient of thermal expansion
PAA	polyamic acid
DGEBA	diglycidyl ether bisphenol A
CEC	cation exchange capacity
DSDM-MT	distearylammonium montmorillonite
PO	polyolefin oligomer
PP	polypropylene
MA	maleic anhydride
PE	polyethylene
LR	liquid rubber
PDMS	polydimethylsiloxane
EPDM	ethylene propylene diene methylene linkage rubber
PLA	polylactide
HBP	hyperbranched polymer
mPE	metallocene blended polyethylene
AN	acrylonitrile
PMMA	polymethyl methacrylate
PPCN	polypropylene clay nanocomposites
OMS	organomethylsilicate
PAM	polyacrylamide
EVOH	ethylvinylalcohol

MAO	methylaluminoxane
TMA	trimethylalkoxide
PAni	polyaniline
PCL	polycaprolactum
PHA	polyhydroxyalkanoate
PBS	polybutylene succinate
DEP	resin
PCN	polymer clay nanocomposites
PS	polystyrene
NCH	nylon clay hybrid
PBI	polybenzoimidazole
OMT	organo montmorillonite
THF	tetrahydrofuran
MeOH	methanol
OLED	organo light emitting diode
OFET	organo field effect
OSC	organic solar cell
ECD	electrochromic device
TPS	thermoplastic corn starch
ORMOSIL	organo modified silicate
ORMOCERS	organo modified ceramics

Author details

Tanushree Choudhury
Chemistry Division, VIT Chennai, Chennai, India

*Address all correspondence to: tanushree.c@vit.ac.in

IntechOpen

References

[1] Othman AB et al. Hybrid materials based on clay and calixarenic derivatives. Journal of Porous Materials. 2019;**26**:493-504

[2] Varadwaj GBB, Parida K, Nyamori VO. Transforming inorganic layered monmorillonite into inorganic-organic hybrid materials for various applications. Inorganic Chemistry Frontiers. 2016;**3**:1100-1111

[3] Ray PZ, Shipley HJ. Inorganic nano-adsorbents for the removal of heavy metals and arsenic: A review. RSC Advances. 2015;**5**:29885-29907

[4] Bhatnagar A, Sillanpaa M. Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment: A review. Chemical Engineering Journal. 2010;**157**:277-296

[5] Choudhury T. Natural dye intercalated clay hybrid material: Clay based nanopigment. Clay Research. 2017;**36**(1):17-22

[6] Takeda H et al. Characterization of zeolite in zeolite-geopolymer hybrid bulk materials derived from kaolinitic clays. Materials. 2013;**6**:1767-1778

[7] Cristiani C et al. Polyamine-based organo-clays for polluted water treatment: Effect of polyamine structure and content. Polymers. 2019;**11**:897-913

[8] Akkari M et al. Organo clay hybrid materials as precursors of porous ZnO/silica-clay heterostructures for photocatalytic applications. Beilstein Journal of Nanotechnology. 2016;**7**:1971-1982

[9] Kim MH et al. Review of clay-drug hybrid materials for biomedical applications: Administration routes. Clays and Clay Minerals. 2016;**64**(2):115-130

[10] Lin AYM, Meyers MA. Interfacial shear strength in abalone nacre. Journal of the Mechanical Behavior of Biomedical Materials. 2009;**2**:607-612

[11] Silva RC et al. Electrochromic properties of polyaniline based hybrid organic/inorganic materials. Journal of the Brazilian Chemical Society. 2016;**27**(10):1047-1057

[12] Son YH et al. Structure-property correlation in iron oxide nanoparticle-clay hybrid materials. Chemistry of Materials. 2010;**22**(7):2226-2232

[13] Yacoub E. Hydrogel-clay hybrid materials for pesticide and nutrient retention. Laboratoire Mapiem (EA4323) Materiaux Polymeres Interface. Available from: http://mapiem.univ-tln.fr/-PhD-Thesis-.html

[14] Van Olphen H. Clay Colloid Chemistry. New York: Interscience Publishers; 1963. pp. 59-83

[15] Kozak M, Domka L. Adsorption of quarternary ammonium salts on montmorillonite. Journal of Physics and Chemistry of Solids. 2004;**65**(2-3):441-445

[16] Umemura Y. Layered structure of hybrid films of an alkylammonium cation and a clay mineral as prepared by LB method. Thin Solid Films. 2003;**426**:216-220

[17] Sinha Ray S, Okamato M. Polymer/layered silicate nanocomposites. Progress in Polymer Science. 2003;**28**:1539-1641

[18] Riechle WT. Catalytic reactions by thermally activated synthetic anionic clay mineral. Catalysis. 1985;**94**(2):547-557

[19] Yariv S. In: Yariv S, Cross H, editors. Organo-Clay Complexes and Interaction. New York: Marcel Dekker Inc.; 2002

[20] Ruitz-Hitzky E, Casal B. Crown ether intercalations with phyllosilicates. Nature. 1978;**276**:596-597

[21] Fripiat JJ, Chaussiden J, Jelly A. Chimie Physiquedes Phenomenes de Surfaces et Application aux Oxydes et aux Silicates. Paris: Masson; 1970

[22] Doner HE, Mortland MM. Benzene complexes with Cu (II) montmorillonite. Science. 1969;**166**:1406-1407

[23] Okada A, Usuki A. The chemistry of polymer clay hybrids. Materials Science and Engineering. 1995;**C**(3):109-115

[24] Zhang W, Liang Y, Luo W, Fang Y. Effect of clay modifying agents on morphology and properties of PMMA/ clay nanocomposites synthesized via gamma ray irradiation polymerization. Journal of Polymer Science Part A: Polymer Chemistry. 2003;**41**:3218-3226

[25] Jash P, Wilkie CA. Effect of surfactants on the thermal and fire properties of PMMA/clay nanocomposites. Polymer Degradation and Stability. 2005;**88**:401-406

[26] Luo JJ, Daniel IM. Characterization and modelling of mechanical behavior of polymer/clay nanocomposites. Composites Science and Technology. 2003;**63**:1607-1616

[27] Stadtmueller LM, Ratinac KR, Ringer SP. The effects of intragallery polymerization on the structure of PMMA-clay nanocomposites. Polymer. 2005;**46**:9574-9584

[28] Zheng X, Jiang DD, Wilkie CA. Methyl methacrylate oligomerically modofied clay and its PMMA nanocomposites. Thermochimica Acta. 2005;**435**:202-208

[29] Zhu J, Start P, Mauritz KA, Wilkie CA. Thermal stability and flame retardancy of PMMA-clay

nanocomposites. Polymer Degradation and Stability. 2002;**77**:253-258

[30] Su S, Jiang DD, Wilkie CA. PMMA, PP, PE nanocomposites formation by melt blending. Polymer Degradation and Stability. 2004;**83**:321-331

[31] Onal M, Srikaya Y, Alemdaroglu T, Bozdogan I. Isolation and characterization of a smectite as a micro-mesoporous material from bentonite. Turkish Journal of Chemistry. 2003;**27**:683-693

[32] Kocsis JK, Gryshchuk O, Frohlich J, Mulhaupt R. Interpenetrating vinylester/epoxyresins modified into organophilic layered silicates. Composites Science and Technology. 2003;**63**:2045-2054

[33] Artzi N, Nir Y, Narkis M. Structure and properties of EVOH/clay nanocomposites. Polymer Composites. 2003;**24**(5):627-639

[34] Silva TF et al. Silylated montmorillonite as nanofillers for plasticized PVC nanocomposites: Effect of the plasticizer. Applied Clay Science. 2014;**99**:93-99

[35] Sohn JI, Lee CH, Lim ST, Kim TH, Choi HJ, Jhon MS. Viscoelastic and relaxation characteristic of PS/clay nanocomposites. Journal of Materials Science. 2003;**38**:1849-1852

[36] Yoon JT, Jo WH, Lee MS, Ko MB. Effect of comonomers and shear on the melt intercalation of styrenics/ clay nanocomposites. Polymer. 2001;**42**:329-336

[37] Zhang G, Li YJ, Yan D, Xu Y. Nylon 10, 10-MMT nanocomposites made by intercalating polymerisation. Polymer Engineering and Science. 2003;**43**(1):204-213

[38] Hofmann B, Dietrich C, Thomman R, Friedrich C, Mulhaupt R. Morphology and rheology of PS clay

nanocomposites. Macromolecular Rapid Communications. 2000;**21**:57-61

[39] Huang SH, Paeng SW, Kim JY, Huh W, Lee SW. Synthesis of allylester resin tethered to layered silicates by in-situ polymerization and its nanocomposites. Polymer Bulletin. 2003;**49**:329-335

[40] Wang S, Hu Y, Song L, Wang Z, Chen Z, Fan W. Preparation and thermal props of ABS-MMT nanocomposites. Polymer Degradation and Stability. 2002;**77**:423-426

[41] Chaudhary DS, Prasad R, Gupta RK, Bhattacharya SN. Clay intercalation & influence on crystallinity of EVA based clay nanocomposites. Thermochimica Acta. 2005;**433**:187-195

[42] Li B, Hu Y, Zhang R, Chen Z, Fan W. Preparation of poly (vinyl alcohol)/layered double hydroxide nanocomposite. Materials Research Bulletin. 2003;**32**:1567-1572

[43] Strawhecker KE, Manias E. Structure and properties of poly (vinyl alcohol)/Na$^+$ MMT nanocomposites. Chemistry of Materials. 2000;**12**:2943-2949

[44] Tseng C, Wu J, Chang F. Crystallisation behavior of syndiotactic PS nanocomposites for melt and cold crystallisation. Journal of Applied Polymer Science. 2002;**86**:2492-2501

[45] Zhang G, Shichi T, Takagi K. PET clay hybrids with improved tensile strengths. Materials Letters. 2003;**57**:1858-1862

[46] Ko MB. Effects of acrylonitrile content on the properties of clay dispersed poly (styrene-co-acrylonitrile) copolymer nanocomposite. Polymer Bulletin. 2000;**45**:183-190

[47] Brahim C, Ammari F, Meganem F. Involvement of hybrid materials based on natural clay and poly (vinylchloride)

into extraction of metal cations. Polimery. 2017;**62**(3):187-192

[48] Mallick PK, Zhou Y. Yield & fatigue behavior of PP & PAM-6 nanocomposites. Journal of Materials Science. 2003;**38**:3180-3190

[49] Gu A, Chang FC. Preparation of PI/clay hybrid films. Journal of Applied Polymer Science. 2001;**79**:289-294

[50] Xu R, Manias E, Snyder AJ, Runt J. Biomedical PU layered silicate nanocomposites. Macromolecules. 2001;**34**:337-339

[51] Hu Y, Song L, Xu J, Yang L, Chen Z, Fen W. Synthesis of PU/clay intercalated nanocomposites. Colloid Polymer. 2001;**279**:819-822

[52] Chang JH, Uk AY, Ryu SC, Giannelis EP. Synthesis of PBT/clay nanocomposites thro' in-situ interlayer polymerization. Polymer Bulletin. 2003;**51**:69-75

[53] Chang JH, Park DK. Various organo clays based nanocomposites of PET. Polymer Bulletin. 2001;**47**:191-197

[54] Ianchis R et al. Synthesis and properties of new epoxy-organo layered silicate nanocomposites. Applied Clay Science. 2011;**52**:96-103

[55] Silva AA et al. Nanostructure and dynamic mechanical properties of silane functionalized montmorillonite/epoxy nanocomposites. Applied Clay Science. 2011;**54**:151-158

[56] Huskic M, Zigon M, Ivanokovic M. Comparison of the properties of clay polymer modified by silane and by quarternary ammonium salts. Applied Clay Science. 2013;**85**:109-115

[57] Huang G-B, Ge CH, He B-J. Preparation, characterization and properties of amino functionalized montmorillonite and composite layer-by-layer assembly with inorganic

nanosheets. Applied Surface Science. 2011;**257**:7123-7128

[58] Kim Y et al. New sulfonic acid moiety grafted on montmorillonite as filler of organic-inorganic composite membrane for non-humidified proton exchange membrane fuel cells. Journal of Power Sources. 2010;**195**:4653-4659

[59] Romanzini D et al. Effect of clay silylation on curing and mechanical and thermal properties of unsaturated polyester/montmorillonite nanocomposites. Journal of Physics and Chemistry of Solids. 2015;**87**:9-15

[60] Mishra AK et al. Characterization of surface modified montmorillonite nanocomposites. Ceramics International. 2012;**38**:929-934

[61] Chavarria F, Paul DR. Comparison of nanocomposites based on nylon 6 and nylon 66. Polymer. 2004;**45**:8501-8515

[62] Kawasumi M, Hasegawa N, Kato M, Usuki A, Okada A. Preparation and mechanical properties of PP clay hybrids. Macromolecules. 1997;**30**:6333-6338

[63] Gultek A, Galip Icduygu M, Seckin T. Preparation and characterization of PBI clay hybrid materials. Materials Science and Engineering. 2004;**B107**:166-171

[64] Rehab A, Salahuddin N. Nanocomposite materials based on PU intercalated into montmorillonite clay. Materials Science and Engineering. 2005;**A399**:368-376

[65] Yao KJ, Song M, Hourston DJ, Luo DZ. Polymer/layered clay nanocomposites: 2 polyurethane nanocomposites. Polymer. 2002;**43**:1017-1020

[66] Hu Y, Song L, Xu J, Yang L, Chen Z, Fan W. Synthesis of polyurethane/clay intercalated nanocomposites. Colloid & Polymer Science. 2001;**279**:819-822

[67] Gu A, Chang FC. Novel preparation of PI/clay hybrid films with low co-efficient of thermal expansion. Journal of Applied Polymer Science. 2001;**79**:289-294

[68] Kornmann X, Lindberg H, Berglund LA. Synthesis of epoxy-clay nanocomposites: Influence of the nature of the clay on structure. Polymer. 2001;**42**:1303-1310

[69] Van Den Oever MJA, Elbersen HW, Keijsers ERP, Gosselink RJA, De Klerkengels B. Switchgrass as a reinforcing fiber in PP composites. Journal of Materials Science. 2003;**38**:3697-3707

[70] Mallick PK, Zhan YX. Yield & fatigue behavior of PP & PAM-6 nanocomposites. Journal of Materials Science. 2003;**38**:3183-3190

[71] Garcia Lopez D, Picazo O, Merino JC, Pastor JM. PP clay nanocomposites. European Polymer Journal. 2003;**39**:945-950

[72] Weibing X, Liang G, Zhai H, Tang S, Hang G, Pang WP. Preparation & crystallization behavior of PP/PP-g-MAH/org-MMT nanocomposites. European Polymer Journal. 2003;**39**:1467-1474

[73] Li J, Zhou C, Gang W, Wei Y, Ying T. Preparation and linear rheological behavior of PP/MMT nanocomposites. Polymer Composites. 2003;**24**(3):323-331

[74] Collar EP, Laguna O, Areso S, Garcia-Martinez JM. Succinyl fluorescein grafted atacted PP as an interface modifier in PP/talc composites. European Polymer Journal. 2003;**39**:157-163

[75] Kato M, Okamato H, Hasegawa N, Tsukigase A, Usuki A. Preparation and properties of PE clay hybrids. Polymer Engineering & Science. 2003;**43**(6):1312-1316

[76] Kuo S, Huang W, Huang S, Kao HS, Chang FC. Synthesis & characterization

of in-situ blended metallocene PE clay nanocomposites. Polymer. 2003;**44**:7709-7719

[77] Shin SYA, Simon LC, Soares JBP, Scholz G. PE clay hybrid nanocomposites. Polymer. 2003;**44**:5317-5321

[78] Zheng H, Zhang Y, Peng Z, Zhang Y. Influence of clay modification on the structure and mechanical properties of EPDM MMT nanocomposites. Polymer Testing. 2004;**23**:217-223

[79] Li J, Zhou C, Gang W. Study on nonisothermal crystallization of maleic anhydride grafted PP/MMT nanocomposite. Polymer Testing. 2003;**22**:217-223

[80] Zheng X, Jiang DD, Wilkie CA. Polystyrene nanocomposites based on an oligomerically modified clay containing maleic anhydride. Polymer Degradation and Stability. 2006;**91**:103-113

[81] Wang KH, Choi MH, Koo CM, Choi YS, Chung IJ. Synthesis & characterisation of maleated PE/ clay nanocomposites. Polymer. 2001;**42**:9819-9826

[82] Chao Chen Em M et al. PE/clay hybrid materials: A simple method to modulate the optical properties. Polimeros. 2016;**26**(1):38-43

[83] Teichler A et al. Inkjet printing of chemically tailored light emitting polymers. European Polymer Journal. 2013;**49**(8):2186-2195

[84] Manickandan Nair KC, Thomas S. Interface modification on the mechanical properties of PS-sisal composites. Polymer Composites. 2003;**24**(3):332-343

[85] Saxena M, Gauri VS. Studies on bamboo polymer composites. Polymer Composites. 2003;**24**(3):428-436

[86] Papargyri SA, Cooke RG, Papargyris DA, Botis A, Papapolmeron G, Papargyris AD. Kaolin clay matrix composites. British Ceramic Transactions. 2003;**102**(5):193-203

[87] Thwe MM, Liao K. Environmental effects on bamboo-glass/PP hybrid composites. Journal of Materials Science. 2003;**38**:363-376

[88] De Carvallo AJF, Curvello AAS, Agnelli JAM. Composites of thermoplastic starch and kaolin. Carbohydrate Polymers. 2001;**45**:189-194

[89] Okada K, Mitsunaga T, Nagase Y. Properties and particle dispersion of biodegradable resin/clay nanocomposites. Korea-Australia Rheology Journal. 2003;**15**(1):43-50

[90] Hussain M, Simon GP. Phosphorous-clay polymer nanocomposites for fire performance. Journal of Materials Science Letters. 2003;**22**:1471-1475

[91] Rodlert M, Christopher JG, Garamszegi L, Leterrier Y, Grunbauer HJM, Manson J-AE. Hyperbranched polymer/ MMT clay nanocomposites. Polymer. 2004;**45**:949-960

[92] Ratna D, Becker O, Krishnamurthy R, Simon GP, Varley RJ. Nanocomposites based on a combination of epoxy resin, hyperbranched epoxy, and a layered silicate. Polymer. 2003;**44**:7449-7457

[93] Nassar EJ, Neri CR, Cale EPS, Serra OA. Functionalised silica synthesized by sol-gel process. Journal of Non-Crystalline Solids. 1999;**247**:124-128

[94] Kickelbick G. Concepts for the incorporation of inorganic building blocks into organic polymers on a nanoscale. Progress in Polymer Science. 2003;**28**:83-114