Sjournals
Scientific Journals
Scientific Journal of Review (2013) 2(11) 296-328
ISSN 2322-2433
doi: 10.14196/sjr.v2i11.1056

Contents lists available at Sjournals
Scientific Journal of REVIEW
Journal homepage: www.Sjournals.com

Review article

Recent developments in clay- polymer nano composites

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ARTICLE INFO

Article history,
Received 13 November 2013
Accepted 24 November 2013
Available online 29 November 2013

Keywords,
Polymer nanocomposites
Organo clay
Thermoplastic polymers
Nano composites

ABSTRACT

The present review deals with recent developments on synthesis and characterization of polymer nanocomposites (PNCs) derived from organo clay (OCL) with selected thermosetting and thermoplastic polymers of industrial relevance. To compatibilize with polymer matrix, clays are modified with organophilic functionalities. The clays modified in this way are known as organoclay (OCL). The most popular methods for clay modification are executed through their cation exchange with quaternary ammonium salts bearing alkyl, vinyl, imidazolium, tallow alkyl functionalities. Crown ethers alkylsilanes, and zwitterions are also reported as clay modifiers for development of PNCs. As an alternative strategy, functionalized polymer matrixes are developed for compatibilization with clays to produce high performance PNCs. This strategy although is under developing stage , grants potential expectations towards development of PNCs from both class of polymer matrix with improved mechanical, thermal, flame retardant and barrier applications.

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Contents

Abbreviations

ABS: Acrylonitrile-butadiene-styrene
AFM : Atomic force microscopy
CF: Carbon fiber
DMTA: Dynamic mechanical thermal analysis
DSC: Differential scanning caloriemetry
EVA: Ethylene vinylacetate
FT-IR: Fourier transformed-Infrared
HDPE: High density polyethylene
HDT: Heat distortion temperature
LDPE: Low density polyethylene
LLDPE: Linear low density polyethylene
LR: Liquid rubber
MDPE: Medium density polyethylene
MMT: Montmorrilonite
NMR: Nuclear magnetic resonance
NR: Natural rubber
OCL: Organoclay
PA : Polyamide
PCL : Polycaprolactum
PE: Polyethylene
PE-g-MA: Polyethylene-graft-malic anhydride
PHRR: Peak heat release rate
PI: Polyimide
PNCs: Polymer nanocomposites
PP : Polypropylene
PPS: Poly(p-phenylene sulfide)
PS: Polystyrene
PVC: Polyvinyl chloride
PVDF: Polyvinylidine fluoride
PU: Polyurethane
QAH: Quaternary ammonium halide
SAN: Styrene-acrylonitrile copolymer
SBR: Styrene butadiene rubber
SEM: Scanning electron microscopy
SR: Synthetic rubber
SSR: Semi-synthetic rubber
TEM: Transmission electron microscopy
Tg: Glass transition temperature
TGA: Thermogravimetric analysis
VER: Vinylester resin
XRD: X-Ray diffraction

1. Introduction

Polymer nanocomposites (PNCs) are the class of composite materials comprising at least one of their components so called fillers bearing nanometer size scale (< 1000 nm) dispersed into a polymer matrix. Although the term PNCs represents a novel field in material science, PNCs have actually been used for centuries by the nature. Using natural materials and polymers such as carbohydrates, lipids and proteins, nature produce physically strong PNCs as vital components of bones, shells and natural structures. The physical, chemical and biological properties of the PNCs are largely related to physical characteristics of polymer matrix, their composition, dimensions of fillers, compatibility of fillers with polymer matrix, interfacial interactions between polymer matrix and nanofiller phase (Hussain et al., 2006; Bitinis et al., 2011; Faghihi et al., 2013).

Over past decades, significant progress is made on development of clay containing PNCs using various thermosetting and thermoplastic polymer matrix (Fig. 1) The development of PNCs for particular class of application is best exercised through appropriate combination of filler and polymer substrates (Das et al., 2011; Zuzana et al., 2012). Conventional fillers such as talc, calcium carbonate, fibers etc, often used in large amount as reinforcement in the polymer matrix for improvements in their physical, chemical and biological characteristics. Larger loading of fillers imparts brittleness or loss of opacity to resulting PNCs. Among various varieties of fillers those belonging to the class of phyllosilicates such as MMT, bentonite clays are the most accepted fillers for development of PNCs based on synthetic and biopolymers. The size, compatibility and thickness of individual clay layers plays important role for development of well exfoliated PNCs with enhanced optical clarity. Toyota cars, in collaboration with Ube in 1991 commercialized timing belt covers fabricated from clay/ nylon-6 based PNCs. In subsequent years, Unitika introduced nylon-6 based PNCs for engine covers on Mitsubishi's engines. In August 2001, General Motors and Basell announced the application of polyolefin based PNCs as a step component for Safari cars manufactured by General Motor Company and Chevrolet Astro vans. This was followed by the application of these PNCs in the doors of Chevrolet impellers (Zhang and Fridrich 2003; Ray and Okamoto 2003; Xia and Song (2006).

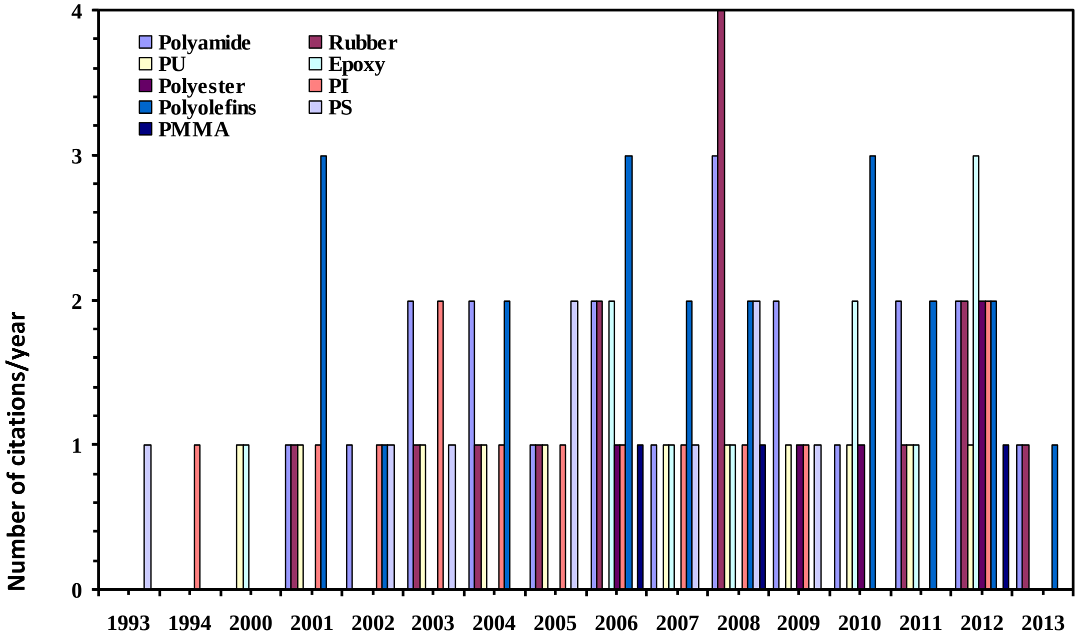

Fig. 1. Progress in the development of clay containing PNCs from various thermosetting and thermoplastic polymers.

More recently, noble polymers have developed clay/polypropylene based PNCs for fabrication of seat backs in the Honda Acura, while Ube have developed clay/nylon-12 PNCs for fabrication of automotive fuel lines and fuel system components. Nylon 6/MMT based PNCs demonstrated significant improvements in tensile strength, modulus and heat distortion temperature. Gilman (1997) found revolutionary fire retardancy associated with PNCs and subsequently cars equipped with a PNCs part were launched in 1989 (Gao 2004; Okada and Usuki 2004).

2. Clay thermoset nanocomposites

Thermoset are those materials made by macromolecules joined together by chemical bonds, acquiring a highly crosslinked polymer structure. Common thermosetting polymers under current industrial applications are polyamides, polyimides, epoxies, vinyl ester and phenolic resins. Now-a-days, thermosetting polymers are well accepted as a matrix for development of high performance naval and aerospace structures Thermosetting polymers are normally produced and formed in the same step. Upon heating, thermosetting polymers are become soft, but cannot be shaped or formed to any great extent, and will definitely not flow. The highly crosslinked structure produced by chemical bonds in thermoset materials, is directly responsible for their high mechanical and physical compared with thermoplastics or elastomers materials. On the other hand this highly crosslinked structure provides high brittleness, insolubility, creep behavior, along with poor elasticity and flame retardency of these materials. For such reasons, thermosetting polymers have extensively been investigated for their modification through reinforcing inorganic and organic fillers (Irfan 2012; Guerra et al., 2013).

Polymer thermoset nanocomposites derived through compatibilization of OCL with thermosetting polymers have recently been of great interest as a radical alternative to conventional PNCs due to applications for development of coatings, laminates, automobile and aerospace structures and biomedical implants. Over past decades, research and development has been greatly focused by both academia and industry towards exploration of PNCs bearing enhanced extent of clay polymer bindings for their prolonged applications. According to composition, PNCs are the hybrid materials in which nanoscopic clay particles, typically < 1000 nm are dispersed in an organic polymer matrix. Smectite clays (e.g. MMT), belonging to the structural family called 2:1 phyllosilicates, are the main choice for designing PNCs due to their low cost, high abundance, and rich intercalation chemistry that allows for their chemical modifications to improve the compatibility with the polymer matrix (Gonzalez et al., 2009; Bitinis et al., 2011).

One of the major problems in preparing the proposed class of PNCs is the hydrophilicity of the clay that makes the clay less compatible with the organic polymers. Many factors can influence the dispersion and exfoliation of clays in polymer matrix. The final properties of the PNCs depend on the choice of the mixing technique and the achieved degree of exfoliation of the clay platelets. Most polymers, however, are hydrophobic and are not compatible with hydrophilic clays. In this case, pretreatment of either the clays or the polymers is necessary. The most popular methods for clay modification are the use of amino acids, organic ammonium or tetra organic phosphonium halides to convert the clay to organophilic surface (Usuki et al., 1993; Peter et al., 1999; Ray and Okamoto 2003; Carrado 2000; Faucheu 2010).

Several efforts were made to modify the various varieties of clays with surfactants, functionalized hetrocyclic molecules, organic polymers to achieve their better compatibility with polymer substrates. The clays modified in this way are known as OCL. For those polymers without any polar functional groups, such as PP, it is common to apply the techniques of grafting polar functional groups onto the polymer chains or adding graft-copolymers during processing. For example, maleic anhydride grafted PP has been used to produce clay/PP based PNCs directly (Kato et al., 1997; Quang and Donald 2006) (Table 1).

The following three methods are developed to produce PNCs. The solution-induced intercalation is the straight forward method for preparation of PNCs. This method involves pre-swelling or exfoliation of clay in a compatible solvent and the solution so formed is added to polymer suspended in the similar or another solvent. The polymer enters into the clay gallery and intercalated PNCs are formed from which the solvent is removed by heating or under vacuum. The large quantities of volatile solvent necessary for this approach make it less attractive as an industrial process. This approach poses difficulties for the commercial production of PNCs for most engineering polymers because of the high costs of the solvents required and the phase separation of the synthesized products (Vaia et al., 1993). The second method based on In situ polymerization involves inserting a polymer precursor between clay layers and then expanding and dispersing the clay layers into the matrix by polymerization. Melt intercalation, the third route, is particularly attractive to industry because a molten thermoplastic is blended with the OCL. The efficiency of intercalation using this method may not be as high as that of insitu polymerization and the composites produced contain partially exfoliated layered structure. However, the approach can be applied by the polymer processing industry to produce PNCs based on traditional polymer processing techniques, such as extrusion and injection molding. In addition to these three major processing methods, other fabrication techniques have been also developed. These include solid intercalation (Gao et al., 2001), co-vulcanization (Usuki et al., 2002), and the sol-gel method (Gao 2004; Musto et al., 2004; Quang and Donald 2006).

Table 1
Clay modifiers employed for various polymer matrix for development of PNCs bearing specific applications.

Clay modifier	Polymer matrix	Application of PNCs	References
aDDAH	PI	Gas permeability	Yano et al.,1993)
ADHH	SAN	Clay dispersion	Benali et al., (2008)
QAH	PA6	Clay dispersion	Benali et al., (2008)
QAH	PA6	Clay dispersion	Araujo et al., (2011)
QAH (photo initiator)	PU/PA	Clay dispersion	Qin (2009)
QAH	EP	Flame retardency	Brown et al., (2000)
QAH	Polyester	Clay dispersion	Dalir et al., (2012)
QAH	PI	Barrier properties	Pinnavaia et al., (1994)
aDDAH	PI	Thermal properties	Krishnan et al., (2007)
cODAH	PP	Mechanical properties	Garcia et al., (2003)
QAH	PI	Thermal properties	Alam et al., (2009)
QAH	PE	Flame retardency	Chungui et al., (2005)
aDDAH Alkylsilane	PE	Thermal properties	Qian et al., (2009)
QAH	MDPE	Thermal properties	Sargolzaei and Akbarabady (2010)
QAH	EVA	Clay dispersion	Tasdelen (2011)
VBTAH	PS	Clay dispersion	Moet and Akelah (1993)
VBTAH	PS	Clay dispersion	Fu and Qutubuddin (2001)
Crown ether	PS	Flame retardency	Yao et al., (2002)
QAH	PS	Thermal properties	Wang et al., (2003)
IHe	ABS	Storage modulus	Modesti et al., (2007)
QAH	PS	Thermal properties	Yang et al., (2008)
QAH	SAN	Mechanical properties	Michael et al., (2010)
Octadecyldimethyl betaine	PMMA	Storage modulus	Meneghetti and Qutubuddin (2006)

[a] Dodecylammonium halides
[b] Alkylammonium (dihydroxy) halides
[c] Octadecylammonium halides
[d] Vinylbenzyltrimethylammonium halide
[e] Imidazolium halides

Functional polymers as compatibilizer have also been used to achieve the PNCs with enhanced dispersion of OCL. In this context, ethylene-vinyl acetate (Marco et al., 2004), PE-g-MA (Sibold et al., 2007; Lew et al., 2004), chlorinated PE (Tasdelen 2011), PP-g-MA (Hwang et al., 2008; Perez et al., 2010; Barbosa et al., 2012) were extensively studied as compatibilizer for OCL. Most recent approach of achieving enhanced dispersion and compatibility of clays with polymers is based on reaction chemistry that involves grafting of functional macromolecules onto polymer backbones. This route provides PNCs with improved thermal, mechanical, barrier properties and flame retardency.

SEM and XRD are widely used to characterize the dispersion state of the nanoparticles in the polymer matrix. Due to high resolution, TEM is suitable only at nanoscale which is not necessarily representative of the entire composite sample at the macroscale. Moreover, sample preparation for TEM analysis is quite complex, time consuming and costly. On the other hand, SEM allows observations of the internal structure of PNCs at larger scales than TEM (Moet and Akelah 1993; Yun et al., 2008; Nigam et al., 2010). The micro-scale could reveal the size and distribution of agglomerates in a more representative sample. Rheology is a widely used for the study of the dispersion state which defines the nanostructure of the mixture between the conventional, the intercalated, or exfoliated PNCs (Borse and Kamal 2009; Bensadoun et al., 2011). Combined to rheology, SEM is a good indicator of the dispersion of nanoparticles in the resin and may also confirm the level of exfoliation (Carrado 2000; Valerio et al., 2005; Quang and Donald 2006; Vermoge 2007; Choudalakis and Gotsis 2009; Mansoori et al., 2012).

2.1. Clay/polyamide nanocomposites

Yano et al., (1993) synthesized PI hybrid with MMT clay mineral from a dimethylacetamide solution of poly (amic acid) and a DMAC dispersion of MMT intercalated with an ammonium salt of dodecylamine. MMT of stacked silicate sheets about 2000 A in lengths, 10 in thickness. In this hybrid, MMT is dispersed homogeneously into the polyimide matrix and oriented parallel to the film surface. Only addition of MMT (2 wt %) brought permeability coefficients of various gases to values less than half of those of ordinary (PI).

Gloaguen and Lefebvre (2001) prepared polymer/clay based PNCs which display unique properties, even at low clay content, by comparison to more conventional mineral filled polymers. Two systems were considered in the present study: the rest one consists of nylon 6/clay hybrids in which in situ polymerization is aimed at obtaining a nylon matrix strongly bonded to the delaminated clay platelets. The second one is prepared by melt dispersion of OCL derived from MMT in polypropylene, which should in principle result in a reduced degree of polymer-clay interaction. Dynamic viscoelastic analysis was indeed indicative of a noticeable difference when referring to the molecular dynamics of the Tg. Plasticity results, in which volume strain was recorded by video-extensometry, showed extensive cavitational behavior while retaining a fairly large strain at break, as long as deformation is performed above the Tg of the matrix.

Mehrabzadeh and Kamal (2002) prepared PA6/clay, HDPE/clay, and HDPE/ PA6/clay based PNCs. XRD, DSC, and FT-IR measurements reveled enhancements in the crystallization of the γ-form of PA6. The clay has served as a nucleation agent and caused a reduction of spherulitte size. SEM analysis of fracture surfaces showed the reduction in the particle size of PA-6 and changes in the morphology of HDPE/PA6/clay based nanocomposites.

Liu et al., (2003) prepared PA11/ OCL based PNCs by melt-compounding. XRD and TEM indicated the formation of the exfoliated PNCs at low clay contents (< 4 wt %) and a mixture of exfoliated and intercalated PNCs at higher clay contents. TGA and DMTA as well as tensile test showed that the degree of dispersion of nanoclay within polymer matrix plays a vital role on property improvement. The thermal stability and mechanical properties of the exfoliated PA11/clay based PNCs at lower clay content were superior to those of the intercalated ones with higher clay contents, due to the finer dispersion of OCL into the PA11 matrix.

Pramoda et al., (2003) prepared PA6-clay by melt compounding and studied the thermal degradation and evolved gas analysis TG–IR. The thermal decomposition of PA6 and its clay based PNCs takes place with the evolution of the cyclic monomer (caprolactam), followed by other volatile gases like CO2 and NH3, which are characterized by the presence of oligomeric products with nitrile and vinyl chain ends in the FT-IR spectra. The onset temperature for degradation is 12 C higher for PA6 with 2.5 wt % of clay loading than that for neat PA6, whereas, the onset temperature for degradation remained almost unchanged for samples with higher clay loading (i.e. 5, 7.5 and 10 wt % clay).

Srinath and Gnanamoorthy (2004) prepared nylon clay based PNCs by melt intercalation technique. The abrasive wear resistance and wear mechanism of polymer clay based PNCs was reported. Abrasive wear resistance was studied against the SiC abrasive paper. Presence of nanoclay has contributed reductions in the ductility and abrasive wear resistance of PNCs.

Kashiwagi et al., (2004) have investigated the thermal and flammability properties of PA6/clay (2 and 5% by mass fraction) based PNCs to determine their flame retardant performance. The gasification process of the PNCs samples at an external radiant flux of 50 kW/m2 in a nitrogen atmosphere was observed. The residues collected at various sample mass losses were analyzed by TGA, TEM and XRD to determine the content of the residue and to understand the flame retardant mechanism of the PNCs. The analysis of the floccules of blackened residues shows that up to 80% by mass of the residues consists of clay particles and the remainder was thermally stable organic components with possible graphitic structure. Furthermore, clay particles were stacked in the carbonaceous floccules residues and the d-spacing of the clay platelets was in the range of 1.3–1.4 nm as compared to the well exfoliated original sample. The accumulation of the initially well-dispersed clay particles in the sample on the burning/gasifying sample surface was due to two possible mechanisms. One was recession of the polymer resin from the surface by pyrolysis with the de-wetted clay particles left behind. Another mechanism was the transportation of clay particles pushed by numerous rising bubbles of degradation products and the associated convection flow in the melt from the interior of the sample toward the sample surface. Numerous rising bubbles may have another effect on the transport of clay particles. Bursting of the bubbles at the sample surface pushes the accumulated clay particles outward from the bursting area and forms the island-like floccules instead of forming a continuous net-like structure of clay filled protective layer. Therefore, both PA6/clay based PNCs samples did not produced the sufficient amounts of protective floccules to cover the entire sample surface.

Feng et al., (2004) prepared PP/ PA6 blends composed of poly(propylene) (PP) and PA6 /clay based PNCs by twin-screw extrusion and melt-drawn into ribbons by a ribbon extrusion process. The influence of clay on the morphology of PP/PA6 ribbons was investigated by means of field-emission SEM and optical microscopy. The results show that at low clay content (3, 5 wt %), PA6 exhibited continuous lamellar structure in PP as pristine PA6 did in a PP/PA6 blend.

Jang and Wilkie (2005) studied the degradation pathway of polyamide 6 (PA6)/clay based PNCs as a function of clay content. Well-dispersed PNCs were obtained by simple melt blending between OCL and PA6. PNCs exhibit a large reduction in peak heat release rate, 60%, measured by cone calorimetry. There were no significant differences in the evolved products during thermal degradation of PA6 and PA6/clay based PNCs in terms of composition and functionality.

He et al., (2006) prepared polyamide 1,1/clay based PNCs by melt-blending, followed by melt-extrusion through a capillary. TEM showed that the exfoliated clay morphology was dominant for low nanoclay content, while the intercalated one was prevailing for high nanoclay loading. Melt rheological properties of PA11 based PNCs have been studied in both linear and nonlinear viscoelastic response regions. In the linear regime, the PNCs exhibit much higher storage modulus (G´) and loss modulus (G'') values than neat PA-11. The values of G´ and G'' increase steadily with clay loading at low concentrations, while the G' and G'' for the sample with 5 wt % nanoclay showed an inverse dependence and lie between the modulus values of the samples with clay (1 and 2 wt %). This was attributed to the alignment/orientation of nanoclay platelets in the intercalated PNCs induced by capillary extrusion. In the nonlinear regime, PNCs showed increased shear viscosities when compared with the neat resin. The dependence of the shear viscosity on clay loading have analogous trend to that of G' and G".

Zhang et al., (2006) prepared both PA12/clay and polyamide 6–polyamide 66 copolymer (PA 6/6, 6)/clay based PNCs by melt intercalation. The incorporation of modified clay (4-5 wt %) largely increased the strength, modulus, HDT and permeation resistance to methanol of the polyamides but decreased the notched impact strength. Incorporation of nanoclay decreased the melt viscosities of both the PA 12 and PA 6/6 based PNCs. Incorporation of the nanoclay increased the crystallinity of PA 6/6, 6 but had little effect on that of PA 12, which explained the clay obviously increased the Tg of PA 6/6, 6 but hardly had any effect on that of PA 12. The dispersion and orientation of both the nanoclay and the polyamide crystals were studied with TEM, SEM, and XRD. The nanoclay was exfoliated into single layers in the PNCs, and the exfoliated clay layers had a preferred orientation parallel to the melt flow direction.

Zou et al., (2007) observed morphological changes in poly(p-phenylene sulfide) (PPS)/polyamide 66 blends due to addition of small amount of clay. The morphology of polymer blends was changed gradually from sea–island into co-continuity and lamellar supra molecular structure, as increasing of clay content. Clay was selectively located in the PA66 phase, and the exfoliated clay layers formed an edge-connected network. The change of morphology was not caused by the change of volume ratio and viscosity ratio. This has been explained well explained by the dynamic interplay of phase separation between PPS and PA66 through preferential adsorption of PA66 onto the clay layers and through layer–layer repulsion. This provides a means of manipulating the phase morphology for the immiscible polymer blends. The mechanical and tribological properties of PPS/PA66 blends with different phase morphologies (different clay contents) were studied. Both tensile and impact strength of the blends were found obviously increased by the addition of clay.

Samyn et al., (2008) prepared PA6 based PNCs exhibiting different nanomorphologies by melt blending PA6/clay. NMR results were consistent with TEM images but the advantage of NMR has served as representative of the whole sample and provided a precise quantification. PA6 based PNCs exhibited significant reduction of peak heat release rate but the morphology has not played any significant role. They have clearly shown that if dispersion was achieved, polymer/clay based PNCs should exhibit flame retardant properties.

Lin et al., (2009) prepared PA66/clay based PNCs in twin screw extruder at 270°C. Samples were analyzed using SEM and TEM to examine the morphology development of clay inside nylon down the length of the extruder. It was found that the clay aggregates were quickly broken into smaller tactoids and then even nanometer size clay bundles and single clay platelets in the first mixing section. The structure changes in the second mixing section were much less significant. XRD analysis of the PNCs showed small or disappearance of, characteristic XRD (001) peaks, which indicates partial exfoliation, or complete exfoliation, respectively, of clay inside PA matrix.

Lewin (2010) obtained a UL-94 V-0 rating and an oxygen index value of 29.7 by treated with PA6 with monomeric pentabromobenzyl acrylate) (7 wt %) and presented the simultaneous application of a brominated flame retardant and an organically layered silicate for the flame retardency of PA6. By adding OCL (10 wt %) and pentabromobenzyl acrylate (10wt%), the V-0 rating remained, indicating cooperation between pentabromobenzyl acrylate and OCL. Higher concentrations of OCL result in a decreased UL-94 rating. The size and mass of drops formed in the UL-94 test increased with OCL, suggesting an increase in the viscosity and density of the pyrolyzing matrix. The effect of the Br additive on PHRR was similar, but smaller than that of clay.

Araujo et al., (2011) prepared PNCs from PA6 where clay was modified with three quaternary ammonium salts to derive the respective OCL. The XRD and SEM revealed intercalation of salt molecules in clay layers and represented a good interaction with polymer, showing the formation of intercalated and/or partially exfoliated structures. The PNCs showed similar thermal stability compared to pure polymer.

Kredatusova and Brozek (2012) prepared PNCs by direct addition of polyesteramide solution to MMT. PEA matrices were obtained by the anionic copolymerization of ε-Caprolactam and ε- caporolactone containing 20–100 mol % of ε- caporolactone units. The matrices were used to test the exfoliation of two clay varieties (Cloisite 30B and Cloisite 25A). The extent of exfoliation was dependent on the mutual interaction of polymer, solvent and clays. The degree of MMT-solvent interaction was assessed from the swelling factor and basal distance through wide angle XRD . The polymer-solvent interaction was determined from limiting viscosity numbers measured for each solvent used.

Rathi (2012) prepared PA66/clay based PNCs with inorganic additives by melt blending method. Inorganic additives such as potassium nitrate, zinc borate and magnesium hydroxide along with organic phosphinate were used to study their effect on thermal behavior of PA66/clay based PNCs. The PNCs were characterized by XRD which confirms the formation of intercalated and/or exfoliated PNCs. The thermal degradation behavior of PNCs was studied by TG-DTA, DSC and FT-IR. PA66/30B based PNCs was thermally stable over temperature range beyond 450°C with increase in char yield. DSC curve of PA66/30B shows an endothermic peak at 452°C with higher heat of absorption (378 J/g) during the decomposition stage due to intercalation of PA66 between the 30B interlayer. The All PA66 based PNCs liberated char residue at 400°C indicating the presence of nitrile group in the degradation products of PA66. The addition of zinc borate along with organic phosphinate induced a change in path of decomposition of polymer, leading to higher char formation which may protect the polymer from burning.

Stoeffler et al., (2013) compared the efficiency of three melt compounding methods for preparing polyamide 12 (PA12)/untreated clay composites. Conventional extrusion was compared with two water-assisted extrusion methods and respectively involving injection of water in the polymer/clay stream or injection of aqueous clay slurry in the polymer stream. The dispersion of the MMT in composites was analyzed at the microscale and at the nanoscale using optical, SEM and wide angle XRD . The results showed that injection of aqueous clay slurry in the polymer stream was the most efficient method for preparing PA12/untreated clay composites, although clay particles remained mainly dispersed at the microscale. This method allowed for a drastic size reduction of the microparticles, accompanied by enhancements by 10 % in tensile modulus and tensile strength (compared with equivalent composites obtained by conventional extrusion). The influence of the pH of the aqueous clay slurry was also investigated: neutralization of the clay slurry generated finer dispersions, probably resulting from a better pre-exfoliation of the clay in the water medium. PA12/MMT composites were also prepared as control samples. When an adequate surface treatment was selected, nanoscale dispersion of the clay platelets was easily achieved. In this case, composites prepared by conventional extrusion showed overall similar properties as their equivalents prepared using injection of water in the polymer/clay stream.

2.2. Clay /elastomer nanocomposites

An elastomer is any material which is able to regain its initial shape when a deforming force is disconnected such as natural or synthetic rubber. Rubber was first known elastomer brought to Europe in 1493 from the America by Columbus, but it remained little more than a novelty for over 200 years. Interest eventually began to grow, and in 1770 Joseph Priestley noted its ability to rub out pencil marks, hence the name 'rubber'. This was followed by a rapid growth in technical developments and applications in the 19th century. Rubber began to be used as containers, flexible tubing, elastic bands and waterproofing, spurred by developments from Charles Macintosh and Thomas Hancock. Charles Goodyear's discovery of vulcanisation using sulphur increased the natural strength and durability of rubber by cross-linking the molecules of the soft gum rubber into a tougher material. Following the discovery of Good Year, fillers of several varieties were used for the modification of elastomers making them durable against mechanical stress, heat flammable atmosphere and environmental degradation (Morton 2000; Yang et al., 2014).

Manchado et al., (2003) investigated the effect of the incorporation of a bentonite on the vulcanization kinetics of natural rubber by means of both cure-meter testing and DSC under dynamic and isothermal conditions. The vulcanization curves showed that the modified clay behaved as an effective vulcanizing agent, that accelerated the vulcanization reaction of the elastomer. A marked decrease in the induction time and optimum cure time of the elastomer were observed in presence of OCL. Although the octadecylamine itself accelerated the vulcanization process, the octadecylamine-modified clay gave rise to a further noticeable increase in the vulcanization rate, which attributed to a synergetic effect between the filler and the amine. Moreover, in presence of the OCL, a dramatic increase in the torque value was obtained because of the formation of a higher number of cross links, which could be attributed to the confinement of the elastomer chains within the silicate galleries and consequently to better interactions between the filler and the rubber. However, no significant changes were observed in the unmodified clay composite. These results were in concordance with those obtained by DSC. In addition, the activation energy of the vulcanization process was also calculated by means of both techniques. A clear decrease in the activation energy was observed when the OCL was added to the PNCs.

Hasegawa et al., (2004) prepared ethylene propylene rubber–clay based PNCs (EPR–PNCs) by melt-compounding of maleic anhydride modified EPR (EPR-MA) with MMT. Silicate layers of MMT were found to exfoliate and homogeneously dispersed into the nanometer level in the PNCs as revealed by TEM. EPR–PNCs exhibited higher tensile moduli compared to EPR-MA and composites containing conventional fillers such as carbon black talc. The storage moduli of EPR–PNCs were also higher than those of EPR-MA and the conventional composites. Creep resistances of EPR–PNCs were much improved compared for EPR-MA. Improvement of these properties was caused because dispersed silicate layers have much large interface with the EPR matrix and was strongly restrain the EPR polymer chains.

Liang et al., (2005) prepared isobutylene–isoprene rubber/OCL based PNCs (IIRCN) by solution or melt intercalation (S-IIRCN or M-IIRCN).The dispersion states of clay layers in these PNCs were investigated by TEM and XRD. TEM images demonstrated that both exfoliated and intercalated nanoscale clay layers co-exist in these PNCs and the aspect ratio of clay layers in S-IIRCN was larger than that M-IIRCN. XRD patterns reveal the increase in basal spacing of clay from 2.2 nm for the original organically modified silicates to 4.2 nm for those dispersed in the composites, probably due to intercalation of some rubber macromolecules into the galleries of clay layers. Compared with corresponding micro-composites and pure IIR vulcanizate, the prepared PNCs exhibited outstanding mechanical performances and improved gas barrier properties, which were likely attributed to the nanometer scale dispersion and high aspect ratio of clay layers. In addition, the properties of PNCs prepared by solution intercalation were superior to those of PNCs by melt intercalation.

Wang et al., (2006) investigated the rheological properties of liquid polybutadiene rubber/ OCL based PNCs gels by rheological experiments, focusing on the effects of clay exfoliation and orientation-disorientation as well as polymer-clay interaction and temperature. Both irreversible and reversible viscosity transitions were observed in the temperature range from 26 to 136 °C in steady shear experiments on as-prepared and exfoliated samples. These transitions depend strongly on the end groups, molecular weight of the liquid rubber and the shear field. The irreversible transition was attributed to the exfoliation of the clay and the reversible transition can be understood as a shear-induced orientation-disorientation transition of the clay sheets. Polymer-clay interaction was confirmed to be a key controlling factor of the orientation-disorientation transition, whereas the shear field plays a critical role to induce such a transition.

Alex et al., (2006) synthesized the skim natural rubber latex protein based PNCs through coagulating the clay mixed latex to a consolidated mass by formic acid, followed by drying and vulcanization like a conventional rubber vulcanizate. XRD studies revealed that PNCs exhibited a highly intercalated structure up to a loading of 15 parts per hundred rubbers of OCL. TEM studies showed a highly exfoliated and intercalated structure for the natural rubber latex based PNCs at loadings of 3-5 per hundred rubbers. The presence of clay resulted in a faster onset of cure and higher rheometric torque. The rubber recovered from skim latex had high gum strength, and a low amount of OCL (5 per hundred rubbers) improved the modulus and tensile strength of natural rubber latex. The high tensile strength was supported by the tensile fractography from SEM. Thermal ageing at 70°C for 6 days resulted in an improvement in the modulus of the samples where the effect was greater for unfilled natural rubber latex vulcanizate. The maximum degradation temperature was found to be independent of the presence and concentration of OCL.

Jacob et al., (2008) prepared natural rubber latex layered clay based PNCs with low loadings of nanoclay using conventional compounding technique. A higher loading of clay resulted in processing difficulties due to viscosity build up. X-ray analysis showed that PNCs in which layered silicate layers were either delaminated or ordered as in an intercalated structure. Partially exfoliated structure was observed from TEM of PNCs with 3 per hundred rubber nanoclay. The transport properties were measured in toluene at 303 K. A higher decrease for the diffusion coefficient for PNCs directed the presence of tortuous path for the diffusing molecules. Thermodynamic parameters showed a better compatibility for the silicates with rubber resulted in the formation of an elastomeric network. Gas permeability results of the PNCs suggested a better barrier resistance for oxygen molecules even in lower loading of nanoclay.

Sun et al., (2008) prepared a novel PNCs by traditional rubber mixing with MMT and vulcanizing process. The dispersion of the layered silicate in rubber matrix was characterized by XRD and TEM. Clay not only accelerated the curing process, but also improved the mechanical and aging resistance properties of natural rubber latex. The improvements in properties were caused by the fillers attributed to partial intercalation of clay by natural rubber latex macromolecules. DMTA results showed a decrease of tan δ and increase of TG when the OCL was added to rubber matrix.

Jia et al., (2008) developed nano-dispersed clay into rubber matrix and 3-aminopropyltriethoxysilane by latex compounding method. Bis(triethoxysilylpropyl) tetrasulfide was then incorporated into 3-aminopropyltriethoxysilane -modified nanocomposites by mechanical blending. The structure and properties of the PNCs were investigated by XRD, FT-IR, TEM, SEM, DMTA and mechanical testing. The results showed that a chemical bridge between organically modified clay and rubber matrix through Bis (triethoxysilylpropyl) tetrasulfide was built during vulcanization. Thus a high performance of styrene–butadiene rubber/clay based PNCs was gained by such a two-step method, which illustrated eight times higher modulus at 300% strain and seven times higher tensile strength compared with cured pure rubber.

Pojanavaraphan and Magaraphan (2008) prepared natural rubber /clay aerogel based PNCs via freeze–drying technique. The pristine clay was introduced in 1-3 parts per hundred rubber in order to study the effect of clay in the natural rubber latex matrix. The dispersion of the layered clay and the morphology of the PNCs were determined by XRD and SEM. XRD patterns indicated the formation of intercalated and exfoliated structures at loadings of 1-3 per hundred rubber clay. SEM studies revealed the formation of clay aerogel structure at 3 per hundred rubber clay loading. The increment hardness of PNCs compared with pure natural rubber latex signified excellent polymer/filler interaction and the reinforcing effect of the clay to rubber matrix. This was supported by an increase in maximum rheometric torque and crosslink density. The crosslink density of clay-filled natural rubber latex vulcanizate was found to increase with the pristine clay content in both thermal and microwave curing methods. However, microwave-cured 2 and 3 per hundred rubber-filled natural rubber latex vulcanizate exhibited higher crosslink density than those which were thermally-cured under the same curing temperature. In addition pristine clay accelerated the thermal decomposition of natural rubber latex by showing a slight decrease in onset and peak decomposition temperatures along with clay content.

Lowe et al., (2011) investigated the fabrication of PNCs by OCL during mixing into natural rubber latex. Natural rubber latex /OCL based PNCs show more intercalation and exfoliation and increased tensile modulus at higher filler reinforcement. Unlike MMT, funmodified clay was dispersed well in natural rubber latex. The results revealed that organo-modification improves compatibility but did not affect the microstructure of PNCs.

Ghari and Shakouri (2012) prepared two natural rubber latex based PNCs with MMT and swelled OCL (SMMT) using melt intercalation method. The effect of these two MMT on the morphology, rheometery and mechanical behaviors of natural rubber latex has been evaluated. Scorch times for the MMT-filled compounds were very short compared to unfilled compounds. A more pronounced effect was achieved by using SMMT as reinforcing agent. The obtained results reveal that PNCs reinforced by SMMT have more adequate morphology, rheometery and mechanical behaviors as well as swelling resistance. The microstructure of the natural rubber latex/MMT systems was studied by XRD and SEM. The results showed that the optimized value of filler in dual fillers-based PNCs systems was equal to 10 per hundred rubber nano-calcium carbonate. Natural rubber latex based PNCs containing SMMT and nano-calcium carbonate was showed 44.5% increase in tensile strength, 14.4% stress improvement at 100% strain, and only 3% increase in elongation at break compared to pure natural rubber latex.

Hrachova et al., (2013) investigated the effect of various modifiers on the structure and properties of clay/natural rubber based PNCs with the aim to evaluate the effect of size and structure of the modifier. They prepared PNCs by melt intercalation method. No improvement of mechanical properties was observed for small organic cation however, stress and strain at break of clay/rubber based PNCs was increased with rising number of octyl chains in the interlayer spaces of OCL. The PNCs exhibited hybrid structure as revealed by XRD, TEM, and SEM.

2.3. Clay/polyurethane nanocomposites

Polyurethanes are thermosetting polymers derived from polymerization di-isocynate and diols. Commercially, polyurethanes are versatile materials for fabrication of sheets and foam. For high temperature and barrier application polyurethane are transformed in to their composite through reinforcing clays.

Chen et al., (2000) synthesized a novel segmented polyurethane (PU)/clay by PU and OCL. 12-Aminolauric acid (12COOH) and benzidine (BZD) were used as swelling agents to treat NaMMT and for forming OCL (12COOH-MMT and BZD-MMT) through ion exchange. The nanometer-scale silicate layers of OCL were completely exfoliated in PU in the cases of 12COOH-MMT/PU (1, 3 and 5 wt %) and in the cases of BZD-MMT/PU (1 and 3 wt %) based PNCs as confirmed by XRD pattern and TEM studies. The segmented structures of PU were not interfered by the presence of the silicate layers in these PNCs as evidenced by their glass transition and degree of phase separation from DSC and FT-IR measurements. A two-fold increase in the tensile strength and a three-fold increase in the elongation were found for BZD-MMT/PU (1 wt %) as compared to that of pure PU.

Ma et al., (2001) synthesized an elastomeric polyurethane/clay (PU/clay) based PNCs based on poly (propylene glycol) (PPG), glycerol propoxylate, and toluene-diisocyanate by intercalative polymerization technology. The results of WAXD studies showed that the gallery distance of clay in the hybrid was enlarged from 1.9 to 4.5nm. Introducing clay in the PU matrix resulted in an increase in both the tensile strength and elongation at beak. At clay content of 8 wt%, the tensile strength and elongation at break were two times and five times respectively to that of the pure PU. The clay intercalative route to the synthesis of PNCs also affected the thermal properties of the PNCs.

Zhang et al., (2003) studied the water absorption of MMT by using TGA and FT-IR, and investigated a removal method through boiling with toluene. The morphology, thermal dynamic mechanical properties and mechanical tensile of synthesized PU/MMT was investigated by WAXD, FT-IR and DMTA techniques and found that intercalated PU/MMT based PNCs was reinforced and toughened by the addition of nanometer-size MMT layers.

Caoa et al., (2004) prepared polyurethane (PU) /MMT based PNCs with organically modified layered silicates by in situ polymerization and foams were prepared by a batch process. Clay dispersion of PU based PNCs were investigated by XRD and TEM. The morphology and properties of PU based PNCs and foams greatly depend on the functional groups of the organic modifiers, synthesis procedure, and molecular mass of polyol because of the chemical reactions and physical interactions involved. The presence of clay results in an increase in cell density and reduction of cell size compared to PU foam. In the PU with high molecular mass polyol, a 68°C increase in TG, 65% increase in compressive strength and 78% increase in modulus were observed with the addition nanoclay(5 wt %). Opposite effects were observed in PU based PNCs foams with highly cross linked structure.

Kim et al., (2005) investigated the reaction behavior and physical properties of polyurethane (PU)/clay based PNCs. OCL was used as nanofillers to formulate the PNCs. DSC used to study the reaction behavior of the PU/clay based PNCs systems. The reaction rate of the PNCs increased with clay content. The reaction kinetic parameters of proposed kinetic equations were determined by numerical methods. The Tg of the PU/clay based PNCs systems increased with clay content. The thermal decomposition behavior of the PU/clay based PNCs was measured using TGA. XRD and TEM data showed the intercalation of PU resin between the silicate layers of the clay in the PU/clay based PNCs.

Tan and Nie (2007) synthesized intercalated clay/polyurethane based PNCs by UV irradiation. OCL containing initiator groups were prepared by cationic exchange process which acted as both suitable intercalant and photo initiator. These modified OCL were then dispersed in the mixture of urethane acrylate and hexanediol diacrylate in different loading, then situ photo-polymerized. Intercalated and exfoliated PNCs structures were evidenced by both XRD and TEM. Thermal properties and morphologies of the resultant PNCs were also investigated.

Patro (2008) synthesized PNCs of rigid polyurethane foam with unmodified vermiculite clay. The clay was dispersed either in polyol or isocyanate before blending. The viscosity of the polyol was found to increase slightly on the addition of clay up to 5 pphp (parts per hundred parts of polyol by weight). The gel time and rise time are significantly reduced by the addition of clay, indicating that the clay acts as a heterogeneous catalyst for the foaming and polymerization reactions. XRD and TEM of the polyurethane composite foams indicated that the clay was partially exfoliated in the polymer matrix. The clay was found to induce gas bubble nucleation resulting in smaller cells with a narrower size distribution in the cured foam. The closed cell content of the clay PNCs foams increases slightly with clay concentration. The mechanical properties are found to be the best at 2.3 wt % of clay when the clay was dispersed in the isocyanate.

Qin (2009) synthesized a novel quaternary ammonium photo initiator ion exchanged with MMT. An ordered swollen structure of the intercalated MMT was evidenced by XRD, FT-IR and TGA. The photo initiator molecules were anchored in the interlayer space of MMT. These photo initiator-modified MMT were then dispersed in urethane acrylate oligomers and in-situ photo polymerized yielding exfoliated PU-MMT based PNCs. The photo polymerization kinetics was monitored by real-time infrared spectroscopy. XRD and TEM revealed that the modified MMT layers were uniformly dispersed in PUA matrix.

Xu et al., (2010) developed shape memory PNCs of PU/clay by melt mixing of PU and nano-clay. Based on nano-indentation and micro-hardness tests, the strength of the PNCs increased dramatically as a function of clay content, which attributed to the enhanced nanoclay–polymer interactions. Thermomechanical experiments demonstrated good mechanical and shape memory effects of the PNCs. Full shape memory recovery was displayed by both the pure PU and PU-clay based PNCs.

Pinto et al., (2011) prepared biodegradable PU by aqueous PU dispersion having poly caporolactone and poly (ethylene glycol). MMT particles were delaminated within the waterborne to produce PNCs. The triamcinolone acetonide, an important corticoid drug, was dispersed into the PNCs followed by drying step to produce an implantable drug delivery system.. WAXS and SAXS results suggested that triamcinolone acetonide and clay did not dramatically change the morphology phase of the polymer although they can interact with each other. The presence of MMT particles in PNCs reduced the rate of triamcinolone acetonide release as compared to pure polyurethane and enhanced the mechanical properties of polymer.

2.4. Clay/epoxy nanocomposites

The term epoxy has been widely adapted for many uses beyond fiber reinforced polymer composites. Epoxies are of current interest as general purpose adhesives, binder in cements, non-skid, industrial coatings, potting and encapsulating media. Epoxies are the excellent matrix for pressure vessels, pipes, rocket housings, recreational equipments. Epoxy adhesives are created by the reaction of oxirane group with curing agents bearing carboxyl, amine or anhydride linkages. Nanocomposites of epoxy are developed to enhance their flame retardency, thermal stability and to reduce their inherent brittleness. (Sharma 2013; Apicella et al., 2013).

Brown et al., (2000) examined the role of various quaternary ammonium-modified MMT (OCL) epoxy/diamine based PNCs. Utilization of a hydroxyl-substituted quaternary ammonium modifier affords flexibility to combine both catalytic functionality which increased the intra-gallery reaction rate, with enhanced miscibility toward both reagents. The use of a low-boiling solvent to enhance miscibility and processability of the initial mixtures was shown not to alter the structure or properties of the final PNCs. Also, the use of autoclave techniques enabled fabrication of high-quality specimens containing up to 20 wt % organically modified layered silicate. Finally, exfoliated and partially exfoliated epoxy/diamine based PNCs were produced with enhanced heat-distortion temperature and increased flammability resistance.

Wang et al., (2006) developed a novel approach assisted with solvent to disperse clay into epoxy matrix. The dispersion of clay was examined by means of optical microscopy, WAXS and TEM. Batches of cured samples containing silane modified clay (1-3 wt %) were prepared and their thermal/mechanical properties were studied by DMTA, mechanical tests. Improvements on storage, Young’s moduli and fracture toughness were improved with incorporation of silane modified clay.

Ray et al., (2006) fabricated vinyl ester resin matrix composites with loadings of OCL (1, 3, 5 and 10 wt %) The composite samples were characterized through XRD, FT-IR, DMTA, TGA, and SEM. The clay samples as well as the clay-resin composites were investigated by XRD. From the shift in the peak positions and the change in d-spacing values, it was evident that there was intercalation in the 10 wt% composites, whereas exfoliation occurred in the 1, 3, and 5 wt % composites. The flexural strength and the breaking energy of all the composites were decreased compared with the unfilled resin, but there was an increase in flexural modulus value by 13 %. From the DMTA of the 3 and the 5 wt % composites, it was observed that the loss modulus value was higher in the 3 wt % composites, but the TG was slightly higher in the 5 wt% composites. Thermal degradation behavior was also improved in the 5 wt % composites compared with the 3 wt % composites.

Auad et al., (2007) developed an epoxy-phenolic resin suitable for use as a composite matrix was reinforced with modified MMT. Characterization by XRD and TEM demonstrated that intercalated PNCs were formed with an inter-gallery distance of approximately 10 nm. The influence of nanoparticles on tensile strength and modulus, fracture toughness, and impact toughness was measured and compared with the un-reinforced polymer. The results revealed that the maximum enhancement in stiffness and toughness was achieved with filler content (2.5 wt %).

Ha et al., (2008) investigated the effect of the MMT concentration on the tribological behavior of MMT/epoxy based PNCs. Wear tests were performed on MMT/epoxy based PNCs with four different clay concentration levels to characterized the improvement in wear behavior due to the MMT concentration. In order to examine the tribological mechanism depending on the clay concentration level, SEM analysis was performed on the worn surfaces after the wear tests. The results showed that the friction coefficient of MMT/epoxy based PNCs with a low MMT concentration was larger than that of PNCs with a high MMT concentration. It is believed that the phenomena occur due to the action of MMT as a reinforcement and lubricant material and reduce the wear rate with increasing MMT concentration.

Avilaa, et al., (2010) synthesized carbon fiber/epoxy-nanoclay and carbon fiber/epoxy-graphene nanosheets through ultrasonic mixing in acetone followed by a shear mixing with hardener. TGA indicates an average decrease on peak mass loss around 41% with the addition of small amount of nanoparticles. The sample plates were exposed to a heat flux of 800 $kW.m^{-2}$ for a period up to 120 seconds. The addition of nanoclay has contributed an increase on impact peak force of 11.69%.

Nigam, et al., (2010) synthesized and characterized the PNCs consisting of epoxy resin with inorganic as well as OCL. Confirmations of intercalation and exfoliation characteristics of these fillers into the cured epoxy resin matrix have been investigated by WXRD and AFM. SEM was adopted to assess the nature of filler dispersion, size of the agglomerates and the polymer-filler adhesion. While significant improvement in the mechanical properties was observed, the thermo-oxidative stability of the composites showed marginal improvement.

Lingaraju, et al., (2011) developed nanoparticles reinforced plastics. The tensile strength, impact strength, flexural strength and hardness of PNCs were studied in accordance with ASTM standards. The clay and silica used in the present system were treated with 3-aminopropyltriethoxysilane. The effect of variants in sliding speed, time and applied load on the wear behavior of PNCs was studied by measuring the weight changes and observing the surface features by SEM. In the experiments with wear test pin having flat face in contact with hardening rotating steel disc, sliding speed, time and loads in the range of 640–1000 RPM, 300–900s and 5–25 N respectively was used. It is observed that wear rate was increased with applied load, time and sliding speeds.

Wu, et al., (2012) investigated the flame retardency of epoxy /tetraphenylphosphonium modified layered silicate PNCs combined with low-melting silicate glass. The total heat evolved was changed insignificantly as neither relevant additional carbonaceous charring nor flame inhibition occurs. However, flame retardancy was clearly observed due to an inorganic-carbonaceous surface protection layer. Peak heat release rate reduction less than expected was observed when additives were combined. The morphology of fire residue was investigated by SEM on different length scales and turns out to be the key to understanding the efficiency of flame retardancy. The fire residue of PNCs showed a layered structure; whereas separated columns limit the barrier properties for epoxy/ tetraphenylphosphonium (5 wt %) modified layered silicate epoxy based PNCs on the micrometer scale.

Isitman, et al., (2012) prepared OCL based PNCs by ultrasound-assisted solution intercalation technique based on PS containing brominated epoxy and a combination of brominated epoxy and antimony oxide. Aspects of nano-morphology and nano-dispersion were investigated by XRD and TEM whereas flammability and reaction to fire were evaluated using limiting oxygen index and mass loss calorimeter tests. PS/brominated-epoxy-blend-based PNCs showed mixed intercalated–exfoliated nanomorphology where polymer-intercalated crystallites predominantly exist in PS matrix and exfoliated silicate layers reside on PS/brominated epoxy phase boundaries and within brominated epoxy domains. OCL was found to impart a compatibilization effect on PS and dispersed brominated epoxy, which facilitates uniform distribution of a fine flame retardant phase within the matrix. Reduction of the rate at which decomposition products evolve into the gas phase, OCL based PNCs showed notable reductions in peak heat release rate and increases in limiting oxygen index. The gas-phase hot radical entrapment by halogenated flame retardant system was coupled with the condensed-phase physical action of dispersed OCL, which increased the overall fire-retardant effectiveness. Fire-retardancy of PNCs based on PS/brominated epoxy blends were attributed to nano-confinement and tortuous pathway effects of OCL rather than to carbonaceous char formation proposed earlier for PS/ OCL systems without conventional flame retardancy.

Ratna, et al., (2012) investigated the effects of OCL neat VER. OCL, Cloisite10A and Cloisite 30B were dispersed into neat organic VER by using a ultrasonic method. Morphology of the dispersed OCL particles in the PNCs formed during polymerization was characterized by XRD and found that intercalated PNCs formed. The thermal properties such as decomposition and TG % weight retention and tan δ were determined by TGA and DMTA. A decrease in TG was found in both VER /Cliosite10A and VER /Cliosite30B based PNCs.

Abdelwahab, et al., (2012) investigate the hybridization of VER and OCL aiming at enhancing the thermal and mechanical properties of VER. The polymerization of VER in the presence of OCL has been studied by DSC and FT-IR. The morphology of the hybrids has been studied by XRD. The transparency of the hybrids in the form of films studied by UV-VIS spectra indicated that the transparency depends on the OCL content. The inclusion of clay into VER led to enhance the hardness, however, with increasing the amount of reactive diluent, the surface hardness decreased.

2.5. Clay /polyester nanocomposites

Polyesters are the long-chain polymers chemically composed of an ester (85 wt %) and a dihydric alcohol and a terephthalic acid". Polyesters are durable against most chemicals, stretching and shrinking, wrinkle resistant, mildew, abrasion resistant and are well known to constitute extremely strong fabrics and fibers. Polyesters are modified with fillers due to their limited thermal stability and flame retardency thereby showing potential for use in the automotive, transportation, and packaging industries (Scheirs and Long, 2003; Dalir et al., (2012)

Gianelli, et al., (2006) prepared polyester/clay based PNCs by using polybutylene terephthalate and a co-polyester elastomer as polymeric matrices and a commercial OCL as filler. As verified by XRD and TEM intercalated structures were obtained by mixing the molten polymer with the layered silicate in a co-rotating twin screw extruder. The fire behavior of these materials was investigated by means of cone calorimeter test. Peak heat release rate of 3-mm thick samples measured at 50 kW/m^2 external heat flux was reduced by a factor of 2-3 on addition of OCL to the polymers.

Pereira et al., (2009) prepared layered double hydroxides/unsaturated polyester layered double hydroxide/UP based PNCs and studied the effect of layered double hydroxide on the resin properties. Intercalated layered structures were observed for the different organo- layered double hydroxide loadings (1 and 5 wt %). Incorporation of organo- layered double hydroxide in the resin has reduced the flexural strength of polyester resin while the flexural modulus was unchanged for the layered double hydroxide / UP composites and increased with 1 wt% of layered double hydroxide. Adding 1 wt% of layered double hydroxide to the resin produced an important reduction on the flexural strength, but an increase of the flexural modulus. Mass loss curves show enhanced char formation with the different loads tested while the amount of evolved smoke remains quite unchanged.

Fogelstrom et al., (2010) prepared smooth and transparent films from both the neat and the nanoparticle-filled hyper-branched resins. XRD and TEM corroborated a mainly exfoliated structure in the PNCs films, which was also supported by results from DMTA. Furthermore, DMTA measurements showed a 9-16^{o}C increase in TG and a higher storage modulus-above and below Tg indicating the formation of more cross-linked network. TGA demonstrated the influence of the nanofiller on the thermal properties of the PNCs, where a shift upward of the decomposition temperature in oxygen atmosphere was attributed to the improved barrier properties of the nanoparticle-filled materials.

Gonzaga (2012) prepared PNCs based on an unsaturated polyester resin (UPE) and MMT slurry. Upon increasing the clay content (from 1 to 5wt %) increments of 57% and up to 120% were found in the flexural modulus with respect to that of the resin alone. Using clay slurry, the cross-linking reaction was affected by the clay in such a way that the gelation temperature and the thermal stability were increased. TEM and SEM revealed intercalation of clay into UPE. Furthermore, shear and oscillatory rheological tests revealed the formation of a structure between resin and clay at low shear rates.

Dalir et al., (2012) prepared a large number of polyester based PNCs batches featuring different kinds of surface modifiers and OCL (6 wt %).MMT platelets modified with ammonium ions of different chemical architectures were examined to study the effect of ammonium ions on the extent of surface reactions with long-chain fatty acids. The ammonium MMT was first dispersed and suspended in acetone. This suspension was further esterified with dotriacontanoic (lacceroic) acid to form high density brushes on the clay surface. This led to achieving higher basal plane spacing of the MMT platelets due to the reduction of electrostatic interactions holding them. The outcome of the surface esterification was analyzed by FT-IR and XRD. The esterified ammonium-modified clays were then mixed by five different mixing strategies based on the use of a three-roll mill mixer and/or ultrasonication to obtain the desired polyester-nanoclay dispersion, intercalation, and exfoliation. The dispersion states of the modified nanoclay in polymer were characterized from XRD, SEM, and low and high magnification TEM. The aspect ratio of nanoclay and their morphology after mixing were also confirmed by the comparison of the experimental diffusivity results with those of Fick's diffusion model. Systems having esterified ammonium (4 and 6 wt %) showed ease of processing.

2.6. Clay/polyimide nanocomposites

Polyimides are a class of thermally stable polymers that are often based on stiff aromatic backbones. The chemistry of polyimides is in itself a vast area with a large variety of monomers available and several methodologies available for synthesis. The most widely practiced procedure in polyimide synthesis is the two-step poly (amic acid) process. It involves reaction of a dianhydride and a diamine at ambient conditions in a dipolar aprotic solvent. However, there has been considerable debate on the various reaction mechanisms involved in different synthesis methods and their modifications into nanocomposite materials for high performance applications (Ghosh 1996; Kricheldorf 1998).

Pinnavaia et al., (1994) prepared a new type of clay-PI based PNCs by the self-polymerization of diglycidyl ether of bisphenol A in the galleries of acidic alkylammonium ion exchanged forms of MMT. The acid catalyzed intragallery polymerization process leads to the spontaneous exfoliation to the 10Å-thick clay layers. Intra and extra gallery polymerization processes were distinguishable by DSC. Clay-polyimide hybrid composites were syntheses by the intercalation of polyamic acid in MMT and subsequent thermal conversion to polyimide. In contrast to the completely exfoliated clay-polyether system, the polyimide system contains regularly intercalated clay aggregates in the polymer matrix. The clay-polyimide hybrid composite films exhibit greatly improved CO_2 barrier properties.

Chang and Park (2001) prepared Poly (amic acid)/ OCL hybrids by the solution intercalation method with dodecy-lamine-MMT. A polyimide hybrid was obtained from poly (amic acid) hybrid by heat treatment at various temperatures. The film type polyimide hybrids showed better thermal properties than poly (amic acid) hybrids. Also, the thermal stability of the polymer hybrids was enhanced linearly with increasing clay content (0 to 8 wt %). Tensile properties and gas barriers of the hybrids were enhanced remarkably compared to pristine polymers. Intercalations of the polymer chains in clay were examined through XRD SEM and TEM. TEM revealed that a partially exfoliated structure had been obtained from polyimide/ OCL hybrids.

Abdalla et al., (2002) prepared polyimide-clay based PNCs through blending NaMMT and two organically modified Na+-MMT (2.5 and 5 wt %) in methanol solution. DMA results showed a significant increase in thermo mechanical properties (E' and E'') of PNCs (2.5 wt % of clay) in comparison with the neat polyimide. Increasing the clay loading (5 wt %) degraded these properties. Higher Tg was observed for PNCs with clay (2.5 wt %) compared to the neat polyimide. Flexural properties measurements of PNCs 2.5 wt % of clay showed an improvement in the modulus, strength and elongation.

Khayankarn (2003) prepared a polyimide (PI)–clay based PNCs from a solution of poly (amic acid). FT-IR, TGA, XRD, and atomic absorption spectroscopy were used to verify the incorporation of the modifying agents into the clay structure and the intercalation of the modified clay into the PI matrix. Both PI and PI–clay films were subsequently prepared by solution casting. Only addition of clay (3 wt %) reduced oxygen permeability to less than half that of unfilled PI. Furthermore, this hybrid showed an improvement in electrical re4sistance because of the prevention of electrical tree growth by clay particles.

Yu et al., (2004) prepared a series of PNCs with organosoluble polyimide (PI) and layered MMT by the solution dispersion technique. The organosoluble PI containing non-coplanar moiety in diamine monomer and flexible bridging linkages in dianhydride monomer was synthesize by chemical imidization. The synthesized PNCs were characterized by FT-IR, WXRD, and TEM. The organosoluble PI showed better corrosion resistance compared to polyaniline, poly (o-ethoxyaniline) and poly (methyl methacrylate) by using a series of standard electrochemical corrosion measurements of corrosion potential, polarization resistance, and corrosion current in 5 wt % aqueous NaCl electrolyte. PI-clay based PNCs materials incorporated with low loading of clay were found to further improve corrosion inhibition over pure polyimide. Effects of the material composition on the O_2/H_2O molecular permeability, optical clarity, and thermal properties of polyimide–clay based PNCs materials were studied by UV spectra, TGA, and DSC, respectively.

Krishnan et al., (2005) prepared polyimide-clay based PNCs by the solution-casting method. OCL clay was prepared by treating Na+MMT with three different intercalating agents, namely, piperazine dihydrochloride, 1,3-bis(4-piperidinylpropane) dihydrochloride and 4,4'-bipiperidine dihydrochloride at 80 degrees C. Polyamic acid solutions containing various wt% of OCL were prepared by reacting 4,4'-(1,1'-biphenyl-4,4'-diyldioxy)dianiline with bicycle [2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride in N-methyl-2-pyrrolidinone containing dispersed particles of OCL at 20 ^{o}C. PNCs films were prepared from these solutions by solution casting and heated subsequently at a programmed heating rate. These films were transparent and brown in color. The extent of layer separation in PNCs films depends upon the chemical structure of the OCL. These films were characterized by inherent viscosity, FT-IR, DSC, thermomechanical analysis , wide angle XRD, TEM, Ultraviolet –visible spectra and TGA. PNCs films had superior tensile properties and thermal behavior.

Liang and Campbell (2006) prepared the naturally occurring sodium and calcium cations found in bentonite clay galleries exchanged with lithium cations by heat treatment of the lithium bentonite at 130, 150, or 170°C. Inductively coupled plasma analysis showed that heating the lithium clay at elevated temperatures reduced its cation exchange capacity. Ion exchange of heat-treated clays with either a protonated alkyl amine or a protonated aromatic diamine resulted in decreasing amounts of the organic modifier incorporated into the lithium clay. The level of silicate dispersion in a thermosetting polyimide matrix was dependent upon the temperature of Li-clay heat treatment as well as the organic modification. In general, clays treated at 150 or 170°C and exchanged with protonated octadecylamine or protonated 2, 2′-dimethylbenzidine showed a higher degree of dispersion than clays treated at 130°C or exchanged with protonated dodecylamine. DMTA showed little change in the storage modulus or TGA of the PNCs compared to the base resin. However, long-term isothermal aging of the samples showed a significant decrease in the resin oxidative weight loss. PNCs samples aged in air for 1000 h at 288° C showed up to a 20% decrease in weight loss in comparison with that of the base resin.

Krishnan et al., (2007) prepared bicycle [2.2.2] oct-7-ene-2, 3, 5, 6-tetracarboxylic dianhydride (BCDA)-based PI–clay PNCs from their precursor, namely polyamic acid, by a solution-casting method. The OCL was prepared by treating Na-MMT clay with dodecyltrimethylammonium bromide at 80 °C. Polyamic acid solutions containing various wt% of OCL were prepared from 4, 4′-(4, 4′-isopropylidenediphenyl-1, 1′-diyldioxy)-dianiline and BCDA in N-methyl-2-pyrrolidone containing dispersed particles of OCL at 20 °C. These solutions were cast on a glass plate using a Doctor's blade and then heated subsequently to obtain PNCs films. The PNCs were characterized using FT-IR, DSC, TMA, DMTA, polarizing microscopy, SEM, TEM, XRD and TGA. The Tg of the PNCs was found to be higher than that of pristine polymer. The coefficient of thermal expansion of the PNCs decreased with increasing OCL content. XRD studies indicated that the extent of silicate layer separation in the PNCs films depended upon the OCL content. Tensile strength and modulus of the PNCs containing OCL (1 wt %) were significantly higher when compared to pristine polymer and other PNCs. The thermal stability of the PNCs was found to be higher than that of pristine polymer in air and nitrogen atmosphere.

Jin and Chang (2008) synthesized a series of colorless PI based PNCs films from 2,2'-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA) and 2,2'-bis(trifluoromethyl)-4,4'-diaminobiphenyl (TFDB) with various OCL contents by solution intercalation polymerization to poly(amic acid)s, followed by thermal imidization. The variation with the OCL content on thermomechanical properties, morphology and optical transparency of the hybrids was examined at OCL loadings (0 to 1.0 wt %). The hybrid films showed high optical transparency and almost no color with cut-off wavelengths ranging from 352 and 356 nm. The hybrid PI films showed good thermal properties with a Tg of 280-287oC. Most films did not show any significant thermal decomposition below 490oC.

Alam et al.,(2009) prepared a series of polyimide (PI)-organically modified clay based PNCs to enhance tensile modulus, thermal stability of PI. PI was made from 3, 3', 4, 4'-biphenyl tetracarboxylic dianhydride (BPDA), p-phenylediamine (PDA), MMT, one type of layered clay, was treated by dodecylamine salt to prepare OCL. XRD indicated that OCL layers were exfoliated and dispersed into PI-film. Tensile measurements indicated that small amount of OCL (up to 3 wt %) increased tensile modulus nicely. The Tg of the nano-composites were higher than those of pristine PI. TGA showed that PNCs have higher decomposition temperatures over.

Faghihi et al., (2013) prepared a series of poly(imide-ether)-clay based PNCs materials-based 3,3′,4,4′-benzophenonetetracarboxylic dianhydride and 1,3-bis(4-aminophenoxy)propane and layered MMT/Na+ by in situ reaction through thermal imidization up to 200°C. Poly(amic acid) was prepared through the reaction of 1,3-bis(4-aminophenoxy)propane and 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, and then a thermal plan of imidization was used for the synthesis of PNCs materials. The resulting PNCs films containing 0.5, 1, 3, and 5 wt % of OCL were characterized by FT-IR, WXRD, SEM, and TGA, respectively.

Feyzi et al., (2013) prepared a series of PNCs consist of organic polyimide and OCL content varying (0 to 10 wt %), by in situ polymerization. Polyimide used as a matrix of PNCs was prepared through the reaction of 1, 2-bis (4-aminophenoxy) ethane (BAE) and 3, 3′, 4, 4′-biphenyltetracarboxylic dianhydride (BPDA) in N, N-dimethylacetamide (DMAC). The resulting PNCs films were characterized by FT-IR, XRD, SEM and TGA.

Kim and Chang (2013) synthesized a series of colorless and transparent polyimide hybrid films from bicycle [2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride (BTDA) and bis[4-(3-aminophenoxy)phenyl] sulfone (m-BAPS) with various clay contents, by solution intercalation polymerization to poly(amic acid), followed by thermal imidization. The thermal properties, morphologies, optical transparencies, and gas permeations of the PI hybrid films were examined for OCL loadings ranging from 0 to 40 wt%. Up to a clay loading of 20 wt%, the clay particles were found to be highly dispersed in the PI matrix without any agglomeration of particles. However, for clay content above 20 wt% some agglomerated structures were formed in the polymer matrix. The thermal and oxygen barrier properties of the PI hybrid films were improved by increasing the OCL content from 0 to 40 wt%.

3. Clay/thermoplastic nanocomposites

The first man-made thermoplastic was an invention by Alexander Parkes who unveiled Parkesine at the 1862. Thermoplastic have ultimate tensile strength and maximum stress. Thermoplastics are the organic materials that melt when heated. They should be differentiated from thermoset materials which cure, or become set, when they were heated. Thermoplastic materials were melt processable and formed when by a melted or viscous phase. Thermoplastics have wide ranging properties. Depending upon their chemistry they can be very much like rubber, or as strong as aluminum. Thermoplastics are light weight, (densities of 0.9 to 2 gm/cc). Some thermoplastic materials can withstand up to 600 F, while others retain their properties at -100 F. Some thermoplastic materials have no known solvents at room temperature. Most thermoplastic materials were excellent insulators, both electrical and thermal. On the other hand thermoplastic composites can be made to be electrically conductive with the addition of carbon or metal fibers. In general the combination of light weight, high strength, and low processing costs make thermoplastics well suited to many applications (Omar, 2013).

3.1. Clay/polyolefin nanocomposites

Kawasumi et al., (1997) prepared polypropylene (PP)-clay hybrids (PPCH) by simple melt-mixing of three components, i.e., PP, maleic anhydride modified polypropylene oligomers (PP-MA), and clays intercalated with stearylammonium to generate OCL. The dispersibility of 10Å thick silicate layers of the clays in the hybrids was investigated by using a TEM and XRD. It is found that there were two important factors to achieve the exfoliated and homogeneous dispersion of the layers in the hybrids the intercalation capability of the oligomers in the layers and the miscibility of the oligomers with PP. Almost complete hybrids were obtained in the case where the PP-MA has both intercalation capability and miscibility. The hybrids exhibit higher storage moduli compared to those of PP especially in the temperature range from TG to 90 °C. The highest relative storage modulus at 80 °C of the hybrid based on a mica and the miscible PP-MA was as high as 2.0 to that of PP and was 2.4 to that of the PP/PP-MA mixture, which was considered to be the matrix of the PPCH.

Usuki et al., (2002) prepared ethylene propylene diene methylene linkage rubber (EPDM)-clay hybrids by mixing with EPDM and MMT via vulcanization process. By using thiuram and dithiocarbamate for the vulcanization accelerator, EPDM-clay hybrid was prepared successfully. In this EPDM-clay hybrid, the silicate layers of the clay were exfoliated and almost dispersed to the monolayers. The tensile strength of the EPDM-clay hybrid loading 4 wt % clay exhibited 2.0 times higher value compared to that of neat EPDM at 25°C. The storage moduli (E /) of the EPDM-clay hybrid were also higher than that of neat EPDM. The gas permeability of EPDM-clay hybrid decreased 30% as compared with neat EPDM.

Garcia et al., (2003) obtained and studied the PP clay based PNCs by using two different coupling agents, diethyl maleate and MA, two different clays, a commercial MMT (nanomer 130, TC) and a sodium bentonite purified and modified with octadecylammonium ions into OCL. The relative influence of each factor, matrix and clay modification was investigated from structural analysis SAXS, TEM and mechanical characterization.

Marco et al., (2004) prepared PNCs based on OCL and PE by melt processing using ethylene-vinyl acetate as compatibilizer. The degree of intercalation spacing was determined by XRD. Thermal degradation behavior was studied through TGA and chemical evolution in solid residue was studied with FT-IR. During thermal degradation of the PNCs the formation of a protective layer on the polymer surface was observed caused by a charring process of

PE, which is normally a non-char-forming polymer. The protective effect of the char/clay layer against thermal oxidation was observed by monitoring the retention of long chain structure of PE.

Chungui et al., (2005) prepared PE/clay composites by melt compounding of PE and OCL with different intercalating agents. Wide angle XRD and TEM revealed that PE/OCL based PNCs formed when using a reactive intercalating agent, while only conventional microcomposites were obtained from the common alkylammonium intercalated clay. Mechanical testing indicated that the reinforcement in the PNCs was more effective than that in their conventional counterparts. The thermal stability and flammability of the PE/clay based PNCs were measured by TGA and cone calorimeter test. By adding OCL (2 phr), the peak heat release rate of the PNCs was reduced by 54%. Further studies indicated that the improvement of flammability was due to the formation of a clay-enriched protective char during combustion.

Yuan et al., (2006) described the effect of two concentrations of clay nanoparticles on the nonisothermal crystallization behavior of the intercalated PP–clay based PNCs. That indicated crystallization peak temperature of PP–clay based PNCs was marginally higher than neat PP at various cooling rates. Furthermore, the half-time for crystallization decreased with clay content, implying the nucleating role of clay nanoparticles.

Zaragoza et al., (2006) prepared clay based PNCs using a twin screw extruder. They have studied the flammability of the heterophasic PP-EP/ Ethylene-vinyl acetate (EVA)/MMT based PNCs. Both the fluidity of the EVA phase and compatibility conditions between PP-EP and EVA were used in order to obtain the required PNCs. Products exhibited the partially exfoliated/intercalated nanoclay dispersion. TGA indicated that nanoclay retard thermal degradation depending on nanoclay concentration. The retarding process was assigned to the exfoliation and dispersion of the silicate layers which impeded heat diffusion to the macromolecules. Thermal studies, under non-isothermal crystallization, indicated the lack of influence of OCL on the thermal behavior. Flammability characteristics were however affected by the nanoclay layers which overall generated flame retardation both in the EVA host and in PNCs.

Modesti et al., (2006) described the thermal properties and fire behavior of PP based PNCs using DSC, DMTA, TGA and glow wire test. In order to study the morphological structure of the materials obtained, TEM and XRD were used. The PNCs were prepared using the melt intercalation technique. The results show that all the properties were strongly influenced by the composition of PNCs, instead the processing conditions greatly affect only the dynamic-mechanical properties. DSC curves show that the crystallinity was deeply influenced by the presence of clay in the matrix, owing to the fact that the filler acts as nucleating agent. DMTA curves show that materials processed at low temperature profile and high shear stress, i.e. when good clay dispersion was achieved, were characterized by an enhanced modulus, thus indicating that the incorporation of clay into the PP matrix remarkably enhances its stiffness and have good reinforcing effects. TGA traces in oxidizing atmosphere show a drastic shift of the weight loss curve towards higher temperature and no variation of the onset temperature. The TGA in inert atmosphere show instead marked increase of this parameter (about 200^{o}C) and no shift of weight loss curves. Glow wire results highlight that PNCs were characterized by enhanced fire behavior.

Qian et al., (2009) prepared the cetyltrimethyl ammonium bromide intercalated MMT(OCL) , by an alkylsilane, dodecyltrimethoxylsilane (CMT) , to improve the miscibility of OCL with PE matrix, involving the grafting reaction between the silane and silanol groups on the edge of clay. The silane modified clays exhibited improved thermal stability due to the replacement of the physically adsorbed ammonium by the covalently bonded silane. The clays were melted with PE. Compared with the composite of PE/CMT. The clay dispersion state was improved and a unique orientation of the clay layered was observed in PE/DMT based PNCs, which was confirmed by XRD and TEM studies. The dispersion state, orientation degree of clay the mechanical and thermal properties of the PNCs were enhanced with the increasing amount of the grafted silane.

Sargolzaei and Akbarabady (2010) studied the thermal stability of MDPE /MMT based PNCs by TGA and DSC methods in a wide range of temperature. The dispersion of the MMT clays on microscopic scales was examined using a TEM. The mass loss from TGA was used to study decomposition temperature in a temperature range from room temperature to 800^{o}C and DSC was used to probe melting and crystallization in a temperature range from room temperature to 300^{o}C. TGA made possible to show that non modified MMT clay and MMT clay modified with alkyl ammonium salt exhibit a significant stabilizing effect on MDPE macromolecules in air atmosphere. DSC shows natural MMT and MMT clay modified with alkyl ammonium salt exhibit a significant change in melting, crystallization, enthalpy and crystalline content of samples. TEM image shows uniform dispersion and intercalation of MMT clays in PNCs.

Huang et al., (2011) observed combination effect between MMT and an intumescent flame retardant to generate OCL for development of LDPE based PNCs. The results from XRD and TEM showed that MMT can achieve better dispersion in LDPE/PSPD blend matrix, and exfoliated LDPE/ intumescent flame retardant /OCL based PNCs were formed. The combination effect of intumescent flame retardant and MMT improved thermal stability and reduced the flammability The peak heat release rate of LDPE/ intumescent flame retardant /OCL was reduced by about 51% compared with pure LDPE. The morphology and composition of residues generated after cone calorimeter test were investigated by SEM and XPS. The SEM showed that the compact and dense intumescent char is formed for LDPE/PSPD/OCL based PNCs after combustion. The results of XPS confirmed that carbon content of char for LDPE/PSPD/OCL increased by the combination effect of PSPD and MMT.

Tasdelen (2011) investigated the influence of the OCL derived from alkylammonium modification of MMT on the ability to form PNCs by melt blending, depending on the processing temperature and the OCL thermal treatment, have been investigated. On one side chlorinated polyethylene/ OCL nanocomposite have been prepared by melt intercalation at 175 ^{o}C and its WXRD pattern revealed that the peak characteristic of the interlayer spacing of the OCL was shifted to lower d-spacing, indicating a collapse of the OCL structure. On the other side, nanocomposites based on Ethylene-vinyl acetate (EVA) copolymer/Cloisite 30B have been prepared by melt intercalation at 140 ^{o}C. At this temperature, exfoliation was observed with the as-received OCL while the same OCL, simply dried at 180 ^{o}C for 2 hours, induced again the formation of a composite with a collapsed structure. The effect of the Cloisite 30B thermal treatment on the morphology and mechanical properties of EVA-based nanocomposites was investigated using XRD and tensile test. In order to shed some light on the origin of this clay interlayer collapse, OCL modified with various ammonium cation bearing long alkyl chains with different amounts of unsaturation were studied using XRD and X-ray photoelectron spectroscopy before and after thermal treatment at 180oC for 2 hours.

Kunkel et al., (2011) prepared the clay-polyolefin based PNCs by in situ polymerization of ethylene or propylene, using a catalyst adsorbed onto the clay. Decreased thermal stability attributed to clay-catalyzed polymer decomposition, while decreased flammability was raised in part from clay-catalyzed formation of a polyaromatic char from olefins trapped in the material by the dispersed nanofiller.

Grigoriadi et al., (2012) prepared LDPE/ layered silicate based PNCs. LDPE-based PNCs, without any polymer modification and with two kinds of clays, one with low aspect ratio (Lp) and another with high aspect ratio (MMT) and characterized using DMTA. Organo silicates (2, 5 and 10 wt%) were added, respectively. XRD was performed on composites obtained by dispersing the organo silicates in unmodified LDPE. The LPDE reinforced with MMT had better performance in the whole temperature range than those with organo-laponite. It was concluded that the relatively high aspect ratio MMT can induce superior dynamic mechanical properties to the LDPE polymer compared to lower aspect ratio organo-laponite. This was linked to the higher active surface area and preferential orientation of longer platelets resulting in higher mechanical enhancement. This behavior was more pronounced up to filler contents of 5 wt%. Further increase of the filler content led to more conventional composites, which hindered the reinforcing ability of the silicates.

3.2. Clay polystyrene nanocomposites

Jang et al., (2001) prepared and characterized a new hybrid organic-inorganic PNCs consisting of ABS terpolymer and a Na+ exchanged MMT by direct intercalation through one-step emulsion polymerization. Those products were purified by successive hot acetone and toluene extraction, respectively, for more than 2 days. The FT-IR spectra for the purified samples revealed the characteristic absorbance as a result of those of ST, butadiene, acrylonitrile, and MMT. XRD of the composites showed the enlarged 001 d-spacing as much as 1.75 nm, but no signals were found for the partial insertion of copolymer chains. The direct intercalation was not accompanied by delamination of the clay interlayer. The TGA confirmed that the onset temperature of decomposition was transferred to the higher temperature region as much as 40-50 °C. Morphological observations by TEM, ESM, and optical micrograph demonstrated homogeneous dispersion of MMT particles in the copolymer matrix.

Yao et al., (2002) prepared crown ether-modified clays (OCL) by the combination of sodium and potassium clays with crown ethers. PS based PNCs were prepared by bulk polymerization in the presence of clays. The PNCs were characterized by XRD, TEM, TGA and cone calorimetry. PNCs can be formed only from the potassium clays; apparently the sodium clays are not sufficiently organophilic to enable PNCs. The onset temperature of the degradation was higher for PNCs compared to PS and the peak heat release rate was decreased by 25% to 30%.

Wang et al., (2003) used monoalkyl-and dialkyl-imidazolium surfactants to prepared OCL from MMT with markedly improved thermal stability in comparison with their alkyl-ammonium equivalents. Increase in the thermal stability affords the opportunity to form syndiotactic PS/imidazolium-MMT based PNCs even under static melt-intercalation conditions in the absence of high shear rates or solvents. Upon PNCs formation, s-PS exhibited an improvement in the thermal stability in comparison with neat s-PS. This crystallization response agrees with s-PS/pyridinium-MMT hybrids and was tentatively attributed to a heterogeneous nucleation action by the inorganic fillers.

Zhao et al., (2005) developed a rheological technique to analyze the clay morphology in PNCs. For this purpose, a series of PS–clay based PNCs with 1, 2-dimethyl-3-n-hexadecyl imidazolium (DMHDI) organically modified clays were prepared. These PS based PNCs investigated and demonstrated a change of pattern in dynamic mechanical spectrum, as a function of the degree of exfoliation, from typical polymer response to a terminal response of storage (G') and loss moduli (G") then to a pattern with double crossover frequencies, and finally to a solid-like response with G'>G" in all frequency ranges. In addition, the rheological response of PS–clays based PNCs made from DMHDI modified clay combined with high-energy sonication , characterized as exfoliated by XRD and TEM was compared with that of PNCs made by dimethyl, benzyl hydrogenated tallow (2MBHT) modified clay.

Zhang et al., (2005) prepared styrenic polymer clay based PNCs through melt blending the polymer with MMT. Polymers used in this study were high impact PS, SAN and ABS. XRD and TEM were used to evaluate the structure of the PNCs. Intercalated PNCs were formed for high impact PS while delaminated PNCs were formed for SAN and ABS. The thermal stability and fire properties were evaluated using TGA and cone caloriemetry, respectively. PNCs formation have a small effect on the thermal stability while the reduction in peak heat release rate was comparable with other PNCs. PNCs had enhanced Young's modulus.

Modesti et al., (2007) prepared ABS /clay based PNCs using an intercalation–adsorption technique from polymer in solution: polymer/clay suspensions were subjected to ultrasonic processing to increase the effectiveness of mixing. Only imidazolium-treated MMT was stable at the processing temperature of 200 °C, used for hot-pressing, whereas alkylammonium modified clays show significant degradation. The morphology of ABS based PNCs prepared was characterized by XRD and TEM. DMTA was used to determine the storage modulus and damping coefficient as a function of temperature, and to investigate the correlations between mechanical properties and morphology of the PNCs.

Greesh et al., (2008) prepared PS-co-butyl acrylate by free-radical random co-polymerization of styrene and butyl acrylate in emulsion in the presence of surface-modified Na-MMT (10 wt %) was modified using different organic modifiers, namely: sodium 1-allyloxy-2-hydroxypropyl (Cops), 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPS), N-isopropylacrylamide (NIPA), and sodium 11-methacryloyloxy-undecan-1-yl sulfate (MET), respectively. The morphology and properties of the PNCs obtained were found to be dependant on the clay organic modifier. XRD and TEM indicated that, PNCs at clay loading (10 wt %) with Cops-, NIPA-, and MET-modified clays, yielded intercalated to partially exfoliated structures, whereas AMPS-modified clay gave a PNCs with a fully exfoliated structure. All polymer–clay based PNCs were found to be more thermally stable than neat poly (Si-co-BA). However, PNCs with intercalated structures exhibited greater thermal stability relative to fully exfoliated ones. Furthermore, PNCs with exfoliated structures exhibited higher storage moduli (GI) than partially exfoliated once, whereas intercalated structure showed the lowest GI values.

Yang et al., (2008) prepared OCL by using ion-exchange method between sodium ions in clay layers and four kind of quaternary ammonium salt. The MMT has the largest d001-spacing, as determined by XRD in modified by di (hydrogenated tallowalkyl) dimethylammonium chloride. PS-MMT based PNCs were obtained by suspension and emulsion polymerization of styrene in the dispersed OCL. The thermal stability of MMT was investigated by TGA.

Michael et al., (2010) developed an efficient extrusion process involving the injection of water while processing to prepare SAN/clay based PNCs with a high degree of nanoclay delamination. The applications of water-assisted extrusion were highlighted in comparison with classical extrusion and roll mill processes. Cloisite R30B (C30B), a MMT clay modified with alkylammonium cation bearing 2-hydroxyethyl chains, and pristine MMT were melt blended with SAN (25 wt% AN) in a semi-industrial scale extruder specially designed to allow water injection. XRD analysis, visual and TEM observations were used to evaluate the quality of clay dispersion. The relationship between the PNCs morphology and its mechanical and thermal properties were investigated. The superiority of the SAN/C30B based PNCs extruded with water has been evidenced by cone caloriemetry and TGA. A substantial improvement of fire behavior and the thermal properties, while a 20% increase of the Young modulus was recorded.

Salehi and Razzaghi (2012) dispersed pristine MMT by the latex-coagulation method and OCLby the melt-intercalation method in SBR, based on the same amount of mineral clay in the composites. Dispersion of OCL was examined by XRD before and after vulcanization and by AFM after vulcanization. It was shown that final structure of nanoclay in the composites was intercalated by both methods, with better dispersion resulting from coagulation of latex over mixing in the melt state. DMTA and tension tests were used to further assess dispersion and polymer–filler interactions. These tests confirmed better dispersion and larger interfacial area for pristine nanoclay in the latex-coagulated rubber through observing lower peak loss factor, higher growth of stress in stretching, and lower elongation at break when compared with those for the based PNCs prepared by the melt mixing.

Greesh et al., (2012) prepared PS–clay based PNCs colloidal particles via free-radical polymerization in dispersion. MMT was pre-modified using different concentrations of cationic styrene oligomeric (‘PS-cationic’), and the subsequent modified PS-MMT was used as stabilizer in the dispersion polymerization of styrene. The main objective of this study was to use the clay platelets as fillers to improve the thermal and mechanical properties of the final PNCs and as steric stabilizers in dispersion polymerization after modification with PS-cationic. The correlation between the degree of clay modification and the morphology of the colloidal PS particles was investigated. The clay platelets were found to be encapsulated inside PS latex only when the clay surface was rendered highly hydrophobic, and stable polymer latex was obtained. The morphology of PNCs material (after film formation) was found to range from partially exfoliated to intercalated structure depending on the wt% of PS-MMT loading. The impact of the modified clay loading on the monomer conversion, polymer molecular weight, thermal stability and thermo mechanical properties of final PNCs was determined.

3. 3. Clay/polyacrylate nanocomposites

Costache et al., (2006) studied the thermal degradation of PMMA and its PNCs in the presence of clays (anionic and cationic) or carbon nanotube have an effect on the degradation pathway. PNCs formations have been established by XRD and TEM. Thermal degradation has been investigated by cone caloriemetry and TGA, and the products of degradation were studied with TG-FT-IR and Gas chromatography/mass spectrometry. They have not seen any marked differences in the degradation products of the polymer and its PNCs, but the degradation of the PNCs occurs at higher temperatures.

Fu and Naguib (2006) prepared intercalated PMMA/clay based PNCs through a solvent co-precipitation method and the effects of MMT on the mechanical properties of PMMA)/clay based PNCs foams were investigated. PMMA/clay based PNCs with well-dispersed nanoclay (0.5 wt %) of showed considerable improvement of mechanical properties; specifically in elastic modulus, tensile strength, and elongation at break. However, with an increased load of clay in the PNCs, the mechanical properties decreased due to the agglomeration of excessive nanoclay. Microcellular foams have been processed with PMMA/clay based PNCs material using a subcritical gas foaming method. When a short foaming time was used, the increased amount of nanoclay induced a greater amount of heterogeneous nucleation during the foaming process and therefore decreased the density of the foam. In contrast, when a longer foaming time was used, foam density increased with a larger nanoclay load due to the higher diffusivity coefficient of CO2 blowing agent. Nanoclay, as nucleation agent and reinforcement filler, changed the foaming behavior and mechanical properties of the PMMA microcellular foams. The microcellular foams made of PMMA/clay based PNCs with 0.5 wt% exhibited an optimized mechanical response under tensile experiments. It is observed that the mechanical properties of PNCs foams were greatly related to the mechanical properties of un-foamed material and foam density.

Yun et al., (2008) developed a new strategy for the preparation of well-dispersed clays in a polymer matrix by a spray-drying method. SEM and TEM measurements showed that the spray-drying process produces clay/polymer microspheres in which the clay was trapped in a well-dispersed state throughout the polymer matrix. The microspheres have been successfully extruded into clay/PMMA based PNCs bulk structures without any perturbation of the well-dispersed clay nanostructure in the original microspheres. TEM and SAXS showed that the clay particles were in the extruded materials range from single platelets to simple tactoids composed of a few stacked clay platelets, indicating an excellent degree of dispersion.

Letaief and Detellier (2009) developed a chemical route for the delamination of kaolinite in a polymeric matrix. The strategy used was based on mixing polyelectrolytes of opposite charges, polyacrylate, with an inorganic polycation resulting from the modification of the internal surfaces of kaolinite. The delamination was carried out by the reaction of sodium polyacrylate (PANa) with kaolinite whose internal aluminol surfaces were previously grafted with triethanolamine and subsequently quaternized with iodomethane (TOIM-K) to form an extended lamellar inorganic polycation. XRD as well as SEM confirmed the complete delamination of the kaolinite particles. 13C MAS NMR showed the removal of the ammonium groups resulting from hydrolysis of the internal surfaces once exposed, and 29Si MAS NMR spectra were in agreement with the retention of the 1:1 aluminosilicate kaolinite layers structures. From the TGA data, the respective wt% of PA and kaolinite in the delaminated PNCs could be estimated to be 61% and 39%, respectively, in the conditions of the particular experiment. The interlayer functionalization of kaolinite was crucial for the success of the delamination procedure. SEM show that some individual kaolinite platelets fold and form curved structures.

Pranav et al., (2010) used the multi-directional 2-D SAXS to quantify the orientation distribution of MMT in melt-pressed PNCs films, containing EVA copolymers as polymer matrices. Different weight fractions of MMT were used to alter the orientation profile of PNCs films, in which the dispersion and morphology of MMT were also characterized by complementary 2-D and 3-D TEM. All PNCs exhibited mixed intercalation/exfoliation clay morphology, where the intercalated structure possessed partial orientation parallel to the in-plane direction of the film. The higher content of the clay loading showed a higher clay orientation. A simple analytical scheme for SAXS data analysis to determine the orientation parameter (P2) was demonstrated..

Mahesh et al., (2011) developed a procedure for preparing nanoclay/vinylester gel coat. Two sets of MMT/vinylester specimens, namely Type 1 and Type 2, were prepared for comparative studies. Type 1 specimens were prepared using ultrasonication only, and Type 2 specimens were prepared using both ultrasonication and twin-screw extrusion. DSC results showed that the Tg of Type 2 specimens are higher than those of Type 1 specimens. TGA results showed that the residual weight of 4 wt % MMT/vinylester of Type 1 was 7.38%, while the corresponding value of Type 2 was 13.5%, indicating lower thermal degradation in the latter. MMT/ vinylester/glass and MMT/vinylester/carbon specimens were fabricated and tested for mechanical and fire retardation behaviors. Type 2 based PNCs laminates showed greater values of tensile, flexural, inter-laminar shear and impact strength, horizontal burning rate, and vertical burning rate than Type 1 based laminates.

Patra et al., (2012) synthesized PMMA/clay based PNCs by ultrasound assisted emulsifier-free emulsion polymerization technique. Ultrasound waves of different power and frequencies were applied to enhance the dispersion of the clay layers with polymer matrix. XRD revealed the increase in interlayer spacing with clay loading. The magnitude of dispersion of the clay in the polymer matrix was detected by TEM. The Young’s modulus, breaking stress, elongation at break, toughness, yield stress and yield strain of the PNCs as a function of different clay concentrations and ultrasonic power were measured. Particle diameter of the PNCs was measured by laser diffraction technique. Oxygen permeability of the samples was studied and it was found that the oxygen flow rate was reduced by the combined effect of clay loading and ultrasound.

4. functionalized precursors for development of pncs

The major technical challenge towards development of clay based PNCs lies in the compatibility of clay with polymer matrix. This leads to the formation of PNCs with improved physical properties making them suitable for wide range of industrial applications. Such compatibility of clay with polymer matrix may be achieved through reaction chemistry based approach based on either of functionalization of clays with polymerizable monomers, attaching the reactive sites over the polymer matrix through graft or block copolymerization [Table 2]. In this context, ethylene-vinyl acetate (Marco et al., 2004), PE-g-MA (Sibold et al., 2007; Lew et al., 2004), chlorinated PE (Tasdelen 2011), PP-g-MA (Hwang et al., 2008; Perez et al., 2010; Barbosa et al., 2012) were extensively studied as compatibilizer for OCL. Most recent approach of achieving enhanced dispersion and compatibility of clays with polymers is based on reaction chemistry that involves grafting of functional macromolecules onto polymer backbones. This route provides PNCs with improved thermal, mechanical, barrier properties and flame retardency.

4.1. Pncs from polymer functionalized clay with thermosetting polymers

Wu et al., (2001) prepared carboxylated acrylonitrile-butadiene rubber (CNBR)-clay mixtures by co-coagulating rubber latex and aqueous suspension of clay .The contents were subsequently combined with a rubber ingredient and vulcanized by a traditional rubber mixing processing procedure. TEM showed that the silicate layers of clay were delaminated or intercalated with CNBR and dispersed in the CNBR matrix at a nanometer level during co-coagulating. XRD indicated that the intercalated amount of CNBR between the layers that were increased with the increase in content of clay in CNBR. The aspect ratio (width/thickness) of the platelet inclusions was reduced and the silicate layers were aligned more orderly during the compounding operation on an open mill. In these PNCs, the particles of silicate layers were dispersed at the nanometer level and the structure was a combination of delaminated and intercalated silicate layers dispersed in the continuous CNBR matrix.

Benali et al., (2008) have prepared PA6/clay based PNCs by "click" reaction. In this method, ring-opening polymerization of ε-caprolactone using propargyl alcohol as the initiator have been performed to produce alkyne-functionalized PA6 and the obtained polymers were subsequently attached to azide-modified clay layers by a "click" reaction. The exfoliated PNCs were characterized by XRD, TGA and TEM.

Benali et al., (2008) prepared exfoliated PNCs by dispersion of polycaprolactone grafted MMT used as master batches in SAN. The polycaprolactone-grafted nanoclay hybrids with high inorganic content are synthesized by in situ intercalative ring-opening polymerization of ε-caporolactone between silicates layers of OCL derived through modification of MMT with alkylammonium cation bearing two hydroxyl functions. The polymerization was initiated by tin alcoholate species derived from the exchange reaction of tin (II) bis (2-ethylhexanoate) with the hydroxyl groups borne by the ammonium cation that nanoclay. These highly filled polycaprolactone based PNCs (25 wt %) were dispersed as master batches in commercial SAN by melt blending. SAN-based PNCs containing nanoclay (3 wt %) were accordingly prepared. The direct blend of SAN/OCL was also prepared for sake of comparison. The nanoclay dispersion was characterized by wide angle XRD, AFM and solid state NMR spectroscopy measurements.

Benali et al., (2008) prepared exfoliated PNCs by dispersion of PA6-g-MMT nanohybrids used as masterbatches. The PA6-g-clay nanohybrids with high inorganic content were synthesized by in situ intercalative polymerization of masterbatches between silicate layers organomodified by alkylammonium cation bearing two hydroxyl functions. The polymerization was initiated by tin alcoholate species derived from the exchange reaction of tin (II) bis (2-ethylhexanoate) with the hydroxyl groups borne by the ammonium cation that generating OCL. These highly nanoclay (25 wt %) filled PCL based PNCs were dispersed as masterbatches in commercial chlorinated PE by melt blending. The formation of exfoliated PNCs was assessed both by WXRD and TEM. The thermal and thermo-mechanical properties were studied as a function of the filler content, by DSC and DMTA, respectively. The mechanical properties were also assessed by tensile tests. The influence of PCL grafting on the properties of these PNCs was investigated by comparison with materials obtained with un-grafted-PCL.

Zulfiqar and Sarwar (2009) synthesized PNCs from reactive thermally stable MMT and aromatic–aliphatic polyamide obtained from 4-aminophenyl sulfone and sebacoyl chloride. Carbonyl chloride terminal chain ends were generated using 1 wt % extra sebacoyl chloride that could interact chemically with the OCL. The distribution of OCL in the PNCs was investigated by XRD, SEM, and TEM. Mechanical and thermal properties of these materials were monitored using tensile testing, TGA, and DSC. The results revealed delaminated and intercalated nanostructures leading to improved tensile strength and modulus up to 6 wt% addition of OCL. The elongation at break and toughness of the PNCs decreased with increasing clay contents. The PNCs were thermally stable in the range 400–450°C. The Tg was increased relative to the neat polyamide due to the interfacial interactions between the two phases. Water uptake of the hybrids decreased upon the addition of OCL depicting reduced permeability.

Naderi et al., (2011) investigated the effect of nanoclay and polyepichlorohydrin-co-ethylene oxide (ECO) content on the microstructure and mechanical properties of PA6/ECO thermoplastic elastomers (TPEs). TPE based PNCs were prepared using PA6, ECO and an OCL by a two-step melt mixing process. First, the PA6 was melt blended with Cloisite 30B and then mixed by ECO rubber. XRD and TEM image showed that the nanoclay platelets were nearly exfoliated in both the phases. The SEM of PA6 with ECO showed that the elastomer particles were dispersed throughout the polyamide matrix and the size of rubber particles was < 3 µm. Introduction of OCL in the PA6 matrix increased the size of dispersed rubber particles in comparison with the unfilled. The dispersed nanoclay results in an improvement of the tensile modulus of the PNCs.

Li et al., (2012) prepared prepolymer composed OCL by reaction of polyol/OCL mixture with toluene diisocyanate. The prepolymer composed with ultrasonic assistant mixture of polyol reactive OCL was reacted with extender and then the PU-urea/MMT (PUU/OCL) based PNCs were obtained. The results showed that at OCL content of 3 wt %, the PU/OCL based PNCs performed super mechanical properties. Because of the presence of OCL, both TG of the soft segment and tan δ of the PUU increased, and the decomposition temperature for the first step and the second step increased respectively. TEM images showed that the OCL particles in the PUU composite exhibit a high degree of dispersion.

Longun (2012) synthesized polyimide (PI)/poly (N-ethyl aniline-co-aniline-2-sulfonic acid)-clay (SPNEAC) based PNCs films containing water-soluble SPNEAC. AFM studies showed a homogeneous distribution of coated clay particles in the PI matrix. The particle sizes varied between about 50 nm and about 220 nm in height and 6–7 µm in length in the PNCs containing SPNEAC (5 wt %). Average surface roughnesses of 0.253 and 34.9 nm were obtained for neat PI and SPNEAC–PI (5 wt %) based PNCs, respectively. The DMTA results show a decreasing Tg of the PNCs with increasing SPNEAC weight fraction. The area under the α-transition peak, which is associated with damping and impact energy, increased with increasing SPNEAC weight fraction. The impact energy of the PNCs was estimated with a viscoelastic model. It increased with increasing SPNEAC weight fraction, and a maximum value of 84.9 mJ was obtained. A 5 wt % addition of SPNEAC improved the impact energy of neat PI films by 300%. SEM micrographs of the PNCs films showed a less compact cross-sectional morphology.

4.2. PNCs from functionalized thermoplastic polymers

Wan et al., (2003) synthesized three kinds of polyvinyl chloride (PVC)/MMT based PNCs by melt blending of PVC with NaMMT and two varieties of OCL. The nanostructure and relaxation behavior of the PVC/MMT based PNCs were studied by WXRD, TEM and DMTA. It was found that partially intercalated and disordered structure formed in PVC/Na+-MMT based PNCs, while partially intercalated and partially exfoliated structures coexisted in the two PVC/OCL based PNCs. The stiffness and impact strength of the three kinds of PNCs were improved simultaneously within 0.5-3.0 wt% MMT with respect to that of bulk PVC. Below 5 wt% MMT content, the three kinds of PNCs retain good optical clarity.

4.3. PNCs from monomer functionalized clay with thermoplastic polymers

Moet and Akelah (1993) prepared PS-MMT intercalates, which were able to swell and disperse in organic solvents, by a cation exchange process by the interaction between the Na+ or Ca2+ cation of MMT and vinylbenzyltrimethylammonium chloride. The resulting vinyl monomer-MMT materials have been identified by XRD, elemental analysis and FT-IR spectra. Free-radical polymerizations of penetrated styrene between the interlayer of 5, 10, 25 and 50 wt% vinyl monomer-MMT resulted in grafted PS-MMT materials. The effect of MMT amounts on the formed PS was determined by extraction with organic solvents, which showed an increase in the grafted polymer formed (0.84–2.94 % wt), and a decrease in the external PS with increasing amounts of MMT. The molecular weight of the external PS was found to be in the range of 22000. The vinyl monomer-MMT and polymer-MMT intercalates were identified by XRD, elemental analysis and FT-IR. Examination of the PS-MMT materials by microscopy and XRD showed spherical particles of nano-size about 150–400 nm, and basal spacing of 1.72–2.45 nm.

Fu and Qutubuddin (2001) synthesized a polymerizable cationic surfactant, vinylbenzyldimethyldodecylammonium chloride (VDAC) for functionalization of MMT and preparation of exfoliated PS–clay based PNCs. OCL was prepared by cationic exchange with VDAC in an aqueous medium. Dispersions of intercalated clay (VDAC–MMT) in styrene monomer formed gels. Shear thinning behavior of the gels was observed via rheological measurements. PS-clay based PNCs were prepared by free radical polymerization of styrene containing dispersed OCL. Exfoliation of MMT in PS matrix was revealed by XRD and TEM.

Meneghetti and Qutubuddin (2006) synthesized PMMA/clay based PNCs via two methods: insitu and emulsion polymerization. The insitu technique follows a two-step process: ion-exchange of the clay to make it hydrophobic, and polymerization after dispersing the functionalized clay in the monomer. The emulsion technique combines the two steps of the in situ method into one by conducting ion-exchange and polymerization in an aqueous medium in the same reactor. The MMT was functionalized with a zwitter ionic surfactant, octadecyldimethyl betaine (C18DMB). Partially exfoliated PNCs, observed by TEM, and were obtained by emulsion polymerization in presence of clay (10 wt. %). Tg of this PNCs was 18 °C higher than pure PMMA. With the same clay content, in situ polymerization produced intercalated PNCs with Tg 10 °C lower than the emulsion PNCs. The storage modulus of partially exfoliated PNCs was superior to the intercalated structure and to the pure polymer.

4.4. PNCs through compatibilizing functionalized thermoplastic polymers with clay

Pralay et al., (2002) prepared intercalated PNCs of PP/ clay by a melt extrusion process using of maleic anhydride modified PP (PP-MA) and MMT. The extent of intercalation of PP-MA chains in the space between silicate galleries increased with crystallization temperature and decreased as clay content increased. As compared to matrix PP-MA, the dispersed clay particles in the PP-MA matrix acted as nucleating agent and lowered the sphereulite formation with increasing clay content as revealed by lights scattering experiments and polarizing optical microscopy. Extensive intercalation occurred during crystallization, especially at high temperature due to the long time for full solidification of the melt. The degree of intercalation of PP-MA chains in the silicate galleries was depending on time in the molten state.

Lew et al., (2004) prepared polyolefin-OCL based PNCs containing a synthetic tetrasilisic fluoromica from metallocene-catalyzed and conventional Ziegler-Natta-catalyzed LLDPE by melt-compounding. The effects of PE-g-MA level, clay concentration, and blending procedure were investigated and compared. Morphology and structural analysis using TEM and XRD suggested the clay exfoliation was more intense in the metallocene LLDPE matrix, conceivably because of the controlled short-chain branching and viscosity effects. When exfoliated, these silicate sheets were shown to restrict the lamellar crystallization, as seen by the decreased in crystallinity using DSC. The DMTA indicated that the three α, β, and γ-relaxations of the LLDPE were affected by polymer chain branching and clay exfoliation level.

Leroux et al., (2005) used 3-sulfopropyl methacrylate as filler for PS. Different PNCs 3-sulfopropyl methacrylate: PS was prepared by bulk polymerization process using low amount of initiator. The two components, filler and polymer as well as the degree dispersion of the reactive filler as a function of its loading in PS were characterized by XRD, 13C NMR, FT-IR, UV–visible, thermal analysis, size exclusion chromatograph. The PNCs were exposed to UV-light in the presence of oxygen. The oxidation photoproducts and the rates of oxidation were compared for the various samples. That indicated the filler was not modifying the oxidation mechanism of the polymer, but had a slight effect on the oxidation rate.

Sibold et al., (2007) synthesized the tailored compounds, based on alkyl-substituted derivatives of succinic anhydride, acid and dipotassium salt to evaluate their role for intercalation of MM Tto generate OCL and the formation of PNCs based on PE in the presence of PE-g-MA as compatibilizer. The samples were prepared via a solution dispersion technique. They have found that these tailored compounds can be intercalated into the layers of MMT and expansion of the lattice was confirmed by WXRD and FT-IR spectra. The higher affinity of the succinic groups for the OCL has been explained as well as the decrease of the polar function influence on the gallery expansion when increasing the hydrophobicity of the organic compounds and acid salt derivative.

Santos (2008) prepared PP based PNCs using MMT with different organic modifiers, and the effect of processing aid on the dispersion of the nanofillers in the PP matrix was evaluated by WXRD, TEM, DSC, TGA, DMTA, and mechanical tests. PNCs of intercalated and partially exfoliated morphology were obtained, mainly when a low amount (1:1) of PP-g-MA/MMT was used. The results of the tests on mechanical properties showed that the clays with larger d001 using polypropylene glycol presented a more considerable gain in impact strength. The PNCs using clays with smaller d001 presented larger modulus when compared with those of pristine PP. The heat deflection temperature, crystallization temperature, and thermal stability of the PNCs were improved compared to neat PP. The DMTA results showed that the MMT improved the modulus of PP, but decreased the Tg.

Hwang et al., (2008) described the possibility of incorporating supercritical carbon dioxide (scCO2) into twin screw extrusion process for the production of PNCs. The CO2 was used as a reversible plasticizer which expected to rapidly transport polymeric chains into the galleries of clay layers in its supercritical condition inside the extruder barrel and to expand the gallery spacing in its sub-critical state upon emerging from dien. The structure and properties of the resulting PNCs were characterized using WXRD, TEM, rheometry, thermogravimetry and mechanical testing. In the processing of the PNCs with $scCO_2$, optimum scCO2 concentration and screw speed which maximized the degree of intercalation of clay layers were observed. The WXRD result reveals that the PP/PP-g-MA/clay system treated with $scCO_2$ has more exfoliated structure than that without treatment, which is supported by TEM result. $ScCO_2$ processing enhanced the thermal stability of PNCs hybrids.

Koh et al., (2010) prepared PVDF/clay based PNCs membranes by phase inversion method through controlling retention time to apply for lithium ion secondary batteries. Increased membrane porosity with macro voids was observed at increasing retention time. Partially intercalated structures of PVdF / clay based PNCs membranes were confirmed by XRD analysis. PVdF membranes containing various kind of clay showed increase of membrane modulus compared to the pristine PVdF.

Perez et al., (2010) prepared PP clay nanocomposites by using the method of mixing in the molten state in extruders with OCL(5 wt %) with and without PP-g-MA. The DSC, TGA, XRD, TEM, and DMTA of PNCs were characterized. All PNCs prepared in intercalated state as corroborated by XRD and TEM. The TEM and XRD were not affected by the presence of clay, PP-g-MA. The incorporation of clay and compatibilizer agent has increased the thermal stability.

Barbosa et al., (2012) prepared PNCs using the technique of melt intercalation, starting from a concentrated polar compatibilizer (PE-g-MA) / MMT in an internal mixer. The concentrate was incorporated into the matrix of

HDPE by two methods: I) counter-rotating twin-screw extruder and II) co-rotating twin-screw extruder, using two screw profiles. After extrusion, the specimens of the extruded composites were injection molded. The XRD technique was used to analyze the degree of expansion of the prepared clays. To analyze the degree of exfoliation of obtained PNCs, XRD and TEM were used. The influence of processing variables on mechanical properties was studied through the behavior of the modulus and tensile strength of PNCs. XRD and TEM revealed the well dispersion of clay in matrix with presence of intercalated and partially exfoliated hybrid structure for PNCs when the systems were prepared in counter-rotating twin-screw extruder.

Wang et al., (2012) successfully modified the natural bentonite using PMMA-g- PEO comb copolymer. Changes in the surfaces and microstructure of the resultant organo-bentonite were characterized by FT-IR, XRD, TG, SEM and high-TEM respectively. FTIR results indicated the presence of the copolymer on the surface of organo-bentonite. XRD measurements showed that the copolymer molecules were intercalated into the bentonite layers. TG and SEM demonstrated the interlayer of bentonite was intercalated by the copolymers with surface adsorption to a certain extent.

Pakdaman et al., (2013) prepared Silane-g- HDPE by reactive extrusion. The grafted PE was then melt compounded with MMT and PA6 to form ternary PNCs. FT-IR for investigation of grafting efficiency of specimens. Dispersion of clay in the blends and individual polymers were examined by XRD, SAXS and TEM. SEM and dynamic rheology were also used for further study of microstructure along with compatibilization effect of silane grafting and adding MMT in the blends. SAXS and TEM study showed that nanoclay was delaminated by PA6 or Silane-grafted HDPE chains, whereas the intercalation of neat HDPE in clay layers was negligible especially in higher level of clay. The morphological studies indicated that silane-grafted HDPE had hydrophilic characteristics and, therefore, was more compatible with PA6 than neat PE. Furthermore, in the same way adding nanoclay to this blends resulted in more uniform and finer morphology.

5. Conclusion

Remarkable progress has been made on development of organoclay (OCL) based polymer nanocomposites (PNCs) and great claims have been made on their various industrial applications. However, this is recognizable fact that although extensive research on the development of OCL derived PNCs has been made, is still the field is in its infancy, and the main object to apply OCL in industry fields is still for limited applications. Thus, the opportunities for development space are unlimited.

Table 2

Progress in the development of PNCs from reaction chemistry based approach.

Polymer Matrix	Filler	Modifications achieved	Reference
SAN	PA6-g-OMMT	Clay dispersion	Benali et al., (2008)
SAN	MMT	Mechanical properties	Michael et al., (2010)
PP-g-MA	OCL	Storage modulus	Kawasumi et al., (1997)
PP-g-MA	MMT	Clay dispersion	Pralay et al., (2002)
PP-g-MA	MMT	Storage modulus	Santos (2008)
PP/PP-g-MA	MMT	Thermal properties	Hwang et al., (2008)
PP-g-MA	OCL	Thermal properties	Perez et al., (2010)
PE-g-MA	OMMT	Mechanical properties	Barbosa et al., (2012)
PE-g-MA	OMMT	Physical properties	Sibold et al., (2007)
PE-g-MA	OMMT	Physical properties	Lew et al., (2004)
MMA-MA	OCL	Mechanical properties	Garcia et al., (2003)
PVDF	MMT	Membrane strength	Koh et al., (2010)
PS-co-butyl acrylate	OCL	Storage modulus	Greesh et al., (2008)
PANa	OCL	Clay dispersion	Letaief and Detellier (2009)
CPE	OCL	Clay dispersion	Tasdelen ., (2011)
PMMA-g-PEO	OCL	Clay dispersion	Wang et al., (2012)
Silane-g- HDPE/ PA6	OCL	Clay dispersion	Pakdaman et al., (2013)

From our point of view, the following directions deserve attention in the near future: (1) development of new low cost strategies for functionalization of clays with quaternary ammonium salts, crown ethers alkylsilanes, and zwitterions (2) preparation of novel functional hyperbranch, dendritic, block or graft polymers as a substitute of existing clay modifiers to achieve improved clay/polymer compatibility (3) tailoring the properties of polymeric clay modifiers through various reaction chemistry based strategies; (4) opening novel class of interdisciplinary application fields for OCL derived PNCs , especially applicable as transparent films, gas barrier devices, various engineering and biomedical applications.

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