A SHORT REVIEW ON THE SILYLATED CLAYS - POLYMER NANOCOMPOSITES: SYNTHESIS, PROPERTIES AND APPLICATIONS

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Abstract

Surface functionalization of clay mineral with organosilane has been the subject of numerous researches in recent years, because silylated clays exhibit remarkable properties suitable for potential applications in environmental engineering and materials science. This review summarizes and examines the different strategies of covalent modifications of clay's minerals surfaces, such as montmorillonite, closite, saponite, vermiculites, magadiite, halloysite and kaolinite. Interlayer silanol (Si—OH) groups can be covalently modified with various organoalkoxysilanes including thiol and amino groups. Furthermore, the modification mechanism, the effects of surfaces properties and their multifunctional applications such as filled polymer nanocomposites are also investigated.

Keywords: clay minerals, organosilanes, silylation, nanocomposites, polymer, adsorption.

1. Introduction

The covalent modification of clay surfaces by coupling with organosilane has attracted considerable interest because the great importance of silylated products in the fields of environmental engineering (catalysis, adsorption, biosensor...) [1-3] and nanocomposite materials [4-6]. Generally, several methods were employed in the functionalization of clay mineral surfaces, for example intercalation of inorganic cationic species such as quaternary ammonium or phosphonium salts [7,8], or silylation reactions with silane coupling agents [9]. In the case of organophilization, the most used surfactants are quaternary ammonium salts, which can expand the interlayer spacing and enable the layered silicate to interact analogously with the bulk hydrophobic polymer [7,10]. Recently, there have been many studies focusing organophilic clays for production of polymer/clay nanocomposites [11], for the development of new routes of organophilization [8], for petroleum drilling fluids [12] and for use as adsorbents of organic micro-pollutants [13]. However, the various alkyl and aryl-ammonium salts are known to have poor thermal stability through Hoffman-degradation. In this respect, the applicability of non-covalent modifications in the processing of polymer/clay nanocomposites is limited [4,14,15]. For these reasons, silylation reaction is an efficient method to modify clay minerals surfaces [16]. This chemical modification using organosilane is based on the condensation reaction between the silanols resulting from the hydrolysis of organosilane and the reactive Si—OH and/or Al—OH groups located at the interlayer, external surface and at the broken edges of clay minerals [17,18], providing new functions (e.g., –SH, –NH₂) for the obtained organoclays.

Based on the above considerations, in this review we detailed and discussed the synthesis and characterization of nanomaterials based on covalently modified clay minerals and their multifunctional applications.

2. Structure of swelling clays and reactive sites for silane grafting

The commonly used clay minerals in the synthesis of surface grafted organoclays are smectites, such as layered montmorillonite [19]. Their crystal structure consists of layers made up of two siloxane tetrahedral (Si—O—Si) sheets sandwiching one octahedral metal...
oxide (M–O or M–OH; M = Mg or Al and so forth) sheet [20]. Such structure allows the
phyllosilicates to possess unique physicochemical characteristics such as swelling capacity,
cation exchange capacity and high surface area. Moreover, the higher surface of
phyllosilicates provides functional groups such as –Si–O–Si–, –Si–O–OH and Al
(M)–OH. Hydrophobic –Si–O–Si– groups on the tetrahedral silicate (Si–O) sheets can
contribute to the interaction between clay minerals and silylation reagents [21].
For swelling clay minerals such as smectite, the hydroxyl groups at the broken-edges of
tetrahedral and octahedral sheets are suitable to form covalent bonds with silanes molecules.
In addition, silanol groups (–Si–OH) on the interlayer and external basal surfaces can
be condensed with silylation reagents through three sites (e.g. trichlorosilyl groups and tri-
alkoxysilyl (ethoxy and methoxy) groups) [22].

![Figure 1](image-url)

**Figure 1.** Materials design of layered silicates with non-covalent and covalent modifications [22].

3. Chemical functionalizations of swelling clays surfaces

Silylation of swelling clay minerals is one of the frequently used functionalization method to
introduce hydrophobic partition to the clay surface via formation of durable covalent linkage
with silane coupling agent [23, 24]. Thus, the mechanism of silylation reaction involves the
condensation reaction between hydrolysed silanes, such as trichlorosilyl and triethoxysilyl
groups, and the surfaces hydroxyl groups located on the broken edges or on the clay surfaces.
Since the first study of silylation reaction onto clay minerals by (Lippma et al. in 1980) [25] organoclays played an important role in chemical research. Nowadays, many efforts have been devoted on the development of various hybrid nanomaterials based on silylated clays. Meanwhile, Paula T. Bertuoli et al. [26] used 3-aminopropyltriethoxysilane (APTES) for the modification of montmorillonite (Mt) in different dispersion media. The results have led the authors to found that silane molecules were grafted in the interlayer space, external surfaces and/or at the edges of the clay minerals. The process of clay surface silylation by aminosilane is shown in Figure 3. Besides, the effect of solvent nature on silylation of montmorillonite surfaces was carried out by Linna Suet al. [27]. The results indicated that the polarity of the solvents used had an important influence on the extent of grafting of APTES, interlayer structure, and swelling property of the silylated montmorillonites. While, He and co-workers [28] have pointed out that both the interlayer and external surfaces, as well as the broken edges of swelling clay minerals, provide suitable sites for organosilane grafting. As would be expected, grafting of organosilane onto the external surfaces does not affect the basal spacing of swelling clay minerals. Recently, Qi Tao et al. [29] treated a series of saponite clays (Sap) with 3-aminopropyltriethoxysilane (APTES) and investigated the spectral, structural and morphological characters of the silylated saponites by using different characterizations techniques. It was demonstrated that the saponite clay was successfully silylated with APTES.
Grafting of 3-mercaptopropyltrimethoxysilane (MPTMS) onto surface of expandable clay minerals (smectites) is also reported. Besides, Lilian Avila et al. [30] investigated the functionalization of Spanish saponite with 3-mercaptopropyltrimethoxysilane (MPTMS). The grafting process was demonstrated by IR, XRD, SEM and thermal analysis. All data confirmed the successful functionalization and the thermal stability of modified saponite. Additionally, Linna Su, Dehai Yu and Guo et al. [24, 31 and 32] reported the preparation and characterization of organomodified montmorillonite and various other clays by different organosilanes such as 3-aminopropyltriethoxysilane (APTES), 3-methacryloxy propyl trimethoxysilane (MPTMS) and 3-aminopropyltrimethoxysilane (APTMS). Various techniques such as FTIR, XRD, SEM and Thermogravimetric analysis (TG) were employed to confirm the silylation process. A similar organosilylation of halloysite clay nanotubes by using various organosilanes, such as 3-aminopropyltriethoxysilane (APTES), N-2-aminoethyl-3aminopropyltrimethoxysilane (AEAPTMS), 3-mercaptopropyl-trimethoxysilane (MPTMS), 3-bromopropyltrimethoxysilane (BrTMS), vinyltrimethoxysilane (VTMS) and phenyltriethoxysilane (PhTES) was also reported by Andreia F. Peixoto et al. [33].

4. Applications of covalently modified clay minerals

4.1. As the Filler Nanocomposites

Polymer / nanoclay nanocomposites are vital for the development of modern science and technology due to their unprecedented improvement in their performances properties such as; thermal, mechanical, catalytic, flame retardant and gas barrier compared to conventional polymer composite [34-36]. The combination of polymer composite with silylated nanoclay gives a significant improvement in the mechanical and thermal properties of the resultants nanocomposites and led to their use in engineering applications for automobiles, food packaging, aerospace, and electronics [37]. In the meanwhile, many researchers have been attempted to synthesize the polymer/nanoclay nanocomposites. Sousa el al. [38] studied the covalent immobilization of L-Serine derivatives onto three clays with different nature, morphology or crystallite size: montmorillonite (K10), halloysite and laponite. The L-serine derivatives were firstly silylated with 3-triethylsilylpropyl isocyanate coupling agent and then covalently grafted to the clays. It was found that the successful grafting of L-serine derivatives was confirmed by various characterisations such as FTIR, elemental analyses (N, C and Si), X-ray diffraction, $^{29}$Si solid-state NMR and SEM. Furthermore, Bee et al. [23] investigated the functionalization of montmorillonite (Cloisite Na$^+$) and commercial montmorillonite (Cloisite 20A) with 3-aminopropyltrimethoxysilane (APTMS), and they studied its effect on the properties on the poly (methyl methacrylate) (PMMA) compatibility. It was deduced that the best interfacial dispersion and interaction between the nanofillers (3 wt% clay loading) and PMMA matrix are paramount to enhance the mechanical and thermal properties of the resulting PMMA/S—Cloisite Na$^+$ nanocomposites.
Figure 4. Silylation of Cloisite (a), synthesis of PMMA (b) and Illustration of labyrinth pathways in both composite samples (c). [23].

In another study, Scarfat et al. [39] carried out a surface modification of montmorillonite (MMT) by grafting 3—Glycidyloxypropyl) trimethoxysilane, and its use as nanofiller in the melt compounding of low density polyethylene (LDPE) nanocomposites. Higher thermal stability and flame retardant properties of the LDPE nanocomposites were achieved in comparison with the hybrid systems containing magnesium hydroxide (MH) as an inorganic conventional flame re.
Figure 5. The synthesis route of polyethylene, Fire residue structure of the surface and microscopic structure of a) LDPE/8SC1, b) LDPE/55MH and c) LDPE/5SC1/50MH [39].

A comparative investigation between UP/MMT-APTES nanocomposites and the UP/MMT-TMOA nanocomposites was conducted by Vargas et al. [40]. They found that the dispersion being predominant in the 2 wt% APTES-clay loading in UP matrix with a probable little exfoliation; whereas in 10 wt% APTES-clay loading the agglomerates were predominant. On the other hand, the cured UP/APTES at high concentration were slightly more stable thermally than UP and TMOA. In a separate study, Silva et al. [41] reported that the silylated montmorillonite was used as nanofillers for plasticized PVC nanocomposites. The authors found that the presence of Na⁺—montmorillonite, HS—montmorillonite and H₂N—montmorillonite resulted in an increase of the storage modulus without affecting the glass transition temperature. Regarding thermal stability, those different clay minerals plasticized with ESO showed the best results obtained from thermogravimetric analysis, but exerted little influence on this property for PVC plasticised with epoxidised soybean oil (ESO). Zhang et al. [42] prepared modified montmorillonite (MMT) by an intercalation agent containing double bonds and then compounding with Ethylene-propylene-diene rubber via crosslinking reaction to form EPDM/VMMT nanocomposites. The results showed that the presence of crosslinking in the EPDM/VMMT nanocomposites can play a significant role in improving its mechanical properties.
4.2. Rheological Properties

The main reason to incorporate silylated clays into polymer matrices is to develop final nanocomposites with improved rheological and morphological properties [43]. Thus, it’s making attractive candidates in numerous applications including automotive and construction industries [44]. In this context, alternatives approaches have emerged involving the use of silylated clays as one of the most interesting nanomaterial that can be employed to improve the properties of the final nanocomposite due to its functional groups [46].

Asgari [47] studied the functionalization of sodium montmorillonite nanoclay with APTES silane coupling agent and its effect on rheological and mechanical properties of HDPE/clay nanocomposites. It was observed that a loading of 2 wt% modified clay in HDPE (prepared by masterbatch technique) increases the tensile modulus by 15%, which indicating a well dispersed structure of the nanosheets within the HDPE matrix. The well dispersed structure was verified using TEM. In the case direct mixing, the strain at yield did not decrease much while yield stress and tensile modulus increased by 10% and 15% respectively. However, strain at break decreased significantly when using the masterbatch technique. In a another interesting investigation, Raji et al. [48] investigated the rheological, morphological, structural and thermal properties of polypropylene (PP) reinforced with different silylated clays (with APTES and VTMS), such as montmorillonite, halloysite and sepiolite. According
to experimental results, the efficiency of the silylation process as a good way to improve the matrix—fillers interaction was demonstrated by comparing the mechanical characteristics of the clays nanocomposites before and after grafting with organosilanes (APTES and VTMS). The authors found that the loading of all functionalized halloysite in the polypropylene matrix showed an increase in complex viscosity, with higher values presented for functionalized montmorillonite and sepiolite due to the nanoscale dispersion of silylated clay obtained by the exfoliation process using the melt extrusion and to a better interaction between clay nanoparticles and the polymer matrix.

\[
\begin{align*}
\text{propylene} & \quad \overset{\text{Ziegler-Natta polymerization}}{\longrightarrow} \quad \text{polypropylene} \\
\text{H} & \quad \begin{array}{c}
\text{C} - \text{C} \\
\text{H} \quad \text{or metallocene} \\
\text{CH}_3 \\
\text{catalysis}
\end{array} & \quad \text{H} \quad \begin{array}{c}
\text{C} - \text{C} - \text{I}_{\alpha} \\
\text{H} \quad \text{CH}_3
\end{array}
\end{align*}
\]

Figure 7. The synthesis route of polypropylene (PP) [48].

4.3. Epoxy / Modified nanoclay Nanocomposites

Due to high strength, low cost, easy processing, and light weight, epoxy/clay nanocomposites are widely used for potential applications in various industries [48,49]. The growing use of thermosetting epoxy nanocomposites requires the understanding of their mechanical, thermal and lifetime properties [50,51]. One well known approach to maximise the toughness of epoxy polymers is by the addition of clays nanoparticles, which can improve the above properties such as elastic modulus and impact strength of the final epoxy/clay nanocomposite. The enhancement of the mechanical properties of epoxy/clay nanocomposites is dependent on the quality of the clay’s nanoparticles dispersion in the polymeric matrix [52]. Previous investigations have reported the immobilization of silane coupling agents functionalized nanoclays for improvement of various properties such as the mechanical behavior and thermal stability of epoxy/clay nanocomposites. As an example, Khosravi et al. [53] investigated the effects of 3-glycidoxypropyltrimethoxysilane (3-GPTS) modified montmorillonite addition on mechanical response of unidirectional basalt fiber (UDBF)/epoxy composite laminates under tensile, flexural and compressive loadings. It was demonstrated that the maximum improvements were corroborated to the specimens containing 5 wt. % 3-GPTS/Mt resulted in 28%, 11% and 35% increase in flexural, tensile and compressive strengths. In another research conducted by Zabihi et al. [54], they explored the effect of covalent and non-covalent bonding of clay with epoxy matrix on thermal behavior and lifetime of epoxy and its epoxy/o-clay nanocomposites. The results led the researchers to suggest that epoxy/o-clay nanocomposites showed better thermal durability compared to epoxy/s-clay.
According to Jlassi et al. [34] MPTMS-grafted Tunisian bentonite was used as an intermediate for layered bentonite/poly (glycidyl methacrylate) (PGMA) nanocomposites with higher strength and thermal stability. Based on the experimental results, the nanocomposites Epoxy/B−MPS/PGMA showed improved mechanical and thermal properties compared to those of the reference epoxy−pristine bentonite nanocomposite. However, Silva et al. [55] reported the functionalization of sodium montmorillonite (Na−MT) with N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTS) and its use as nanofiller in epoxy matrix cured with triethylenetetramine. The authors found that the nanocomposites display higher storage modulus mainly at temperatures above the glass transition temperature. Park et al. [56] improved the mechanical interfacial properties of montmorillonite/epoxy nanocomposites by treatment with 3-aminopropyltrimethoxysilane (APTES).

4.3. Adsorption of pollutants

Because of their various physicochemical characteristics such as the swelling capacity, high specific surface area and high cation exchange capacity, 2:1 clay minerals have potential applications in a wide variety of chemical aspects such as adsorption of different substances, especially organic and inorganic cations. Moreover, their modifications with organosilanes improve their adsorption capacities [57,58].

Lytuong and co-workers [2,59] reported the grafting of MPTMS onto layered vermiculites, and the obtained products are tested as adsorbents agents of Hg (II) from aqueous solutions. The researchers found that silylated vermiculites exhibited higher adsorption capacities, less affected by variation of ionic strength and pH as a consequence of the strong binding of Hg (II) to the thiols moieties. In another work, de Mello et al. [60] showed the importance of silylation reaction of clay (Brazilian bentonite) on the adsorption of heavy metal ions. Indeed, they demonstrated that silylated clay (Clay−SH) presented a good alternative for adsorption of Ag+ ions compared to the ungrafted sample. Similarly, the removal of Ni (II) from aqueous effluents by thiol-silylated clays (K10) was conducted by Wagner et al. [61]. Furthermore, the imidazole−functionalized three lixiviated
vermiculites, V0.3Cl, V0.5Cl and V0.8Cl can be promising adsorbents for the removal of Cu (II) ions from aqueous solutions [3]. On the other hand, Qin et al. [17] reported the silylation of Al13—intercalated montmorillonite with trimethylchlorosilane (TMCS) and it’s used for removal of Orange II from aqueous solutions. The authors found that the removal of Orange II is based on both the adsorption on the interface and the partition between the water and the interlayer organic phases. Marcela et al. [62] carried out a surface silylation of natural montmorillonite (Mn) by immobilization of 3-aminopropyltrimethoxysilane (APTMS) (Mn–S) and silver (Mn–S–Ag). The adsorption performances of the silylated samples, towards nitrate removal form water were studied as a function of pH, contact time, temperature and adsorbent dosage. The obtained results showed that the adsorption of NO\textsuperscript{-3} occurs over −NH\textsuperscript{3} surface groups without involving the Ag\textsuperscript{+} cation in the adsorption process. According to Chen et al. [63] sodium montmorillonite is silylated with 3-mercaptopropyltrimethoxysilane (MPTMS), and the silylated product is used for the effective uptake of both inorganic (Cu\textsuperscript{2+}, Zn\textsuperscript{2+}) and organic [benzene, toluene, ethylbenzene and p-xylene (BTEX)] pollutants. It was found that the modified clay has high adsorption towards Cu\textsuperscript{2+} ions and BTEX as compared to their unmodified montmorillonite or natural soil. More recently, Jlassi et al [64] have removed 92.8% of Cd(II) from wastewater within 1.5 min, at pH 8 and at room temperature by using Calix[4]arene-clicked clay through thiol-yne addition.

Figure 9. Schematic illustrates the fabrication process of B-S-Calix [64].

4.4. Biological and medical applications

Nanocomposites based on silylated clays are known to exhibit remarkable improvement in thermal, mechanical, rheological, electronic and optical properties. The improvements in these nanocomposites properties have opened up alternative ways to the use these systems, in particular in the field of biology and medicine [65,66]. Therefore, it is clear that the covalent functionalization of clay minerals improved their affinity with biological and medicinal molecules by creating strong interactions (electrostatic attraction and hydrogen bonding) between the introduced functional groups of the grafted silanes and reactive sites of these
molecules [67]. For instance, the combination of organoclays and organic molecules and/or polymers should be a feasible approach to prepare bionanocomposite films.

Over the years, extensive researches are focused on the development of polymer-clay nanocomposites. In particular, Gorrasi [68] reported the preparation of new biodegradable nanocomposites based on pectins and halloysite nanotubes (HNTs) loaded with rosemary essential oil, with good physical properties (mechanical, thermal, barrier to water vapor). They found that these developed systems were potential applied to the formulation of cast films (active packaging) with antioxidant and/or antimicrobial properties. In another study, Biddeci et al. [69] fabricated a new bionanocomposite film with both thermo-sensitive antioxidant and antimicrobial activities by the filling of a pectin matrix with functionalized Halloysite nanotubes (HNT) containing the essential peppermint oil (PO). The authors found that the prepared bionanocomposite films (pectin + HNT/CB[6]/PO) represented a potential and sustainable nanomaterial for food packaging applications with tunable antioxidant/antimicrobial activity.

**Figure 10.** Representation of pectin/HNT/PO films and its antibacterial activity against E. coli and S. aureus [69].

Recently, Massaro et al. [70] reported the successful chemical graft of curcumin on halloysite nanotubes and it’s tested as a dual-responsive prodrug for pharmacological applications. The obtained results highlighted that HNT-Cur prodrug induced high cytotoxicity (antiproliferative characteristics) towards two celllines of hepatocellular carcinoma respect to the pristine HNT or free curcumin. Also in this case, recycling studies proved that the HNT-Cur prodrug can be efficiently used in anticancer therapy without loss of antioxidant properties.

In addition, nanocomposites clay-polymer have been widely used for medical purposes, they have also played an important role in pharmaceutical preparations as excipients functioning as disintegrants, binders and diluents, anticaking agents and thickening, emulsifying, delivery modifiers of active agents and flavour correctors [71-73]. Numerous approaches have been interested in the employment of polymer-clay nanocomposites as transport carriers/vehicles for controlled loading and release of therapeutic molecules (drugs and genes), improving the dissolution profile of a drug and/or increasing the stability of the drug [71]. To evaluate the anticancer activity of modified halloysite, Serena et al. [74] functionalized the external surface of halloysite nanotubes with triazolium salts (f-HNT) and its use as a carrier for curcumin molecules delivery. The results obtained confirmed the encapsulation of curcumin.
species on the triazole moiety into the HNT surface and the drug encapsulation efficiency was
depended on pH of the medium.
In order to improve the carrying of doxorubicin (DOX) on breast cancer site, Yanping et al. [75] studied the conjugating of halloysite nanotubes with poly ethylene glycol and folate (HNTs-PEG-FA) and evaluated its use as a new nano-delivery system. The authors demonstrated that (HNTs-PEG-FA) were presented remarkable inhibition of proliferation and induction of death in MCF-7 cells with positive folate receptor (FR+). In another work, Zheru et al. [76] investigated the grafting of polyamidoamine onto halloysite nanotubes (PAMAM-g-HNTs) for loading of siRNA in order treat of breast cancer via gene therapy. It was found that the obtained PAMAM-g-HNTs showed enhanced cellular uptake efficiency of 94.3% compared with Lipofectamine 2000.
The first example of the chemotherapy study on functionalized bentonite nanoclay was reported by Faezeh et al. [77], who performed experiments on Doxorubicin (DOX) to develop a doxorubicin-bentonite nanoclay complex (DOX-Bent complex) for predicting the potential impact of new drug delivery vehicles on the localized chemotherapy of melanoma cancer. The authors demonstrated that DOX-Bent complex (DB-30:1) was found exclusively in the localized chemotherapy. In particular, Joanna et al. [78] studied the functionalization of Halloysite nanotubes with polyamidoamine dendrimer and its use as a carrier of three model therapeutic compounds-chlorogenic acid and salicylic acid. The results obtained demonstrated that polyamidoamine dendrimer functionalized halloysite nanotubes can be a good candidate for the fabrication of drug delivery systems. Mingxian et al. [79] reported the preparation of chitosan/ Halloysite nanotubes nanocomposite HNTs (HNTs-g-CS) via grafting reaction and investigated their impact as a nano-formulation for the anticancer drug curcumin. It was found that HNTs-g-CS exhibited maximum (90.8%) entrapment efficiency and (3.4%) loading capacity of curcumin, which are higher than those of raw HNTs.

Figure 11. Schematic illustration of the synthetic procedure for HNTs-g-CS (a) and the chemical structure of curcumin (b) [79].

5. Silylation of Kaolinite

Kaolinite is made up of a tetrahedral (T) and an octahedral (O) sheet, which form an anisotropic TO (1:1). Because of the strong Vander Waals forces and hydrogen bonds between adjacent layers of this mineral, it is difficult to directly access to Al–OH of interlayer space in most cases [80,81], and only hydroxyl groups at the edges or surface defects are availables for grafting reactions. To solve this problem, intercalation agents with high dipole such as dimethyl sulfoxide (DMSO) should be firstly intercalated into kaolinite interlayer before the subsequent silylation [82]. Tunney and co-workers [83,84] reported, for the first time, the covalent grafting of organic units, such as alcohols, on the interlamellar aluminum hydroxide sheet of kaolinite to form an aluminum alkoxide sheet (Al—O—C). The authors found that, the modification of the interlayers of kaolinite with methanol and ethylene glycol by first expanding the interlayers with DMSO or NMF and then treating at high temperatures (> 200 °C). The alcohols were grafted the hydroxyl surface of kaolinite through esterification reaction to form Kao—OMe (OEt) organoclay, which were resistant to thermal decomposition in N₂ atmospheres up to temperatures > 350 °C, and also to water hydrolysis.

Recently, several approaches were proposed to silylate kaolinite interlayer surfaces with organosilanes. Linna Su et al. [85] reported the successful silylation of kaolinite with APTES and its use as filler for the preparation of kaolinite/epoxy resin nanocomposites. According to these authors, this silylated kaolinite was specifically employed to improve the storage modulus and glass-transition temperature of the synthesised kaolinite/epoxy resin nanocomposites.

![Figure 12. Structure of functionalized kaolinite/epoxy resin nanocomposites with enhanced thermal properties [85].](image)

Tao et al. [86] studied the effect of silylated kaolinite (KGS) on the curing kinetics of cycloaliphatic epoxy/anhydride system. For this purpose, kaolinite was modified with APTES and the influence of KGS on the curing kinetics of cycloaliphatic epoxy resin was investigated by non-isothermal differential scanning calorimetry at different heating rates. The results led the researchers to suggest that the APTES grafting reactions consume the –OH groups of kaolinite and lead to a decrease in the catalytic efficiency of KGS in the curing of epoxy resin. On the other hand, Zhang et al. [87] were the first to synthesise a novel biodegradable nanocomposite by combining poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBHHx)
and silylated kaolinite though silane linkage. It was demonstrated that the new hybrid nanomaterial showed a significant improvement in its mechanical properties compared to others samples. The loading of silylated kaolinite into PHBHHx polymer matrix caused a marked increase in the toughness and tensile strength from 2.6 to 4.2 MPa and 18.2 to 23.5 MPa, respectively. In addition, the use of Silane-grafted kaolinite (SMKS) as reinforcing nanomaterials for styrene butadiene rubber (SBR) was also done by Zhang et al. [88]. They emphasized on the thermal and mechanical properties. Their findings showed that the nanocomposites SMKS-rubber exhibited a great enhancement in both thermal and mechanical properties compared to samples filled with unmodified kaolinite (ORK).

In a different study by Yuan et al. [89] modified the calcined kaolinite nanoparticle surface via stepwise method using 3-glycidoxypropyltrimethoxysilane (GPS) and dodecylamine. They conducted the controlling of silylation of kaolinite nanoparticle by varying the amount of GPS under almost anhydrous condition. The results proved that the final modified kaolinite, containing both hydrophobic and hydrophilic groups, had produced a more homogeneous dispersion in low polar as well as polar solvents, respectively. However, Duarte-Silva et al. [90] studied the structural and textural properties of metakaolinite and modified kaolinite with tert-butyldimethylchlorosilane and its use as adsorbents for three different proteins such as; α-lactalbumin (A-LA), bovine serum albumin (BSA) and β-lactoglobulin (B-LG). The results showed that Meta–kaolinite had a good retention capacity for A-LA and B-LG, while silylated kaolinite presented a high adsorption capacity for BSA and A-LA at room temperature and pH = 5. In a more recent study, Díaz et al. [91] investigated the effect of kaolinite surface functionalized with tert-butyldimethylchlorosilane (TBSCI) and 3-aminopropyltriethoxysilane (APTES) on protein (bovine serum albumin BSA) adsorption performance. They have proved that the functionalized kaolinite considerably improved its protein (BSA) removal capacity.

**Conclusion**

We here summarized the main properties and related multifunctional applications of silylated clay minerals that have recently been reported in the literature. External, internal surfaces and silanol groups at broken edges of 2:1 clay minerals (smectite) have been chemically modified by silylation reactions using various organosilanes. For 1:1 clay minerals (kaolinite), pre-incorporation with polar compounds is an indispensable step before the further silane grafting. As proved in the literature, the silylated clay minerals are applicable in numerous fields, such as supports of nanoparticles, nanofillers and adsorbents etc.

Controlling surfaces reactivity, choosing silane coupling agents and designing silylation process according to diverse purposes, development of promising nanocomposites based on silylated clays with high performances for potential applications, which are further investigation.

**References**


