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Nanoclay Reinforced Polymer Composites

Nanocomposites and Bionanocomposites

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Editors

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To Our Parents

Parents of Dr. Mohammad Jawaid
Ziaur Rahman (Father)
Late Razia Rahman (Mother)

Parents of Dr. Abou el Kacem Qaiss
Mohammed Qaiss (Father)
Khadija Ghazouli (Mother)

Parents of Dr. Rachid Bouhfid
Lahcen Bouhfid (Father)
Khadija Lograi (Mother)

Preface

Nowadays nanoclay-based polymeric materials display better utilization in different applications. The nanoclay as inorganic fillers results from the exfoliation or the dispersion at nanoscale into polymeric matrices, which allows the improvement of nanocomposites properties by adding small quantities of clay due to the high specific area and the possibility to reach an affinity between the nanoclay and the polymeric matrix. Recent studies reported about fabrication and characterization of nanoclay-based nanocomposites and bionanocomposites, which illustrated better mechanical and thermal properties as compared to nanoclay-reinforced polymer composites. The proposed book is focused on nanoclay-based nanocomposites and bionanocomposites fabrication, characterization, and applications. It will also include the classification of the clay which can be nano-sized, chemically modified, processing techniques of the nanocomposites based on nanoclay. The readers will find complete information about nanoclay modification and functionalization, modification of nanoclay systems, characteristic properties of nanoclay and nanoparticulate-based nanocomposites, modification of nanoclay systems, geological and mineralogical research on clays suitability, role of various polymers and shape of nanoclays on bionanocomposites, effect of nanoclays on gas barrier properties of polymers and co-polymers nanocomposites and different properties of tropical wood polymer nanocomposites, bionanocomposites based on modified montmorillonite and nanocrystaline cellulose, synthesis of natural rubber/palygorskite nanocomposites, hybrid polymer layered silicate nanocomposites, mechanical and thermal properties of halloysite nanotube based nanocomposites, nanoclay-based hybrid composites for advanced functional materials, 3D Smart Materials, biodegradable nanocomposites for soil erosion mitigation and nanoclay reinforced three-phase sandwich composite laminates.

We are highly thankful to all authors who contributed book chapters and provided their valuable ideas and knowledge to this edited book. We attempt to gather all the scattered information of authors from diverse fields in nanoclay-based

nanocomposites and bionanocomposites and finally produce this venture that will hopefully become a success. We greatly appreciate contributors' commitment to support us in formulating ours idea in reality.

We thank Springer Science+Business Media Singapore Pte Ltd. team for their generous cooperation at every stage of the book production.

Serdang, Malaysia   Mohammad Jawaid
Rabat, Morocco   Abou el Kacem Qaiss
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About the Editors

Dr. Mohammad Jawaid is currently working as Fellow Researcher (Associate Professor), at Biocomposite Technology Laboratory, Institute of Tropical Forestry and Forest Products (INTROP), Universiti Putra Malaysia, Serdang, Selangor, Malaysia and also Visiting Professor at Department of Chemical Engineering, College of Engineering, King Saud University, Riyadh, Saudi Arabia since June 2013. He is also Visiting Scientist to TEMAG Laboratory, Faculty of Textile Technologies and Design at Istanbul Technical University, Turkey. Previously he worked as Visiting Lecturer, Faculty of Chemical Engineering, Universiti Teknologi Malaysia (UTM) and also worked as Expatriate Lecturer under UNDP project with Ministry of Education of Ethiopia at Adama University, Ethiopia. He received his Ph.D. from Universiti Sains Malaysia, Malaysia. He has more than 10 years of experience in teaching, research, and industries. His areas of research interests include hybrid-reinforced/filled polymer composites, advanced materials: graphene/nanoclay/fire retardant, lignocellulosic-reinforced/filled polymer composites, modification and treatment of lignocellulosic fibers and solid wood, nanocomposites and nanocellulose fibers, polymer blends. So far he has published six books, 14 book chapters, and more than 140 international journal papers and five published review papers under Top 25 hot articles in science direct during 2013–2015. He is also the Deputy Editor-in-Chief of Malaysian Polymer Journal and Guest Editor of Special issue-Current Organic Synthesis & Current analytical chemistry, Bentham Publishers, UK. Besides he is also reviewer of several high-impact ISI journals of Elsevier, Springer, Wiley, Saga publishers. Presently he is supervising 15 Ph.D. students and five Master students in the field of hybrid composites, green composites, nanocomposites, natural fiber-reinforced composites, etc., and three Ph.D. and two Master students have graduated under his supervision in 2014–2015. He has several research grants at University and National level on polymer composites of around RM 575,000 (USD 159, 722). He also delivered plenary and invited talks at international conferences related to composites in India, Turkey, Malaysia, Thailand, and China. He is also member of technical committee of several national and international conferences on composites and materials Science.

Dr. Abou el Kacem Qaiss is currently working as Director of polymer processing laboratory, at Moroccan Foundation for Advanced Science, Innovation and Research (MAScIR), Institute of Nanomaterials and Nanotechnology (Nanotech), Rabat, Morocco since october 2010. He received his Ph.D. from Université Laval, Québec, Canada. He has more than 20 years of experience in teaching, research, and industries. His areas of research interests include hybrid-reinforced/filled polymer composites, advanced materials: graphene/nanoclay, lignocellulosic-reinforced/filled polymer composites, modification and treatment of lignocellulosic fibers, nanocomposites and nanocellulose fibers, polymer blends. So far he has published one book, four book chapters, and has published more than 30 international journal papers during 2011–2015. He is also reviewer of several high-impact ISI journals of Elsevier, Springer, Wiley publishers. Presently he is supervising four Ph.D. students in the field of hybrid composites, green composites, nanocomposites, natural fiber-reinforced composites, etc., and four Ph.D. and six Master students graduated under his supervision during 2012–2015. He has research grants at MAScIR and Minister of Higher Education, Scientific Research and Training, Morocco (MESRSFC) of around USD 690000. He was a co-chair of the International Polymer Processing Society Meeting (PPS-27) that was held for the first time in Africa and in the MENA region (Middle East and North Africa), in the City of Marrakech, Morocco, during May 10–14, 2011.

Dr. Rachid Bouhfid is a researcher at Moroccan Foundation for Advanced Science, Innovation and Research (MAScIR), Institute of Nanomaterials and Nanotechnology (NANOTECH), Rabat, Morocco. He obtained his Ph.D. in Organic Chemistry under the supervision of Mohammed V. Following his Ph.D., he joined Artois University, France as ATER, and then became Assistant Professor. Dr. Rachid Bouhfid's research are mainly in the field of organic synthesis of functional molecules to use them as modifiers of inorganic fillers and the development of new polymeric nanocomposites based on clay and nanoclay, graphene and natural fibers. He is author/coauthor of more than 65 international scientific publications, one book, four book chapters, and more than 12 patents. He is also reviewer of several high-impact ISI journals of Elsevier, Springer, RSC, Bentham Science, etc. He has co-organized several international conferences in the field of heterocyclic chemistry (Trans Mediterranean Colloquium on Heterocyclic Chemistry TRAMECH-7, Rabat, 2013) and polymer processing (The International Polymer Processing Society Meeting PPS-27, Marrakech, 2011).

Nanoclay Modification and Functionalization for Nanocomposites Development: Effect on the Structural, Morphological, Mechanical and Rheological Properties

Marya Raji, Mohamed El Mehdi Mekhzoum, Abou el Kacem Qaiss and Rachid Bouhfid

Abstract During the last decades, a widespread research has been devoted to organically modified clay minerals as reinforcements for polymer matrices. The most commonly used procedure to prepare organophilic clay is the cation exchange reaction with ammonium surfactant. Nevertheless, this kind of surface modification does not provide an efficient covalent bond between clay minerals and polymer matrices. For these reason, wide variety of silane coupling agents has been used to achieve compatibility and good dispersion between the hydrophilic clay and hydrophobic polymer. In this respect, the obtained polymer/organoclay nanocomposites exhibit significant improvements in their physical and mechanical properties over those of raw polymers. Herein, this chapter is divided into two parts. In the first part, it focus on the effect of silane modification of different clays minerals namely Halloysite, Montmorillonite and Sepiolite by various organosilanes such as 3-aminopropyltrimethoxysilane (A), 3-iodopropyltrimethoxysilane (I), 3-mercaptopropyltrimethoxysilane (S) and triethoxyvinylsilane (T). Although the silylation method, characterization and properties of the silane grafted clays are discussed. The second part is devoted to the preparation of polymer/silane grafted clay nanocomposites by melt compounding using polypropylene as polymer matrix. From the nanocomposites with 3wt% concentration in terms of silane grafted clay produced, the morphological, physical, mechanical, and rheological properties were measured. The results showed that the overall properties of silane grafted clays nanocomposites were increase which is attributed to better interfacial adhesion.

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1 Introduction

Because of the surge in the field of nanotechnology, polymer matrix based nanocomposites have recently become a promising current research field in the worldwide. These new kinds of materials have attracted steadily growing interest in numerous industrial applications, mainly in the transportation sector, building/ construction industries and food packaging plastics (Galpaya 2012). They often exhibit remarkable properties, including unique mechanical and electrical conductivity, high gas and liquid barrier, flame retardant and thermal properties as compared to the neat polymers (Yeh and Hwang 2006).

The development and progression of environmentally friendly/green nanocomposites materials, will not only benefit on the plastic industry, but would lead to reduce the percentage of the expensive polymer used in the manufacture of materials, such as polypropylene, polyacrylic, polyester and epoxies etc. (Alonso et al. 2012). They are hazardous to the environment, non-degradable and take a long time to decompose, which generates huge many environmental problems associated with their disposal, including damage to the environment eco-system, water supplies, and sewer systems as well as to the lakes, rivers and streams. Furthermore, they are non-renewable; and their high price and unstable with impending depletion of petroleum resources (Majeed et al. 2013).

The incorporation of nano-sized particles in the polymer nanocomposites can reduce their production cost, through the substitution of small amount of polymer by a cheap and abundant resource may be organic or inorganic include layered materials such as graphite, and some clay types, or fiber-like materials namely carbon nano-tubes and nano-fibers, cellulose nano-fibers or other types of clay (Šupová et al. 2011). Among these particles loading, the different kinds of clay reinforcement have been proven an unavoidable synergistic impact on the overall performance of the nanocomposites, due to its special structure, which are most thermally stable and it arranged on the nanometer scale with a high aspect ratio and/or an enormously large surface interface with polymer. In this regard, the low cost, less weight, and low moisture absorption and also the low density makes the clay an attractive alternative to organic or petrochemical-based loading (El Achaby et al. 2013).

Since, discovered the possibility to build a polymer clay nanocomposite in the late 1980s (Nguyen and Baird 2007). Several investigations have also been conducted regarding on the development of new advanced and find further applications. The Toyota Research team began the investigations into reinforcing polymers; they found that the incorporation of moderate mineral clay charge into Nylon 6 marked the stimulus for subsequent theoretical and applied over the last decades, followed by Vaia observations (Vaia et al. 1993), that reported it is

possible to melt mixing polymers and clays without organic solvents. These two important results have motivated both academic and industrial labs to focus their attention on the polymer/clay nanocomposites.

2 Clay Minerals: Structure, Properties and Applications

To fully understand the effect of clay reinforcement on the polymer matrix properties, it is important to highlight the clay definition and their structure. The term clay mineral is difficult to define. From chemical point of view, this term signifies a class of the broad category of hydrated phyllosilicates, likewise, based on geological knowledge, this clay making up the fine-grained fraction of rocks, sediments, and soils (Velde 1985). Far from this definition which create some ambiguity until the moment, and for roughly speaking, clay minerals are essentially hydrous aluminosilicates with very fine particle size and a general chemical formula $(Ca, Na, H)(Al, Mg, Fe, Zn)_2(Si, Al)_4O_{10}(OH)_{2-x}H_2O$, where x represents the variable amount of water. Generally, the clay minerals may be broadly classified into two categories: natural and synthetic clays Include Montmorillonite, Hectorite, sepiolite, laponite, saponite, rectorite, bentonite, vermiculite, biedellite, kaolinite, chlorite, as a natural clays and the synthetic one such as various layered double hydroxides, synthetic Montmorillonite, Hectorite, etc. (Kotal and Bhowmick 2015). Figure 1 summarizes the major class of clay.

Generally, The different structures of clay minerals are basically composed of alternating of tetrahedral silica sheets "SiO_2" and alumina octahedral layers "AlO_6" in ratios of 1:1 when one octahedral sheet is linked to one tetrahedral sheet as Kaolinite, Halloysite, or in ratios of 2:1 this structure created from two tetrahedral sheets sandwiching an octahedral sheet such as Montmorillonite and Sepiolite, finally the proportion of 2:1:1 (chlorite), this latter are not always considered as
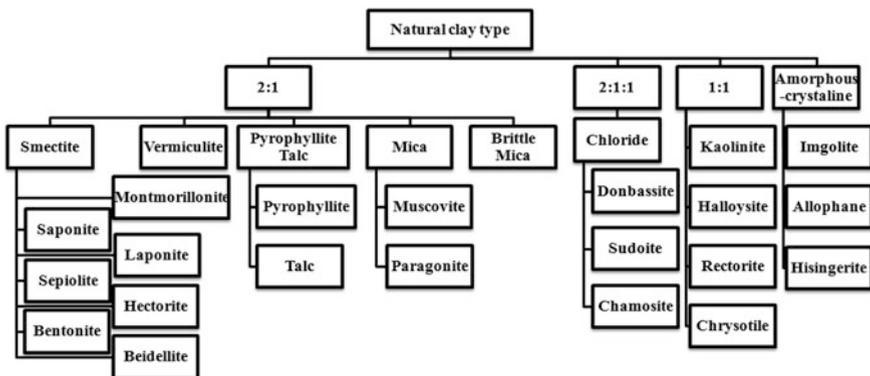
Fig. 1 Natural clay type

clay, sometimes being classified as a separate group within the phyllosilicates (García-López et al. 2010). One side of this lamella remains linked to each other through common oxygen atoms as seen in Fig. 2.

In consequently, the clay platelet undergoes a structural rearrangement to give different structures (nano-fibers, nano-tubes, and plate-like filler) as presented in Fig. 3.

The physical dimension of each platelet may be about 1 nm in thickness and the lateral dimension is varied from 30 nm to several micrometers or even larger, depending on particular silicate, due to an isomorphic substitution of alumina cation (Al^{3+}) within the silicate layers (Nguyen and Baird 2007). For example, in the case of 2:1 structure, the trivalent Al-cation in the octahedral layer is partially substituted by the divalent Mg-cation to form the Montmorillonite structure, given to each layer a net negative charge generated by their difference in valence (Paul and Robeson 2008). The negative charge is counter balanced by the interlayer alkali or alkaline earth metal cation as sodium and calcium ions, when these charges do not balanced and these ions do not fit in interlayer space, the mica will be formed and/or the layers organize themselves to form clay stalks and held together by relatively weak bonding forces of attraction between them as van der walls force, interstitial water and other polar molecules can placed inside the galleries, these latter can be then able to replace by organic cations, via a cationic-exchange reaction in the synthetic

Fig. 2 Clay structure

Fig. 3 Clay structures (nano-fibers, plate-like filler, and nano-tubes)

rout to transforms the hydrophilic-clay organophilic (Taxiarchou and Douni 2014). The gallery or the interlayer space of each kind of expansible clay is depend on the size and type of charge compensating cation and polar molecules on interior surfaces within the crysta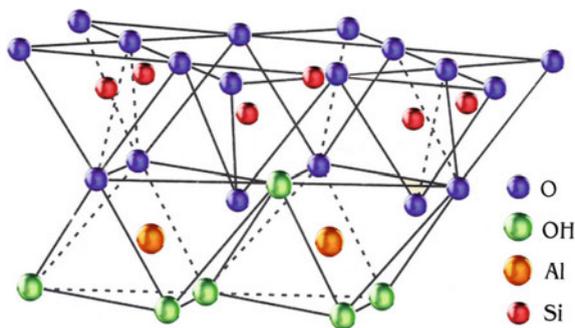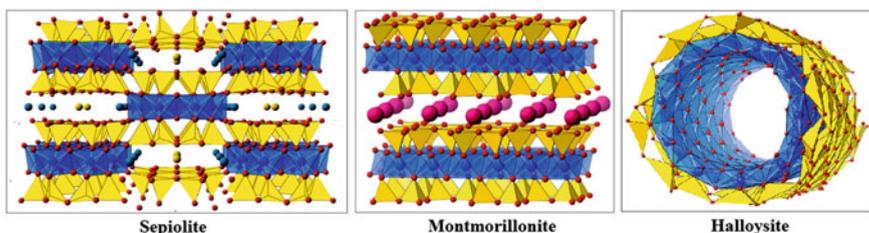l clay structure itself, their presence on the basal planar rendering the clay hydrophilic in the nature (Bergaya and Lagaly 2013). Expansion of the space between two consecutive layers termed interlayers space, imparts high cation exchange capacity (CEC) relative to non-expansible phyllosilicates and most other secondary minerals (Yui et al. 2013).

Cation Exchange Capacity (CEC) is found to be an approximate measure of the amount of readily exchangeable cations neutralizing negative charge in the clay. Otherwise, it designed the capacity of the clay to hold cations, like Al^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Zn^{2+}, Cu^{2+}, Fe^{2+}, Na^+, K^+ and H^{+14}, it usually expressed formerly as milliequivalents per 100 g (meq/100 g), the CEC value differs from one clay to the other (Yui et al. 2013). A comparison of CEC values for some clay variety is provided in Table 1.

There are many methods available to determine the cation exchange capacity (CEC) of clay; any one is reliable employed for all clay powder. However, one possible technique that is used more effectively for all clay types is not dependent on the pH of saturation but is based on cation saturation, primarily the ammonium, sodium, and barium etc. as the index cation (Sanchez-Martin et al. 2006).

One main potential advantage of cation present between the clay layers is to be able therefore effectively replaced by organic cationic surfactant molecules, leads to renders clay useful in the large part of human existence (Hoidy et al. 2009). The initial application of clay minerals was more than 5000 years ago, for rheological additives, as thickeners in coating products, glues, platisols, drilling fluids and for wastewater treatment organoclays are used as thickeners in paints, greases, oil-base drilling muds, polymer composites and nanocomposites also for the purpose of gelling various organic liquids (Hoidy et al. 2009). Although there has been much work in the field of polymer/clay nanocomposites since their appearance (Liu and Wu 2001; Zeng et al. 2005; Mansoori and Hadi 2015), that will be detailed in the next paragraph.

Historical examples of clay nanocomposites applications are abundant in literature. Since antiquity, when Johnston had develop the fundamental concept of active sites and had also identified all the types of sites contributing to clay interaction with other substances, as in organoclays synthesis, include "broken edge" sites and exposed surface aluminol and silanol groups, isomorphic substitutions, exchangeable cations, hydrophobic silanol surfaces, hydration shell of exchangeable cations, and hydrophobic sites on adsorbed organic molecules (Rytwo 2008). The clay minerals become attractive to researchers, engineers and scientists as charge in many polymer industrial applications for commercial use. Thus, the era of clay/polymer nanotechnology can truly be said to have begun. The initial commercial application of clay nanocomposites was the use of clay, especially the Montmorillonite clay system to reinforce nylon-6 nanocomposites (He et al. 2010), used then as timing belt covers for Toyota cars, in collaboration with Ube in 1990 (Gao 2004). Unitika become the second producer of nylon-6 nanocomposites for

Table 1 Ranges of cation exchange capacities for clay

Clay types	Structure type	CEC (meq/100 g)	d-spacing (Å)	Chemical formula	R
Kaolinite	1:1(TO)	3–15	7.14	$[Si_4]Al_4O_{10}(OH)_8 \cdot nH_2O$ (n = 0 or 4)	(Alkan et al. 2005)
Halloysite	1:1(TO)	5–50	7	$[Si_4]Al_4O_{10}(OH)_8 \cdot nH_2O$ (n = 0 or 4)	(Sánchez-Fernández et al. 2014)
Illite	2:1(TOT)	10–40	10	$M_x[Si_{6.8}Al_{1.2}]Al3Fe_{0.25} Mg_{0.75}O_{20}(OH)_4$	(Euigyung et al. 2011)
Chlorite	2:1:1(TOT)	10–40	14	$(Al(OH)_{2.55})4[Si_{6.8}Al_{1.2}] Al_{3.4}Mg_{0.6}O_{20}(OH)_4$	(Bergaya and Lagaly 2013)
Montmorillonite	2:1(TOT)	60–150	12.4–17	$M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$	(Navrátilová et al. 2007)
Vermiculite	2:1(TOT)	100–150	9.3–14	$M_x[Si_7Al]Al_3Fe_{0.5} Mg_{0.5}O_{20}(OH)_4$	(Kotal and Bhowmick 2015)
Hectorite	2:1(TOT)	120	12.4–17	$M_x(Mg_{6-x}Lix)Si_8O_{20}(OH)_4$	(Nguyen and Baird 2007)
Saponite	2:1(TOT)	86.6	12.4–17	$M_xMg_6(Si_{8-x}Alx)Si_8O_{20}(OH)_4$	(Hussain et al. 2006)
Sepiolite	2:1(TOT)	11–12	12	$Mg_4 Si_6 O_{15} (OH)_2 \cdot 6(H_2O)$	(Santos and Boaventura 2008)

engine covers on Mitsubishi's GDI engines in 1996 by using synthetic mica as the nano-fillers (Hussain et al. 2006). After that Chevrolet Impalas developed doors with thermoplastic polyolefin nanocomposite (TPO) (Hussain et al. 2006). This was followed by the announced of a step assistant component for GMC Safari and Chevrolet Astro vans16 as the first application of clay/polyolefin nanocomposites of General Motors and Basell (Tjong 2006). More recently, Noble Polymers has developed clay/polypropylene nanocomposites for structural seat backs in the Honda Acura17, while Ube is developing clay/nylon-12 nanocomposites for automotive fuel lines and fuel system components; the following table summarizes some commercial polymer nanocomposites (Gao 2004).

As summarized in the Table 2, the clay nanocomposites are really commonly used in the wide plastic industry due to its attractive versatility in terms of properties, precisely the synthetic one named organoclay, for instance, the great mechanical nanocomposites (tensile, stress, strain) properties together with a high thermal stability (Singla et al. 2012). The clay nano-fillers also can reduce the gas and liquid permeability (Soheilmoghaddam et al. 2014). Moreover, it can improve the dynamic mechanical performances, as well as the flame retardancy while retaining optical clarity of pure polymer (Ahmed Ben Hassan et al. 2014). Finally, the low cost and density, even at low filler loading (Pavlidou and Papaspyrides 2008).

As already mentioned in last paragraphs, there are six kinds of active sites which are important for explaining the mechanism during the synthesis of an organoclay (Pavlidou and Papaspyrides 2008). This reaction called functionalization is based on the interaction between clay minerals surface and organic components named surfactant through three different possible arrangements for their attachments to clay particles; firstly; the surfactant cations may are intercalated into the interlayer spaces by way of cation exchange and adhere to surface sites via electrostatic bonding-charge interaction, secondly; the surfactant cations and/or molecules are physically adsorbed onto the external surfaces of the particles to better coating the clay particles and finally; the surfactant molecules are located within the interlayer spaces (Pavlidou and Papaspyrides 2008). The studies on the organic surfactant grafted clay have been conducted after the introduction of X-ray diffraction in 1913 using different types of surfactant include (de Paiva et al. 2008): Anionic Surfactants, Nonionic, Cationic ones, and finally a single surfactant molecule display both anionic and cationic dissociations it is called amphoteric or zwitterionic.

These organic components can attach to the clay particles by different way is in depend on clay structure, the first one, is as organic surfactant which goes via ion exchange presented between clay layers (generally sodium and calcium ions) resulting in occupation of an interlayer space of the clay structure by organic molecules that hold positive chains and that will neutralize the negative charges from the clay layers (Beauvais et al. 2009). In order to introduce hydrophobicity and increase the clay basal space, which facilitate their exfoliation in the matrix and also improve the compatibility between the hydrophilic clay and hydrophobic polymer during extrusion. This clay modification called as organomodification, or also organophilization (Mejía et al. 2013). The second way of organic components attachment is as a compatibilizing agent if the clay structure does not contain an

Table 2 Commercial polymer nanocomposites. (Zeng et al. 2005)

Product	Characteristics	Applications	Producer
Nylon nanocomposites	Improved modulus, strength, heat distort temperature, barrier properties	Automotive parts (e.g., timing-belt cover, engine cover, barrier fuel line), packaging (e.g., cosmetics, food, medical, electronics), barrier film	Bayer, Honeywell Polymer, RTP Company, Toyota Motors, Ube, Unitika
Polyolefin nanocomposites	Stiffer, stronger, less brittle, lighter, more easily recycled, improved flame retardancy	Step-assist for GMC Safari and chevrolet Astro vans, heavy-duty electrical enclosure	Basell, Blackhawk Automotive Plastics, General Motors, Gitto Global Corporation, Southern Clay Products
M9™ Mitsubishi's MXD6 nylon	High barrier properties	Juice or beer bottles, multi-layer films, containers	Mitsubishi Gas Chemical Company
ORMLAS	High barrier performance, impact resistance, flame resistance, high clarity	Long-life food tray	Triton Systems
Durethan KU2-2601 (nylon 6)	Doubling of stiffness, high gloss and clarity, reduced oxygen transmission rate, improved barrier properties	Barrier films, paper coating	Bayer
Aegis™ NC (nylon 6/barrier nylon)	Doubling of stiffness, higher heat distort temperature, improved clarity	Medium barrier bottles and films	Honeywell Polymer
Aegis™ OX (nanoclay nylon 6 resins)	Highly reduced oxygen transmission rate, improved clarity	High barrier beer bottles	Honeywell Polymer
Aegis HFX	Highly reduced oxygen transmission rate	High barrier juice, tea, and condiments bottles	Honeywell Polymer
AEGIS CSD	High level of a passive carbon dioxide barrier	High barrier bottles weight	Honeywell Polymer
Specialty Film	Excellent barrier properties to oxygen, flavors, and aromas Provide toughness, strength, tear, and puncture resistance, and resistance to grease and gas penetration	Packaging applications: meat, fresh red meat, poultry, fish, cheese, dried food, and chilled fruit juices	Honeywell Specialty Polymers

(continued)

Table 2 (continued)

Product	Characteristics	Applications	Producer
SET™ nanocomposite nylon 12	Improved stiffness, permeability, fire retardancy, transparency and recycling	Catheter shafts and balloons, tubing, film and barriers, flexible devices	Foster Corporation
Forte™ nanocomposite	Improved temperature resistance and stiffness, very good impact properties	Automotive, furniture, appliance	Noble Polymer

exchangeable cation, which is a graftization of the chemical element that has reactive groups compatible with another reactive groups existing on polymer chain to form the nanocomposite (Ferreira et al. 2011). The overall properties of the nanocomposites based on modified clay characteristics, commonly related on organic molecular mass, type and content of functional groups, organic components/clay proportion, and the manufacturing method (Lee et al. 2012). Among others, the chemical composition and the chain length of the functional groups that interact with the surface of the clays may improve many nanocomposites performance (Xie et al. 2010). The renowned using organic functional groups are Ammonium, phosphonium, imidazolium, Pyridinium, Sulfoniom, and the organosilanes (Leszczyńska et al. 2007). Amongst these latter the organosilanes are known as most favorable compatiblizers or coupling agents for clay fillers because they generally used for providing covalent bonding between clay fillers and polymer matrices, which enhance their interfacial adhesion, and then improve the mechanical properties of the nanocomposites (Sánchez-Fernández et al. 2014). A brief overview on organosilane chemistry and silylation of clay mineral is given below.

3　Oragnosilane Chemistry

Silicon is an essential element which has received a great attention due to is remarkably reactivity and its variety bonding possibilities (Bissé et al. 2005). Silicon is the second most ubiquitous element after oxygen, first, discovered in 1824 by Berzelius (Berzelius 1824). In fact, it is naturally found in the silica (SiO_2) or silicate forms (SiO_4) (Mai and Militz 2004). Silicon as a member of Group 14 in the periodic table shares numerous common characteristics with carbon, but also exhibits different chemical reactivity compared to carbon. Besides, much like carbon atoms, silicon can form four stable bonds with itself and other atoms. In contrast, silicon is more electropositive than carbon, which is much more susceptible of very special and unique chemical reactions. Owing to its dual reactivity, silicon molecule can be synthesized with the ability to bond both organic and

inorganic reactivity (Witucki 1993). Therefore, the unique chemical properties and performance characteristics of silicones give rise to variety of infinite silicon-based materials containing hybrid system of silicon/carbon known as 'Organosilane' (Verdejo et al. 2008).

Historically, it was not until 1907 that Kipping and coworkers reported the first synthesis of organosilane. They initially used organozinc, followed by Wurtz-type coupling (Na), before the use of the famous Grignard reagents to make the silicon-carbon bond as shown in Scheme 1. In 1943, Dow Corning Company began commercial development of organosilane technology, opening a new world in silicone chemistry and applications (Thomas 2011). In order to understand the interaction mechanisms between silane and clay minerals called "silylation", it is first necessary to look on the chemical structure of organosilane as coupling agent. See Scheme 1.

A silane is a monomeric silicon chemical similar to hydrocarbon. It has chemical formula $(R_1R_2R_3R_4)Si$ in which four chemical groups attached to the silicon atom. These groups can be the same or different, inorganic or organic and reactive or nonreactive (Halvorson et al. 2003). To be classified as an organosilane, at least one silane substituent must be an organic group linked to silicon through Si–C bond. Alternatively, organosilanes are currently available and unique class of organic silicon compounds; they can be classified according to their molecular and spacial structures. Organosilanes characterized by the $(R_1R_2R_3)SiX_n$ formula where n can have a value between 1 and 3, they possess a hydrolytically sensitive silicon based functional group SiX_n. Organosilanes compounds can form a variety of different hybrid organic-inorganic structures; they can react with other silanes, with themselves and with both inorganic and organic substrates via complex hydrolysis/condensation reactions. The R groups in organosilanes can be either nonreactive (hydrocarbon chain) or reactive substituent with terminal organofunctional groups (methacrylate, epoxy). These latter types of organosilanes compounds are bifunctional molecules and are referred to as silane coupling agents (Plueddemann 1991). In general, silane-coupling agents can be represented by the chemical formula, $Y–(R_1R_2R_3)–SiX_n$ in which at least one of the organic substituents R_1, R_2 and R_3 has a reactive organofunctional group Y. The most common silane coupling agent structures are functional organotrialkoxysilanes ($Y–R–SiX_3$). Whereas sometimes, the trifunctional SiX_3 group can have only two or one X substituent namely

$$SiCl_4 \ + \ R_2Zn \longrightarrow SiR_4 \longleftarrow SiCl_4 \ + \ RMgBr$$

$$\uparrow$$

$$Na \qquad R = C_2H_5, C_6H_5$$

$$SiCl_4 \ + \ RBr$$
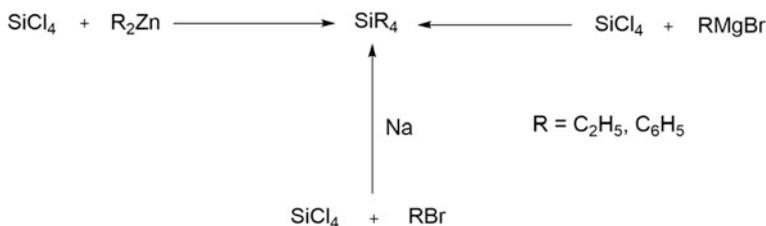
Scheme 1 Synthesis pathway for the preparation of organosilane compounds

Scheme 2 Different types of Functional organosilanes with varying numbers of hydrolyzable substituents on silicon

Trialkoxysilane   Dialkoxysilane   Monoalkoxysilane

Dipodal Silane
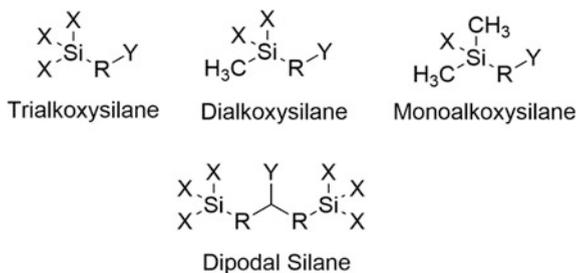
$Y–R_1R_2SiX_2$ and $YR_1R_2R_3SiX$ (Scheme 2). Silylating agents have usually three hydrolysable inorganic-reactive alkoxy groups, e.g., $–OCH_3$, $–OCH_2CH_3$, and one non-hydrolyzable organofucntional group such as amino, vinyl, mercapto. They have also an organo spacer group typically aryl or alkyl separates the organofunctional group from the silicon atom (Ishida and Kumar 1985). Typical commercial examples of silane coupling agents are illustrated in Table 3.

4 Silylation of Clay Minerals

As stated above, silane coupling agents are hybrid compounds with inorganic and organic constituents, they exhibit affinity for both organic and inorganic surfaces and act as a sort of intermediary to form a durable covalent bond between inorganic substrates (namely minerals, metals, cellulose and fillers) and organic polymer (such as thermoplastics or thermosets, rubber) (Weissenbach, Kerstin and Mack 2005). Figure 4 show the bifunctional silane coupling agent mechanism. Due to its unique dual reactivity, silylating agent can be useful for improving the adhesion between the two dissimilar materials (Matinlinna et al. 2013). Such silylating agent can find valuable application in the manufacture of pharmaceutical products, agro-chemicals and in electronics manufacturing (Blum 2003). In addition, any application where silane coupling agents are involved requires the silane molecule to be hydrolyzed and condensed.

Recently, silylation or silane grafting has proved to be an efficient way to modify clay minerals surfaces (Avila et al. 2010). Although, the interaction between hydrophobic molecules and clay could be greatly enhanced by simple grafting of hydrophibic silane groups onto the clay minerals (Takahashi and Kuroda 2011). As a result, the obtained silylation products exhibit suitable application in material science especially in polymer/clay nanocomposites (Isoda et al. 2000). In general, the interactions of silane coupling agents with clay minerals are mainly proceed through different steps. As shown in Scheme 3. Initially, the silane monomers react in the presence of water (hydrolysis) to form reactive, hydrophilic, acidic silanol groups Si–OH followed by partial condensation in which oligomers are formed; during the condensation, silane molecules react with each other forming dimers and

Table 3 Some Commercial silanes coupling agents with different organofunctional groups

Functional group	Chemical name	Structural formula
Epoxy	3-Glycidoxypropyltrimethoxysilane	
Amino	3-Aminopropyltriethoxysilane	
Mercapto	3-Mercaptopropyltrimethoxysilane	
Isocyanate	Tris-(trimethoxysilylpropyl) isocyanurate	
Chloroalkyl	3-Chloropropyltrimethoxysilane	
Diamino	Diaminopropyltrimethosysilane	
Methacryloxy	3-Methacryloxypropyltrimethoxysilane	
Vinyl	Vinyltrimethoxysilane	
Styryl	*p*-Styryltrimethoxysilane	
Acryloxy	3-Acryloxypropyl trimethoxysilane	

Fig. 4 Silane coupling agent mechanism
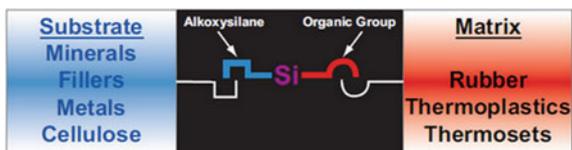
then condense to form siloxane oligomers. Next, the oligomers or monomers silanol are physically adsorbed to hydroxyl groups of clay minerals by hydrogen bonds on the clay surfaces. Finally, under dehydration condensation reaction a robust covalent bond –Si–O–Si– between silanols and hydroxyl groups of clays are formed during a drying process. Moreover, the covalent bond enables a durable
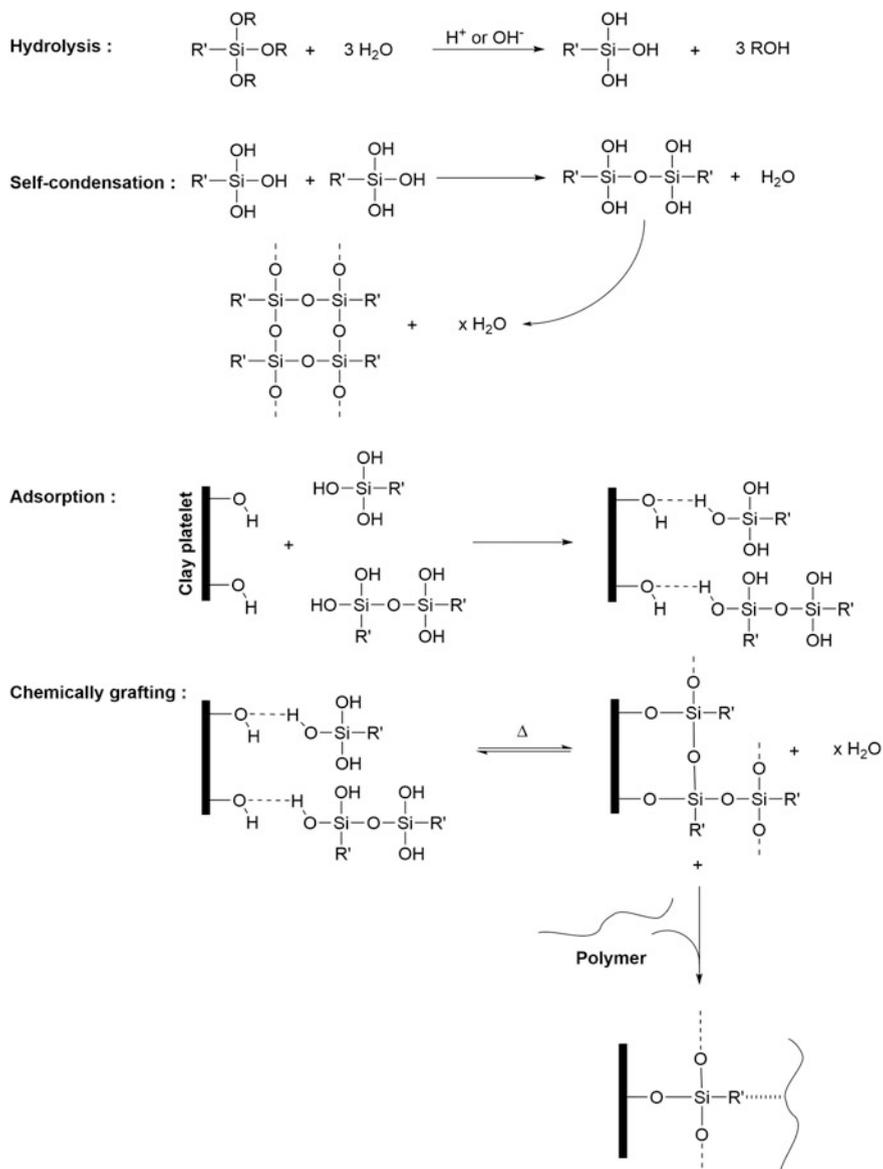
Scheme 3 A plausible mechanism of coupling reaction between silane grafted clay mineral and thermoplastic matrices

immobilization of the organic moieties in the silane grafted products which prevents their leaching into the surrounding solutions. In addition, the R' organofunctional group remains available can react with the polymer matrix, resulting in the

formation of a network among silane, clay mineral and polymer through covalent bonds. Therefore, the resultant polymer/clay nanocomposite exhibits a substantial improvement in their properties including mechanical, rheological and other handling properties (Shanmugharaj et al. 2006; Ha et al. 2007; Shen et al. 2007; Sánchez-Valdes et al. 2009). Certainly, the silanization of the clay mineral can take place at three basic models namely at the interlayer space, external surface and at the edges. The interlayer and edges grafting can increase the distance between the layers. For the external surface, the silylation has no effect on the basal spacing of the clay. Such successful silylation of clay minerals surfaces has been reported, in this case, a great attention was paid to the kind of silanes, the clay mineral structure as well as the influence of the solvents on the grafting reaction. In addition, the silanization reaction can also take place onto organoclay minerals to improve their compatibility with the polymer matrix (Park et al. 2004; Chen and Yoon 2005).

5 Preparation and Characterization of Silane Grafted Clay

In the present chapter, three different clay minerals were reported namely Montmorillonite lamellar structure, nano-fiber sepiolite and tubular Halloysite, a 1:1 layer silicate with rolled structural layers and interlayer water. Initially, the modifications of clays were carried out using four different commercial organosilanes. Although. Toluene was used as solvent for dispersing medium. Scheme 4 shows the chemical structure of the used silanes. Certainly, the choice of organosilane as coupling agent is determined by the nature and chemical structure of the thermoplastic matrices used. In our case, each silane differs by its organic functional groups such as vinyl (T), amino (A), iodo (I), and mercapto (S). These reactive groups can form chemical bonds with polymer materials. In addition, the interaction and the interfacial properties between polymer/clay depend on the type of the non-hydrolyzable organic moiety, which can affect the final macroscopic properties of the material obtained. The method of modifying clays presents; as an example; in this work has been performed in one step. The procedure consisted on dispersing an

Scheme 4 The schematic of the used silanes
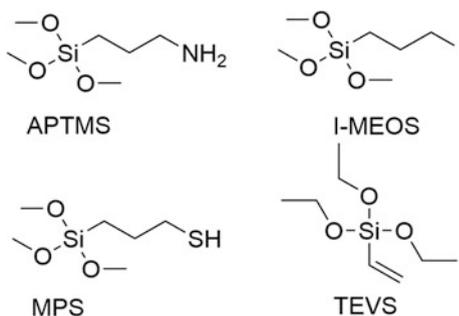
excess of clay (3 g) in 300 ml of toluene at 25 °C under constant stirring followed by sonication for at least 30 min. 3 ml of organosilane was introduced into the above-mentioned mixture and sheared for 24 h at 80 °C. After that, the modified clay was separated from solution by centrifugation at 10.000 rpm. The resultant product was washed using the mixture of ethanol/water for 3 times in order to remove the residual silane and dried at 60 °C in a vacuum oven. The final product was grinded and sieved before use.

5.1 X-Ray Diffraction (XRD)

Once the appropriate silane modified clays were prepared, a number of analysis techniques have been performed including XRD, FTIR, TGA analysis. First, XRD analysis was used to identify the chemical composition and crystallographic structure of the silane grafted clays. Figure 5 present the diffractograms of XRD of clay namely Halloysite, sepiolite and Montmorillonite as well as their four silane grafted -clays samples. As can be depicted from Fig. 5a, all diffractograms of the silane modified-Halloysite are almost identical and show no difference to the raw clays. The five solids are composed principally of two polymorphs of the bilaminar
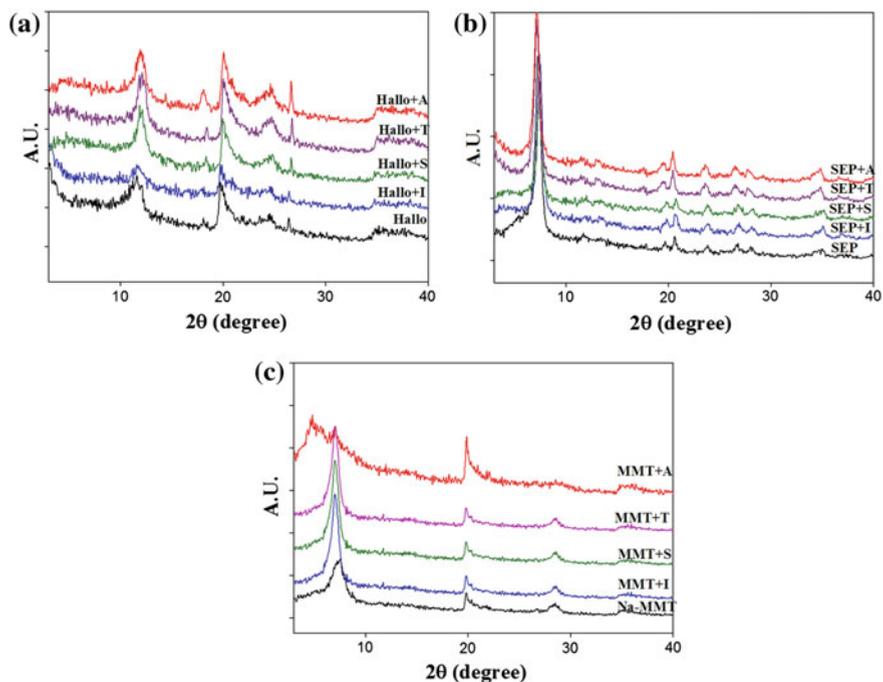

Fig. 5 XRD spectrum of montmorillonite, halloysite, sepiolite, and their silane grafted ones

clay (1:1) dioctahedral Halloysite, in the presence of SiO_2 and $Al(OH)_3$. In addition, both Halloysite-7A, and Halloysite-14A phases were identified. Therefore, during the process of silylation, the modification of Halloysite with different organosilanes did not cause any structural chemical changes compared to other clay minerals (Sánchez-Fernández et al. 2014). On the other hand, Fig. 5b show the XRD pattern of sepiolite which is affected by modification with organosilane. It can be seen that the intensities of some original peaks changed in the position range of 20–40 upon silylation. The variations in XRD diffractograms before and after the silylation of sepiolite show that there is a covalent bond formed by the interaction between sepiolite and different organosilanes, which can be confirmed by FTIR and TGA results (Belver et al. 2013). Figure 5c shows the XRD pattern of raw and silane grafted Montmorillonite. The MMT-A clay display a broad band around of $2\theta = 4.6°$. The interlayer spacing corresponding of the peak of MMT-Na around 1.21 nm which increased to 1.9 nm for the MMT-A clay, according to Bragg's equation (Eq. 1)

$$2\mathrm{dsin}\theta = n\lambda \tag{1}$$

where,

λ is the wavelength of X-Ray, θ is diffraction angle and d is interlayer distance.

It can be concluded that, after clay modification by the organosilane (A), the ATPES molecule was intercalated and grafted to interlayer surface silanol groups. It can be mentioned that d-spacing value indicates a monolayers or paraffin-type arrangement between the aluminosilicate layers. This intercalation constitutes an efficient way to increase surface hydrophobicity which is a fundamental prerequisite for good compatibility between the polymer matrix and the Montmorillonite surface (Shen et al. 2007). For the others silane grafted Montmorillonite spectrum exhibits a broad band in the region between $d = 1.31°$, $d = 1.32°$ and $d = 1.26°$ for MMT-T, MMT-S and MMT-I, respectively. No significant differences were observed in the basal spacing of the latter modified clays. This observation may indicate that there are no interlayers or edges grafting, therefore, the silylation take place at the surface of the Montmorillonite which can be verified by FTIR and TGA results.

5.2 Structural Characteristics (FTIR)

The FTIR spectra of raw clays and the silane grafted ones by A, I, S and T silane molecules are presented in Fig. 6. Figure 6a shows the FTIR spectra of the Halloysite skeleton, The transmittance bands at 3697 and 3623 cm^{-1} in the FTIR spectrum were assigned to the stretching vibration due to O–H stretching of inner-surface hydroxyl groups, O–H stretching of inner hydroxyl groups of the Halloysite, respectively (Frost and Vassallo 1996). The interlayer water is indicated by the H–O–H (adsorbed water) deformation band appears at 1635 cm^{-1} (Bobos et al. 2001). The 1113 cm^{-1} peak was assigned to the stretching mode of Si–O, while
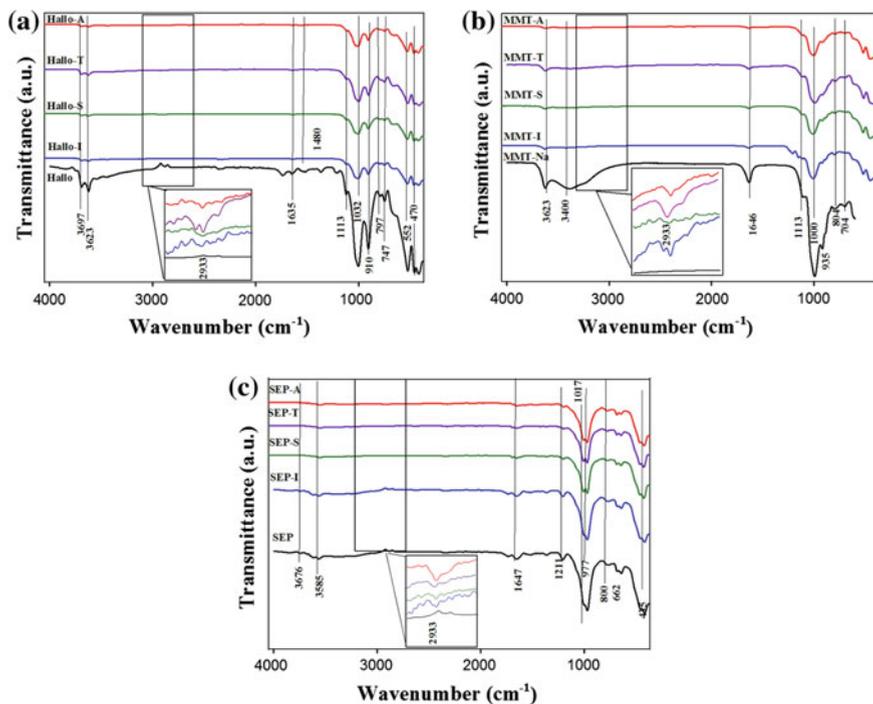
Fig. 6 FTIR spectra of montmorillonite, halloysite, sepiolite, and their silane grafted ones

the band at 1032 cm^{-1} was caused by the stretching vibration of Si–O–Si (Bordeepong et al. 2011). The O−H bending vibrations of the hydroxyl groups are observed at 910 cm^{-1} and Si–O–Si at 470 cm^{-1} confirm the existence of corresponding groups (Szczepanik et al. 2015). The bands attributed to the Al–OH vibrations of the surface hydroxyl groups are observed at 747 and 797 cm^{-1}. The band observed at 538 cm^{-1} was due to the vibration of Al–O–Si (Frost 1995). The Montmorillonite IR spectrum presented in Fig. 6b shows two important bands around 3623 and 3400 cm^{-1} which are indicative to O–H stretching for the silicate and water. The FTIR spectrum of clays, shows a band in the region of 1646 cm^{-1} which is attributed to the –OH bending mode of the adsorbed water (Xie et al. 2011). The characteristic band at 1113 cm^{-1} is assigned to Si–O stretching, and out-of-plane Si–O stretching mode of raw clays (Xie et al. 2011). The band at 1000 cm^{-1} is ascribed to Si–O stretching (in plane) vibration for layered silicates. The IR bands at 935, 804 and 704 cm^{-1} are attributed to Al–Al–OH, and Al–Mg–OH bending vibrations, respectively (Bhattacharya and Aadhar 2014). Figure 6c illustrates the FTIR spectrum of the sepiolite it shows the characteristic band at 3676 cm^{-1}, which is attributed to Mg–OH stretching of hydroxyl groups in octahedral Mg ions located in the interior blocks of natural sepiolite (Alan and İşçi 2014). The coordinated water corresponds of O–H stretching band appeared at 3585 cm^{-1}

and O–H stretching and deformation of zeolitic water bands observed for Sepiolite at 1647 cm^{-1} (Soheilmoghaddam et al. 2014). The Si–O coordination bands at 1211, 1017, 977 cm^{-1} are observed as a result of the Si–O vibrations (Ahmed Ben Hassan et al. 2014). The bands presented around 800 and 662 cm^{-1} are responsible from the O–H deformations and translations, respectively. The two peaks at 1017 and 435 cm^{-1} represent the stretching and bending of Si–O respectively in the Si–O–Si groups of the tetrahedral (Alan and İşçi 2014).

The FTIR spectrum of all silane grafted clays (sepiolite, halloysite and montmorillonite) detect other characteristic signals bands such as two weaker characteristics bands at 2933 cm^{-1} and at 2865 cm^{-1} attributed to aliphatic stretching of CH$_2$ and CH$_3$ groups, respectively. Another band at 1480 cm^{-1} which can be associated to the deformation vibration of CH$_2$ (Herrera et al. 2004), normally present in the mono- and the trifunctional silane molecules. Finally, the presence of silane in the all silane grafted clays spectrum is confirmed, which implies that silane has been grafted into the Montmorillonite, Halloysite and sepiolite structure.

5.3 Thermogravimetric Analysis (TGA)

The thermal degradation of the raw and silane grafted clays were evaluated by thermogravimetric analysis (TGA) to compare the degradation profiles of the different types of clay used as essential parameter in the choice of the technical applications of nanocomposite materials. The thermal decomposition of raw clays and the silane grafted ones by A, I, S and T silane molecules are superposed in Fig. 7. Firstly, the decomposition curves of the raw and silane grafted Halloysite can be divided in three steps as described in the following paragraph. Figure 7a shows the first weight loss for raw Halloysite in the range of 40–140 °C, which is reduced for the silane grafted ones, this lessen indicate an increase in the organophilicity of the Halloysite, while the adsorbed water content at the surface was reduced due to the presence of organosilanes. The second one in the range 200–320 °C can be attributed to the decomposition of silane bonded in the clay, and the decomposition of the oligomerized silane network that was not removed during washing. The last step is between 350–650 °C can be related to the structural dehydroxylation of the Al–OH and Si–OH groups and some additional organic decomposition of the silane grafted onto the Halloysite. Moreover, the higher weight loss shown from silane grafted Halloysites compared to raw Halloysite is consistent with the hydrocarbon chain of the alkyl group from the grafted silane molecules. This also supports the strong chemical interaction of the organosilanes with the Si–O and Al–O groups of Halloysite. The remaining materials at 800 °C (85 %) are of aluminum oxides and silicon oxides present in Halloysite structure. These results confirm the grafting of the silanes on the Halloysite (Carli et al. 2014).