American Journal of Engineering Research (AJER)
e-ISSN: 2320-0847 p-ISSN : 2320-0936
Volume-12, Issue-2, pp-01-16
www.ajer.org
Research Paper Open Access

Clay Particulate Reinforced Polymer Composites: A Review on development of macro-nanocomposites and applications

[a]AdewumiOjoAdemola, [a,b]OladeleIsiakaOluwole and [a]DaramolaOjoOluyemi
[a]Department of Metallurgical and Materials Engineering, Federal University of Technology, PMB, 704, Akure, Ondo State, Nigeria
[b]Centre for Nanomechanics and Tribocorrosion, School of Metallurgy, Chemical and Mining Engineering, University of Johannesburg, Johannesburg, South Africa

ABSTRACT
It has been established that, the development in any nation depends on the available materials. This advancement has been highly promoted by composite material development. The dynamic trends in materials development have been greatly projected in composite materials development where two or more materials are blended to achieve improved properties. Clay is one of the major classes of ceramic materials with its outstanding properties that are required in materials for various applications, predominantly in biomaterials as well as building and construction industries. However, its inherent brittle nature has hindered the prospect of the desired areas of applications as a sole monolithic material. Hence, there is need for several modifications to improve their properties in other to meet their expected demand in any areas of applications. This review was carried out to reveal the versatile usage of clays in polymer composites, their production and also promote further the use of clay in material development for advanced application.

Keywords*: Sustainable materials, classification of materials, clay, polymer, organoclay, composites, intercalation, exfoliation, nanocomposites*

Date of Submission: 20-01-2023 Date of acceptance: 03-02-2023

I. INTRODUCTION

Polymer matrix composites (PMCs) are developed by incorporating reinforcement into the matrix of thermoplastic and thermosetting materials. Their properties such as lightweight, high stiffness, high strength, good corrosion resistance, lesser environmental degradation, excellent thermal insulation, good acoustic damping, excellent design flexibility, and non-magnetic properties have broadened the range of their applications (Oladele*et al.*, 2020;Prabhakar*et al.*, 2018). They are currently replacing conventional materials such as metal, ceramics, polymer and wood in diverse applications that require advanced engineering materials. However, one of its major shortcomings is the dispersion problem. The clay particles in the development of the polymer-clay composites (PCC)contain inclusions (impurities) that impede the clay dispersing in the polymer matrix during the development of the PCC.

Organically modified polymer-clay nanocomposites (PCC) possess high mechanical properties (Zwane*et al.*, 2019;Daitx*et al.*, 2015), thermal properties (Abbasian*et al.*, 2020; Ramesh *et al.*, 2020) and liquid barrier properties (Kezia*et al.*, 2019;Alhwaige*et al.*, 2020) than pure polymers and other conventionally modified microcomposites of clay and polymer.

Before now, expensive clay minerals are often used in preparing microsized dispersion on polymer matrix to bring about the desiredenhanced properties (Sudhakar*et al.*, 2021).Thereafter, sodium montmorillonite (Na-MMt) a natural smectite clay (2:1 phyllosilicate)consisting of aluminosilicate layers with a high aspect ratio and a high surface area were used to synthesize PCC (Kezia*et al.*, 2019).

Based on the mode of dispersion of clay in the polymer matrix, two types of PCC are formed which are intercalated PCC andexfoliated PCC. Clay is found to be occasionally dispersed in intercalated PCC while in exfoliated PCC, clay nanoparticlesare exfoliated from layers due to penetration of polymer chain through the layers. Thus, morphology control depends onthe mode of preparation and the type of organic modifiers used (Yang*et al.,* 2016;Kakarla*et al.*, 2019).

In this review, an attempt is made to evaluate modification methods by reviewing the various preparation/processing for clay-polymer compositesroutes, methods of characterization of the composite materials, how to classify them into different formulations, appraising their excellent properties as well as various applications in the industries.

Modification of Clay Particles

The reaction and dispersion of the clay with most polymer (thermoset/thermoplastics) matrices have been considered to be very difficult as a result of the strong covalent bonds existing between the interlayers of the clay,the hydrophilic nature of the clays and also the electrostatic forces closely hold the stacks of claylayers together. The particles of the clay are made to undergo some modification prior to being made to react or dispersed in polymer matrices for these challenges to solve. The introduction of the hydrophobic characters into the clay minerals which its layered silicates have increased during the modification process by surfactants intercalation will allow the modified clay to flow and dispersed very well in the polymer matrices. There are two types of modification techniques: (i) physical modification and (ii) chemical modification. The physical modification process is all about adhesion of modifying chemicals on the surface of the clay particles. However, physical modification does not alter the clay particles interlayered that much but it helps to slightly improve the properties of the polymer composites produced. The weak van derWaals forces existing between the modifying chemicals and clay particles could be the reason for the marginal improvement in the properties of the polymer composites produced.

On the other hand, the chemical reactions created between the layered silicates and the modifier is being aided by chemical modification. The molecules however, are being modified by adoption of cationic or anionic functional groups in ion exchange process which later improved the capacity of the clay to disperse in polymer. Modified clay particles can be divided into pillared layered clays, organoclays, nanocomposites, acid- and salt-induced Vlasova*et al.*, 2003 as well as thermally and mechanically induced modified clays Basak*et al.*(2012).

The improvedmechanical, thermal, optical, and barrier properties of polymer/nanoclay composite systemsare due to the nano-thick layers existing in the clay material, as well as the largersurfacearea and higher aspect ratio exhibited by clay particles when distributed in polymericcomposites (Wang*et al.,* 2021; Kausar, 2020).

Organoclay which is one of the pillared layered clays has gained so much recognition and application in areas such as cosmetics, chemical, medicine, petrochemical industry and environmental protection. It is used as a sorbent of organic contaminants from the environmentand equally used in wastewater treatment in the textile industry because of the toxicity of the textile dyes and their degradation products on the environment(Chaari, 2011; Tahir and Rauf, 2006).

For a material that could be used for bone biomaterials application to be produced, Zapata et al.(2013) developed silica/clay organoheterostructures to encourage polyethylene-clay nanocomposites by *in situ* polymerization modifying sodium montmorillonite clay with three different unnatural amino acids in order to design intercalated clay structures that will suit the purpose (Katti, *et al.,* 2010). Montmorillonite clayparticle was modified to improve itsthermal properties using Poly(ethylenimine) with a molecular weight of 60000. Bentonite clay was organically modified using the monomerethenyl acetate the exchange of inorganic intralayercations of the clay was achieved using a cationic surfactant (Genamine CTAC). Organoclay modified in this way was integrated inLuviskol, Carbopole and purine. The adsorptive properties of the obtained composites oforganoclays were investigated along with their capability for removing toxic Pb^{2+} from waterin charged systems Stojiljkovic*et al.* (2013). High specific surface, the presence of charge, the existence of a highnumber of macro, micro and submicro pores in the structure of the composite, as well as ahigh number of active centers on its surface cause the material to show good adsorptive characteristics towards Pb^{2+} ions which was confirmed by the decrease of the value of the electrical conductivity. The efficiency of clays modifies many different properties of the polymer, such as sorbancy, ion exchange capabilities as well asthermal and solvent resistance. They gave improved mechanical properties and accelerate the diffusion of oxygen which is important for the packaging industry. To reduce costs and improve the comprehensive waterabsorbing properties of superabsorbent materials based on acrylic monomers, grafting acrylicmonomers onto clay and fabricating a composite consisting of a polymer and clay is a priority. Organically modified clays are recommended as a good option for removal of oil fromproduced water (Oliveira *et al.*, 2012; Mowla*et al.*,2013).

The adsorption for some organic pollutants using bentoniteorganoclay has been studied (Oliveira *et al.*, 2012).Abdelwahab, (2013) reported the modifiedbentoniteas an excellent alternative in the adsorption of hydrocarbon from oil-water emulsionremoval with the highest adsorption capacity (48 mg/g at 2 g/dm3). Additionally, interest inthe synthesis of polymer-clay nanocomposites in tissue engineering is growing as it is cheap,easily available, and environmentally friendly (Chrzanowski*et al.*, 2013). The structure of clay allows the interclaysion of different biomolecules between the clay layers. These biomolecules can bereleased in a controlled manner which can be utilised in drug delivery and cosmetic applications.

The alteration of clay particles is depicted schematically in Figure 4 (Fischer, 2003). TEM images of clay bentonite before and after modificationwith the quaternary ammonium salt of octadecylamine are shown in Figure 5(Motawie*et al.*, 2014).

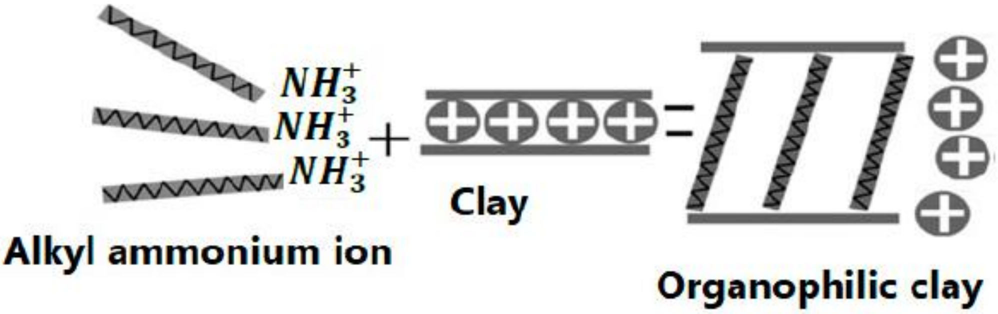

Figure 4: Schematic representation of an ion-exchange reaction (Fischer, 2003)

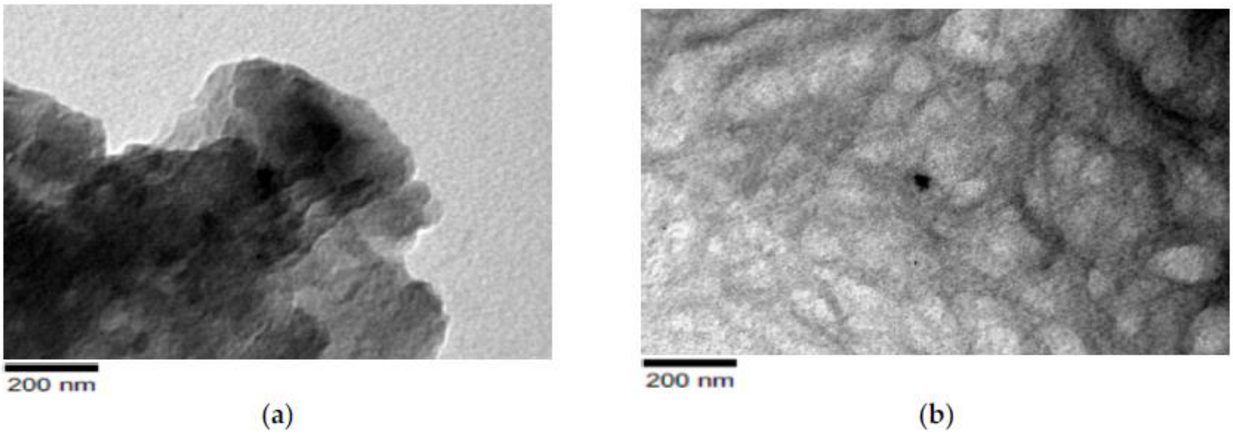

Figure 5:TEM images of organoclay (**a**) before modification and (**b**) after modification with octadecyl amine, reprinted from (Motawie*et al.*, 2014)

Processing of Clay/Polymer Nanocomposites

Solution Blending Method

In this method the solutions of both the polymer and the clay are being prepared separately where the polymer is dissolved in a particular solvent before it is being deployed to use in this method. Likewise, clay also is dispersed separately in the same solvent. Thereafter, the combination of clay and solvent is discharged into the polymer solution. Lastly, the combination of both polymer and clay is homogenized for awhile before they are cast on a Peter dish for the solvent to be evaporated (Jamshidian*et al.*, 2012; Gong *et al.*, 2014).The processes in the solution blendingmethod are being described schematically in Figure 6.

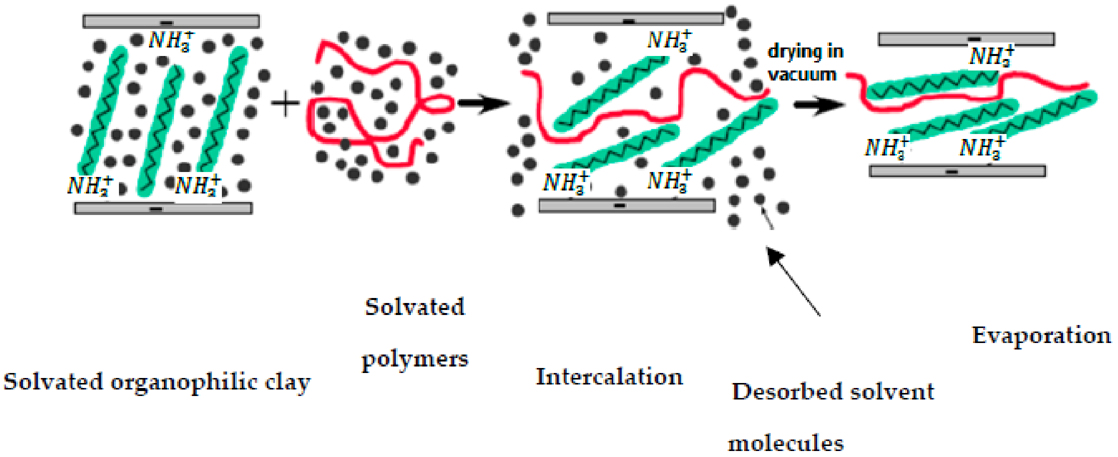

Figure 6: Solution blending for the preparation of polymer/ clay nanocomposite

Melt Blending Method

The melt blending method is used to directly reinforce polymer with clay particles whereby the polymer and clay mix is annealed and it is commonly done at the temperature above the polymer's melting point. This method provides superior compatibility between the layered silicate and the polymer when compare with solution blending approach(Pesetskii*et al.*,2021; Tawakkal*et al.*,2014). The diagram is schematically shown in Figure 7.

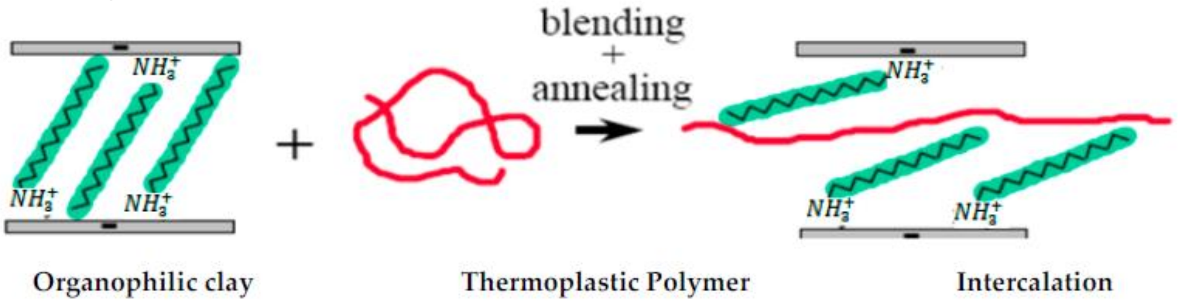

Figure 7: Melt blending technique for the preparation of polymer/clay nanocomposites

In Situ Polymerization Method

In the In Situ Polymerization Method, the organomodified clay is swelled within a liquid monomer or monomer solution, as seen in Figure 8, and then, monomer dispersion occurs into the clay spacing gallery. This is as a result of initiation step that go before a series of polymerization processes, resulting in the development of a hybrid between polymer molecules and organoclay. Next, the polymer molecule is produced through the polymerization process (Ray, 2013). The polymerization process can be prompted by using a source of radiation or thermally, with the appropriate catalyst or initiator as the case may be added before the clay layers expand via an ion exchange process. The polymerization produced a nanocomposite embedded polymer molecules joined to nanoclay(Derdar*et al.*, 2021).

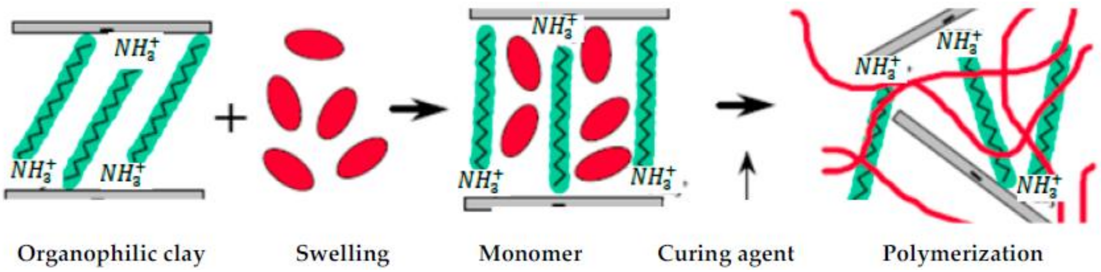

Figure 8: In Situ techniques for the preparation of polymer/clay nanocomposites

Structures of the Nanocomposites PCN

The level of variation in the reaction between the layered silicates and polymer determine the three forms of polymer/clay composite configuration with the clay type, polymer, organic modifier and the polymerization process greatly influencing the level of intercalation and exfoliation of the clay particle (Valapa*et al.*, 2017; Essomba*et al.*, 2019), as discussed below and illustrated in the diagram from Figure 9 which contains transmission electron microscopy (TEM) images (Valapa*et al.*, 2017; Essomba*et al.*, 2019), and wide-angle X-ray diffraction

(WXRD) patterns of the structures of polymer/organoclaynanocomposites (phase-separated, intercalated, exfoliated).

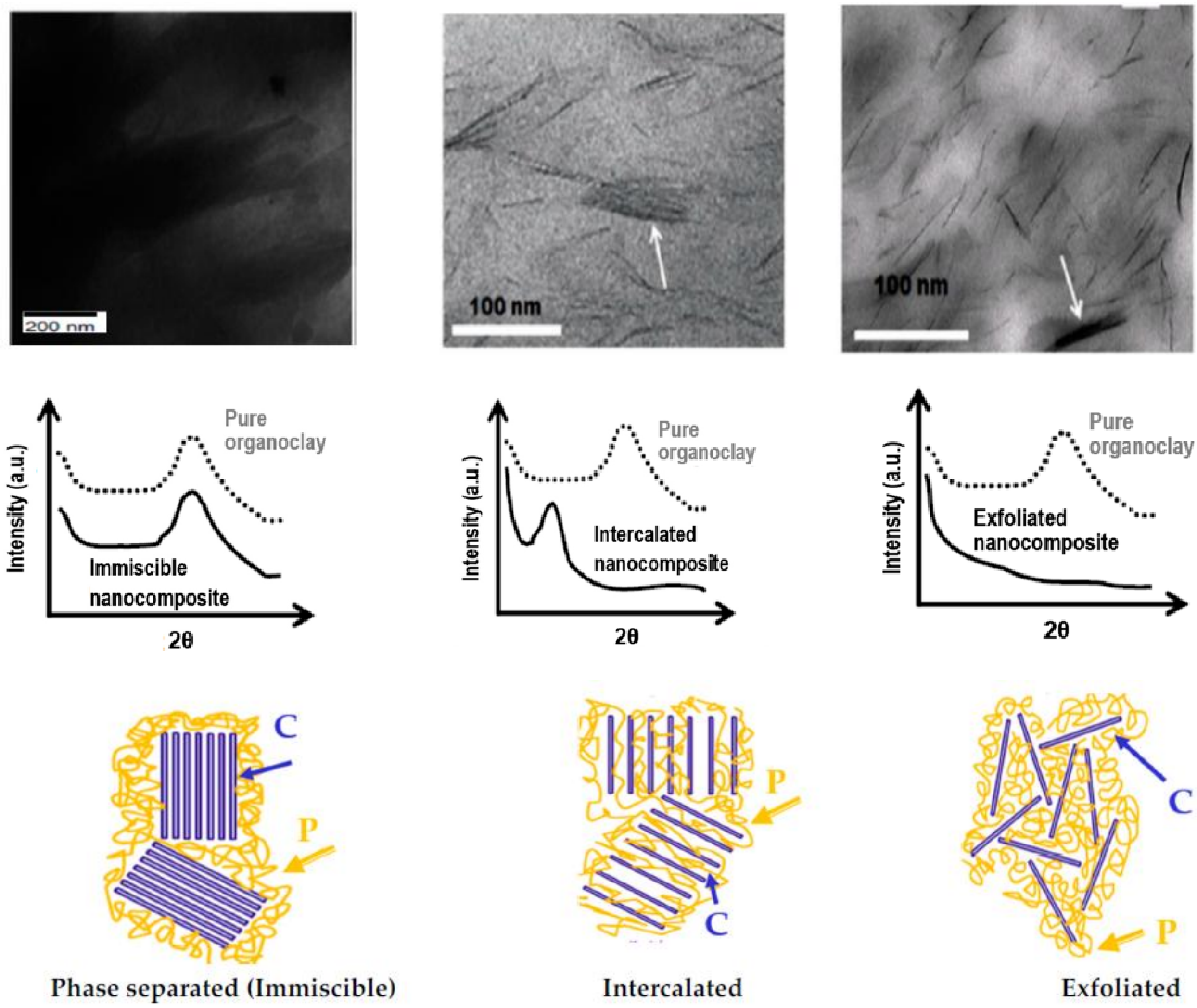

Figure 9**:**Illustration of various structures of organoclays (C) with polymers (P) (**bottom**) and their corresponding WXRD (**middle**) and TEM images (Essomba*et al.*, 2019; Motawie*et al.*, 2014) (**upper**)

Phase-Separated Structure

A phase-separation occurs in a composite when the polymer matrix fails in entering and disperses properly into the spacing between clay layers which happen as a result of incompatibility of clay particles and polymers. The result is a weak interaction between the two phases due to insignificant spacing between layers of clay since clay stacked together and takes form of aggregation around the polymer matrix. This has made the microcomposites developed function in the same way as conventional microcomposites and for the composite to achieve considerable improvement in the area of physical properties, a high clay volume fraction is needed for a good result (Tan and Thomas, 2016).

Intercalated Structure

The intercalation of the polymer into the interlayer spacing between the clay in the course of production of a PCN led to the formation of intercalated structure and the interlayer spacing is therefore increased (Pavlidou and Papaspyrides, 2008). It should be stressed that the well organized clay layers continues in a well-ordered stack between the layers of the clay and polymer matrix and when when the same amount of clay was added, the structure had better characteristics than thephase-separated composite(Yeh and Chang, 2008).

Exfoliated Structure

The total breakdown of clay layers into separate sheets results in a delaminated-exfoliated structure, which is well distributed in the polymer matrix. Due to the homogenous distribution of the completely exfoliated clay layers into the polymer, most of the intended properties (e.g. thermal, mechanical, and barrier)of the resulting polymer nanoclay composite areexpected to increase. In the real sense, obtaining total exfoliation is a difficult task (Kausar, 2020).

The high aspect ratio and intense surface reaction of the clay particles with the polymer chains have made the structure as compared with an intercalated structure, provides the most beneficial enhancement in the resulting polymer nanocomposites characteristics (Kumar *et a*l., 2022).

The exfoliation arrangement is of specific importance since it provides the highest interaction between the polymer and the modified clay by allowing the polymer to access the entire surface of the silicate layers, therefore resulting in the greatest variations in different physical properties. Nevertheless, there is still some debate about whether entirely exfoliated layered silicates occur in the system of polymer–clay nanocomposites, which is confirmed by a significant proportion of polymer nanocomposites in the literature were found to have intercalated or mixed intercalated–exfoliated nanostructures (Jamshidian*et al.*, 2012). This is due to the fact that the silicate layers are highly anisotropic, with side sizes varying from 100 to 1000 nm, and cannot be placed randomly in the polymer matrix even when detached by large spacing (Kumar *et a*l., 2022; Ali *et al.*, 2016).

Morphological Characterization of Polymer-Clay Nanoparticle

X-ray diffraction (XRD) and transmission electron microscopy (TEM) are two complementarytechniques commonly employed to analyze the structures of organically modifiedclay and polymer-clay nanoparticle (PCN) (Gong *et al.*, 2014; Pesetskii*et al.*, 2021). XRD is most typically employed to explore the nanocompositemorphology because it is easy and accessible to use. Using Bragg’s law, this techniquecalculates the gaps between the interlayer spacing of the clay: 2dsin*q* = n*l*, where *q* is theobserved diffraction angle or incident angle, *l* is the wavelength of the X radiation used inthe diffraction experiment, and d is the interlayer distance between layered silicates (Ray and Okamoto, 2003).

Different structures of polymer–clay nanocomposites (phase separated, intercalated,and exfoliated) can be detected by tracking the intensity, position, and, shape of interlayerspacingdiffraction peaks from dispersed silicate layers (Ray and Okamoto, 2003). The structure of the silicateis unaffected in phase-separated polymer–organoclay mixes, and hence, the features oftheorganoclay basal reflections remain unchanged. The intercalated structure of polymerlayeredsilicate on the other hand, causes expanding of the d-spacing in comparisonwith the d-spacing of the used modified clay, resulting in shifted diffraction peak to asmaller angle as Bragg’s law states. The increased interlayer spacing in intercalatednanocomposites implies that the polymer has penetrated the separation and expandedthe layers but the repeating layered structure has been preserved. However, exfoliatedstructures have substantial layer separation which interrupts the coherent layer stackingand no peaks can be observed in the diffraction pattern with the WXRD technique (2_ > 1_) as shown in Figure 10 (Pavlidou and Papaspyrides, 2008). The disappearance of the peaks is either due to extreme separation thatoccurred in the clay layers (i.e., surpassing 8 nm if the exfoliated structure is well ordered)or due to lack of order in the nanocomposite.

XRD provides a reliable technique for establishing the distance between the silicatelayers of the clay before modification and for intercalated polymer nanoclaycomposites(1–4 nm). However, it is imperfect for measuring delaminated and exfoliated PCN as itdoes not produce a peak. In particular, in circumstances where no peak is seen, lack ofpeak may be misunderstood. The XRD patterns of layered silicates can be influenced by avariety of factors, including the concentration and order of the layer silicates. Samples withpoorly ordered layered silicates, for example, will not yield a diffraction peak, and this isthe proper inference from the data. It is not the technique defect if an inaccurate conclusionis reached about the PCN being exfoliated while it is, in fact, very disordered. As a result,lack of an XRD peak just indicates that no peak was seen, it does not establish orcontradict the presence of exfoliated clay layers in the nanocomposite (Morgan and Gilman, 2003).

TEM provides a qualitative comprehension of the interior structureand can supply information on morphology and defect structures in real time in comparison with XRD(Morgan and Gilman, 2003). The clay layers are made of heavy atoms such as Al, Si, and O while thepolymer composed of light elements such as C and H, as well as the spacing gallery which contains light atoms such as Na and Mg, so the layered silicates appear in the TEM imagesas dark lines while the polymer or the gallery appear brighter. As a result, the spacingbetween darker line intersections in TEM images can reflect the distance between the claylayers and the state of dispersion qualitative manner. Thus, utilizing the TEM approach,the morphology of the PCN may be determined clearly, including the state of dispersionand imperfections, as well as either intercalated or exfoliated clay (Pavlidou and Papaspyrides, 2008). The TEM imagesof polyurethane nanoclay composites are shown in Figure 11(Adak *et al.*, 2018).

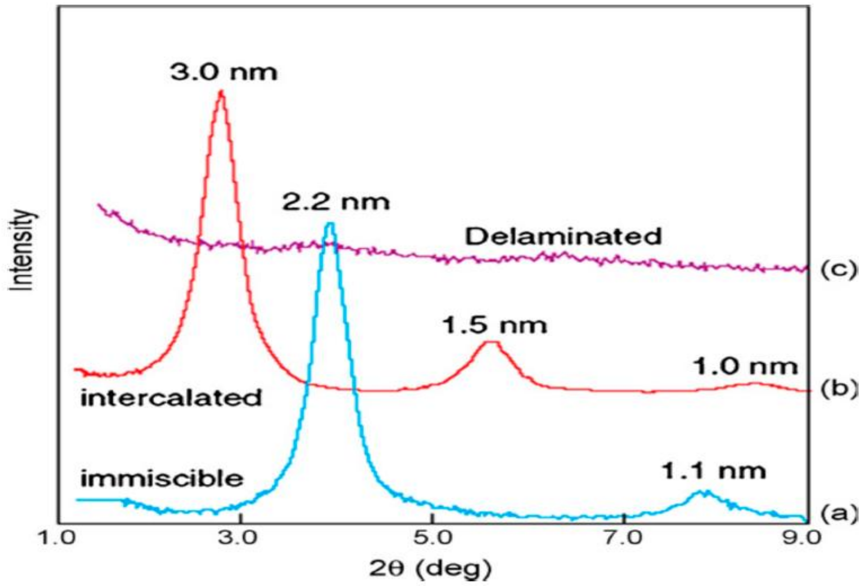

Figure 10:WXRD patterns for polymer/layered silicates: (**a**) polyethylene + organoclay→ phaseseparatedcomposites; (**b**) polystyrene + nanoclay→intercalated composite; (**c**) siloxane + nanoclay→ exfoliated composite (Pavlidou and Papaspyrides, 2008).

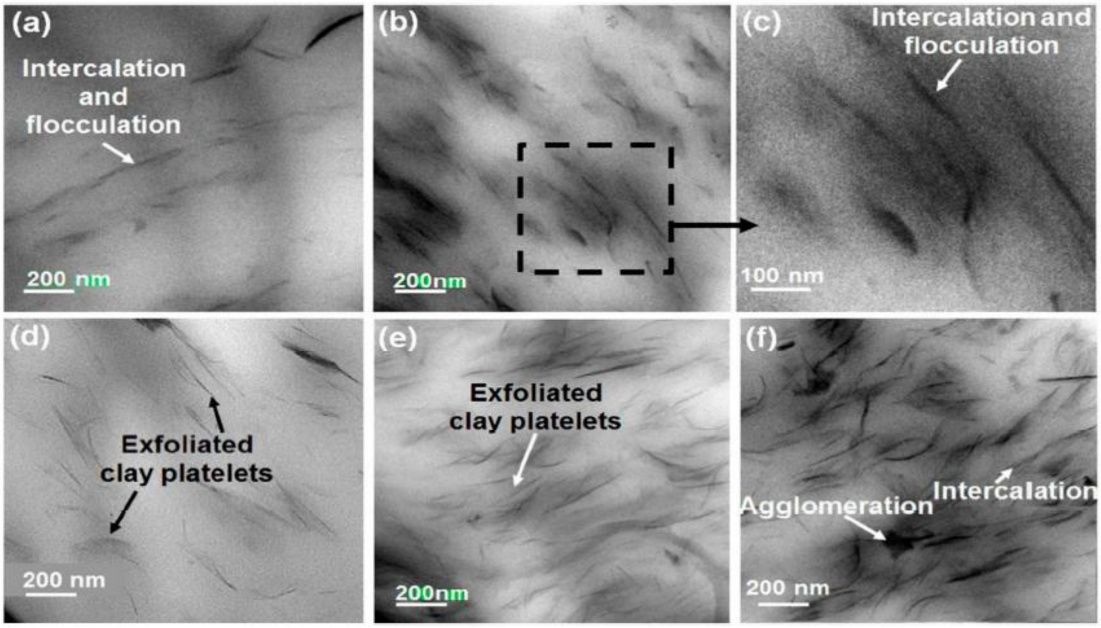

Figure 11:TEM images showing dispersion of clay platelets in CPN: (**a**) PU-CA-1; (**b**,**c**) PU-CA-3;(**d**) PU-C30B-1; (**e**) PU-C30B-3; (**f**) PU-C30B-5 (Adak *et al.*, 2018)..

Properties of Polymer-Clay Nanoparticle

The aim of incorporating layered silicates into different polymers is to improvetheir properties and create PCN with desirable qualities for particular applications. Nanoclaysperform significant and variable enhanced properties at a quite low volume fraction, which helps to preserve more of the faultless beneficial properties of the polymer. The type and properties of the constituents, as well as the processing method and conditions are some of the factors that affect the ultimate properties of polymer–clay nanocomposite(Pavlidou and Papaspyrides, 2008).

Mechanical Properties

The main reason of incorporating inorganic nanoparticles to polymer matrix is the improvement of mechanical properties; therefore, the inorganic nanoparticles are referred to as reinforcing reagents. The improvement procedure is based on high stiffness, higher strain and,higher modulus of the inorganic nanoparticles. It has been observed in most of the studies that the tensile modulus of polymeric nanocomposites made using modified organoclayenhanced significantly, particularly with increasing the loading of the organoclay (Motawie*et al.*, 2014). However, in some cases, when the volume fraction of organoclay surpasses the threshold limit value, young’s modulus decreased, because fully exfoliated structures are changed to partially exfoliated–intercalated structures (Shokrieh et al., 2012).The Toyota research group In the 1980s, reported the reinforcement of the nylon matrix with 4.7 wt% of clay, where the clay can significantly improve the mechanical properties of nylon. They created a nylon–clay hybrid (NCH) with better mechanical and thermal properties than unfilled nylon, including a higher modulus, increased strength, and a lower heat distortion temperature (Penaloza, 2019). Table 1displays an overview of Young’s modulus of polymer–clay nanocomposite experiments that have been undertaken for different polymermatrices

Table 1.Young’s modulus for different polymer–clay nanocomposites.

Polymer Type	Pure Polymer Modulus (GPa)	Nano-Clay (wt.%)	PCN Modulus (GPa)	Ref.
Polyester	2.870	5	3.79	Kornmann*et al.*, 2000
Polyamide	2.450	7	3.46	Tyan*et al.*, 2000
Nylon	6 1.200	5	2.43	Shelley *et al.*, 2001
Epoxy	2.050	5	3.00	Luo and Daniel, 2003
Polypropylene	1.760	7	2.70	Kim *et al.*, 2007
Polyurethane	0.025	13	0.45	Kaushik*et al.*, 2009
Polycarbonate	2.300	4	3.00	Gelineau*et al.*, 2015
Polylactic acid	3.600	5	4.80	Gelineau*et al.*, 2015
Polyvinyl chloride	0.209	4	0.54	Kabalan*et al.*, 2019
LDPE	1.050	5	1.09	Yas*et al.*, 2020

Any parameter that influences the degree of intercalation and exfoliation, similar to modulus, has a significant effect on the tensile strength of nanocomposites. Another impact of nanoclay filler on nanocomposites’ mechanical characteristics is the elongation at break value, which is influenced by the interfacial reaction between the polymer and layered silicates. Burmistr*et al.*(2005) reported a comparative study of mechanical properties such as tensilestrength, Young’s modulus, and elongation at break (%) for polypropylene (PP), polystyrene (PS), and polyamide (PA) matrices reinforced with organo-modified clay, results of which are shown in Table 2.

Table 2: comparative study result of mechanical properties such as Tensile strength, Young modulus and elongation at break (%) for (PP), (PS) and (PA) Matrices.

Table 2: Mechanical properties of some polymer–clay nanocomposite

		UnmodifiedClay				OrganoClay	
Polymer	Content (wt.%)	Tensile Strength (MPa)	Elongation at Break (%)	Young’s Modulus (MPa)	Tensile Strength (MPa)	Elongation at Break (%)	Young’s Modulus (MPa)
Polyamide 6	0	30.86	28.75	1.070	30.86	28.75	1.07
	1	39.84	22.15	1.790	46.17	35.00	1.61
	2	36.76	18.31	2.000	76.12	34.61	2.10
	5	32.71	10.81	3.020	32.71	10.81	3.02
Polypropylene	0	14.48	61.33	0.230	14.48	61.33	0.23
	1	12.77	80.00	0.159	19.36	133.00	0.14
	2	15.50	90.67	0.178	21.08	157.21	0.13
	5	6.73	40.00	0.168	20.27	26.67	0.76
Polystyrene	0	17.50	13.53	1.290	17.50	13.53	1.29
	1	18.80	25.00	0.750	21.15	39.51	0.53
	2	18.45	19.75	0.930	22.34	42.15	0.53
	5	16.50	8.17	2.030	17.72	12.34	1.43

Thermal PropertiesofPolymer Matrix Composites

The thermogravimetric analysis is commonly used to determine the thermal stability of polymeric composites (TGAs). The weight loss as a function of temperature due to the production of volatile compounds during high-temperature degradation is measured. Nonoxidative degradation happens when the samples are heated in an inert gas flow, whereas oxidative degradation occurs when the materials are heated in air or oxygen. Clay addition into the polymer matrix was reported to improve thermal stability in general (Cherifi*et al.*, 2018).

The thermal stability of a polystyrene–clay nanocomposite was reported by Vyazovkin*et al*.(2004). When compared with pure PS, polystyrene nanoclay composites have a 30–40 °C greater degradation temperature than neat PS. Other researchers have found that the type of clay modifier used can influence the thermal stability of modified organoclay and their polymer nanocomposites (Derdar*et al.*, 2021; Baniasadi*et al.*, 2021).

The thermal properties of solvent-based polyamide-imide (SBP) clay nanocomposites are shown in Figure 12, and the starting temperature of thermal degradation and temperatures corresponding to 5 and 10% weight loss are illustrated in Table 3(Naderi-Samani*et al.*, 2017).

The TGA thermogram of pure poly ethyl cyanoacrylate PECA and PECA–montmorillonite MMT nanocomposites, with various weight percent 1, 3, 5, and 7% of the modified MMT, is shown in Figure 13(Fekry*et al.*, 2021). All samples had their decomposition temperatures determined at 10 and 50 percent mass loss (T10 and T50), and the char residues were estimated using the TGA curve and given in Table 4. At T10, all composites decomposed at 9, 2, 6, and 7 °Chigher than pristine PECA for 1, 3, 5, and 7 percent (wt./wt.) composites, respectively. AtT50, all composites showed higher decomposition temperatures than pure PECA by 11, 17,12, and 14 °C, respectively, for 1, 3, 5, and 7% composites. At 350 °C, PECA has asmaller residue mass than all produced composites, and the residual mass grew at the level of MMT added increased (Fekry*et al.*, 2021).

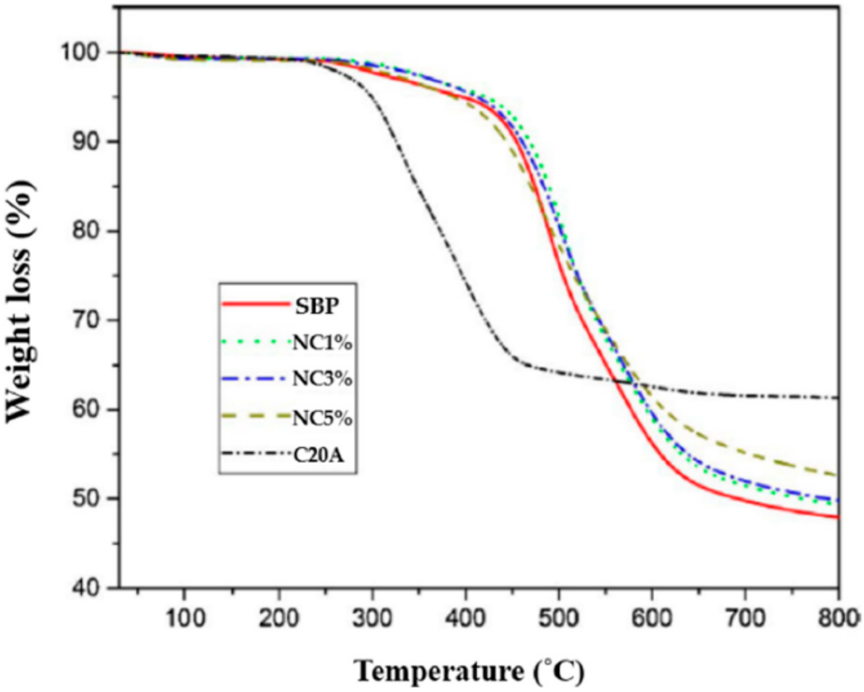

Figure 12:TGA of neat SBP, organoclay and nanocomposites.

Table 3: TGA data of neat SBP and different nanoclays (Naderi-Samani*et al.*, 2017)

Organoclay(wt.%)	T0 (°C)	T5 (°C)	T10 (°C)
Neat SBP	249	397	454
1	285	422	469
3	272	414	461
5	254	387	433

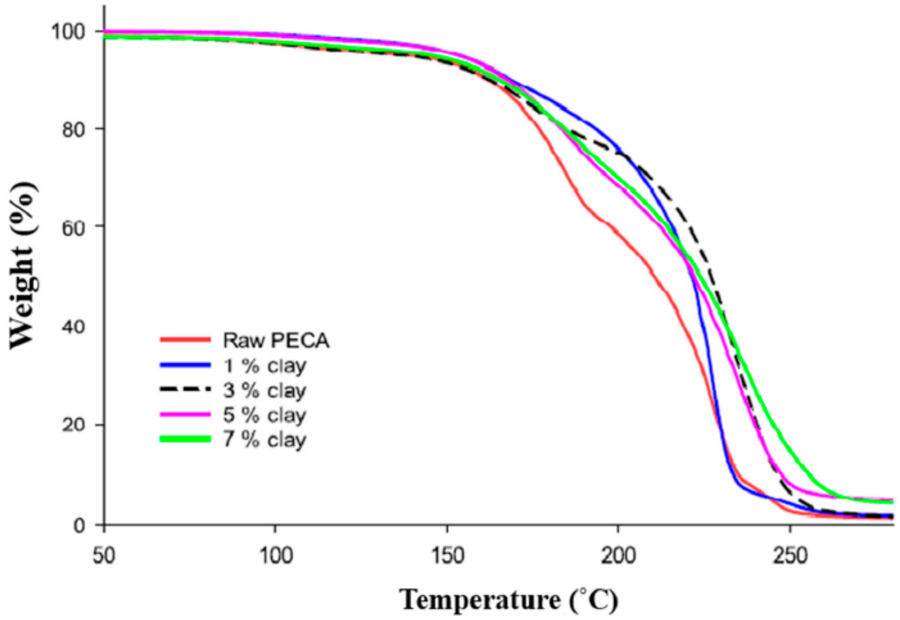

Figure 14: TGA of pure PECA and PECA–modified Mt composites with different wt% (Fekry*et al.*, 2021)

Table 4:Thermal properties of pure PECA and PECA–modified Mt composites with different

Modified MMT(wt.%)	T10 (°C)	T50 (°C)	Char Residue at 350 °C
Pure PECA	160	210	0.94
1	169	221	1.39
3	162	227	1.24
5	166	222	4.37
7	167	224	3.85

Gas Barrier Properties

One of the majorimpacts of clays on polymer matrix propertiesisthe drastic enhancement of polymer barrier qualities (Abdallah and Yilmazer, 2011). Because of the clay sheets impermeability naturally, polymer barrier characteristics are being improve by clays via generating a maze or convoluted path that slows gas molecule movement through the polymer matrix (Figure 14).The level of tortuousness formed by layered silicates in the propagation path of theirmolecules through the polymer matrix determines the degree of barrier enhancement.

The tortuous factor is defined by the proportion of the actual distance traveled by adiffusive molecule to the shortest distance traveled by a diffusive molecule (thickness of nanocomposites film). The gas barrier properties of the polymer matrix can be greatly influenced by the percentage of the clay spread in the polymer matrix. If the lateral length of the layered silicates is increased in addition to the level of intercalation or exfoliation more barrier improvement in the polymer will be achieved. The concept of barrier capabilities of PCN versus the transport of gases and vapors havebeen described in numerous studies (Tan and Thomas, 2016; Koh*et al.*, 2008). Table 5summarizes the findings of severalinvestigations on the water vapor permeability of polymer–clay nanocomposites(Z˙ enkiewicz*et al.*, 2010; Duan*et al.*, 2013; Giannaks*et al.*, 2008; Alix*et al.*, 2012).

TORTUOUS PATH

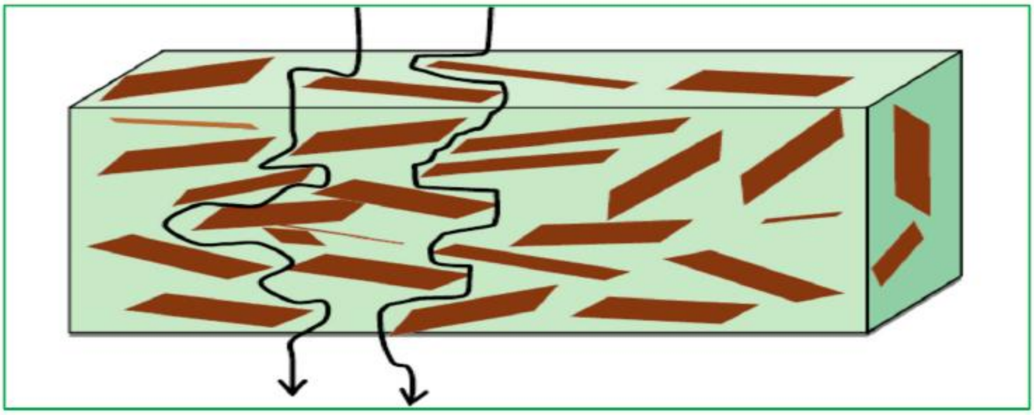

Figure 15: Schematic representation of the mechanism tortuous of improved barrier mechanism by the addition of clay platelets

NON FLAMMABILITY

The chemical structure of layered silicates makes clay particles completely fire resistant. The fire resistance property of the Nanoclay has made it useful in the manufacture of materials in which non-flammability is much more needed. These nanoclays are imcorporated into rubbers and other polymers as reinforcement to make them less flammable (Kiliaris and Papaspyrides, 2010). Also, when compared with traditional procedures, other advantages such as modest filler loading are sufficient to accomplish flame retardancy. These non-halogenated flameretardant additives are made out of polymer–clay nanocomposites (Sanchez-Olivares *et al.*, 2013). A flame retardant nanocomposite was made by intercalation process using common smectite clay montmorilloniteand was called flame retardant hide powder. To make flame-retardant leather, this hide powder was mixed with animal skins. Furthermore, leather's thermal stability was improved (Hiujian*et al.*, 2012). Clay minerals are effective flame retardants in a variety of polymer materials, particularly leather, making them appropriate for the creation of furnishing material in the aeronautic industry (Sanchez-Olivares *et al.*, 2014).

One of the most useful bench-scale approaches for characterizing the flammability properties of diverse clay-based polymer nanocomposites is the cone calorimeter test. Two essential metrics for evaluating fire safety are heat release rate HRR and peak heat releasePHRR. HRR is regarded as the fire's driving force, whereas PHRR denotes the location in a fire where heat is most likely to spread or ignite nearby items (Kiliaris and Papaspyrides, 2010).

Applications of Polymer-Ceramics Nanocomposites

The fuel efficiency, low emission, low cost, high performance and lighter weight are among the factors considered for PNCsbased on clay nanoparticles as filler in the automotive industry and more so, for the lightweight materials to be sustained for automobile application and other commercial purposes, more research into the available polymer resources like waste plastics has been put into considerations. Recently, workwas carried out to promote the use of secondary materials rather than creating new ones for the growing global demands for new materials (Oladele*et al.*, 2020; Owa*et al.*, 2020).

The first commercial product of polymer/clay nanocomposites was initiated by Toyota Motors using nylon 6clay nanocomposites in the early 1990s. Organo-modified nanoclay was incorporated into polyamide 6 as the polymer matrix in designing a timing-belt cover.This happened to be the first commercialproduct of polymer–clay nanocomposites.

A timing belt is a part of an internal combustionengine that has the function of controlling the timing of the engine's valves. The timingbeltcover developed in the process performed admirably in comparison with plastics, with good stiffness, excellentheat stability, and lack of wrapping. Accordingly, the vehicle's weight was drasticallyreduced (Zeng*et al.*, 2005). Another company (Unitika Co.) employed nylon 6 nanocomposites for engine covers on MitsubishiGDI engines in approximately the same years that Toyota introduced CPN (Panchuk*et al.*,2020). Because of the significant progress being made in the sector over the years, more vehicle companies began touse PCNs. GM and partners Basell, Southern Clay Products and Blackhawk Automotive Plastics for example initiated External vehicle body parts manufactured from common thermoplastic olefin (TPO) combined with nanoclay. This TPO nanocompositewith a minimum nanoclay weight percent (2.5 wt. %) was very rigid and significantlylighter than, vehicle parts filled with 10 times the quantity of unmodified clay

(Gul*et al.*, 2016). Themost important parts of automobiles where polymer–clay nanocomposites are employed areshown in Figure 15(Galimbert*et al.*, 2013).

The increased barrier properties of the nanoclay-reinforced polymers have caught the attention of the food packaging sector of the economy.Properties such as Advances in barrier properties to water vapor, gases such as nitrogen, oxygen, carbon dioxide and aromatic compounds have recentlybeen investigated for PNCs, as well as to enhanced thermal and mechanical properties.

The nanoclay-reinforced polymers have started displacing neat polymers in food packaging. Because of the impermeability of the neat polymers that make them unfriendly to the environment. Mitsubishi and Nanocor under the trade name Imperm® N had produced high-barrier polyamide nanoclay composite.A 1000 times reduction in oxygen transfer rate was documented in a nanoclay PET bottle when it compared with pristine PET (Bandyopadhyay and Ray, 2017). Additionally, a water-based coat consisting of nano-vermiculite polyvinylalcoholnanocomposites was successfully produced under the trade name nano seal, NanoPackInc.

also, the cosmetics, food, medical, and electronics packaging industries have experienced the development and application of nylon 6/nanoclaynanocomposites with improved barriers, mechanical, and thermal properties (Gul*et al.*, 2016).

Figure 16:The most essential parts of an automobile where nanocomposites are used

Flame Retardant Applications

Ability to minimize the content of flame retardant substances at the same time reducing the degradation ofphysical and mechanical qualities at the same level as flame retardants make the layered silicates efficient for this purpose. Various sectors of the economy including the leather industry have adopted the application of PCN as a flame retardant, makingit appropriate for the manufacture of upholstery material in the aerospace industry (Sanchez-Olivares *et al.*, 2014).

furthermore, combination of organo-modified clay with standard halogenated or non-halogenated flame retardants have been used in production of wires and cables with flame resistance and retardancy (Lee *et al.*, 2005). Daramola*et al.* (2016) studied the tensile and hydrophilic properties of low-density polyethylene/ titania composites. Authors demonstrated that an optimum combination of mechanical and hydrophilic properties of low-density polyethylene for water-based applications can be achieved by filling the matrix with 1–3 volume % of TiO2 particles and 0.5 µm in size.

Drug Delivery Applications

Polymer-clay nanocomposites have been seen as materials seriously being used in the field of medicine and biological in area such as injured or lost organs and tissues. Missing organs have been found to be recovered using PNCsin the field of Tissue engineering. As poregeometry, pore membrane morphology, and connection between pores of nanostructuredmaterials are critical for growth, cell implantation, emigration, mass transit, and tissue formation,these materials have been proven to be useful in biomedical applications (Ma, 2004).

Another major medical application of nanoclay-reinforced polymers is in the area of drug delivery systems, which is one of the key areas of application. The design of a drug delivery system includes loading a specificconcentration of medication into a specified delivery system and releasing the medicine atthe desired pace to the target site. In managing the distribution and release of medicine for Alzheimer's disease, efforts have been made to go by adsorption or intercalation of the medicines in montmorillonite clay (Yang *et al.*, 2001).

Other areas that polymer/clay composites could be used includes; Self-supported polymer gel electrolytes (PGEs) based on poly (vinylidene fluoride)(PVDF)–clay nanocomposite, with 0–4 wt.% loading of the modified clay, has been fabricated,and their electrochemical properties in lithium-ion batteries were investigated.The evaluation of PGE performance in Li/LiMn2O4 cells illustrates the accessibility ofPVDF-modified clay nanocomposites-based PGEs for lithium-ion battery applications (Prasanth*et al.*, 2013).

The improvement in physical and chemical properties has made polymer–clay nanocomposites (PCN) to have more diverse applications, including water treatment. Due to the ease of preparation, effective cation exchange process, stability, high aspect ratio, and minimum toxic effects (Unuabonah and Taubert, 2014), PCNs possess a high fluctuation and adsorption ability and an incredible life cycle for water purification (Guo*et al.*, 2018). The development of PCNs for the purpose of the removal of organic and inorganic pollutants from hydrous solution have been carried out by several researchers, and they have been proven to be beneficial in the removal of organic and inorganic pollutants (Kara *et al.*, 2016; Yildiz and Senkal, 2016; Liu *et al.*, 2017; El-Korashy*et al.*, 2016; Amari*et al.*, 2021).

II. CONCLUSION

This work revealed the relevance of clay materials in the development of advanced materials for various applications in conjunction with polymer. The brittle nature of clay but with good compressive strength, refractiveness and environmental compactibility have aided their used in polymer matrix for the development of materials and products of high quality for human consumption. This review therefore, shows the pathway for more advancement materials' development using polymer and ceramics in other to achieve properties that are not feasible with the individual materials.

REFERENCE

[1]. Abbasian, M., Seyyedi, M. and Jaymand, M.: Modification of thermoplastic polyurethane through the grafting of well-defined polystyrene and preparation of its polymer/clay nanocomposite.*Polym Bull* 77, 1107–1120 (2020).

[2]. Abdallah,W. and Yilmazer, U.: Novel thermally stable organo-montmorillonites from phosphonium and imidazoliumsurfactants.*Thermochim.Acta* 525, 129–140 (**2011**).

[3]. Abdelwahab, E.: Modified activated carbon and bentonite used to adsorb petroleum hydrocarbons emulsified in aqueous solution. *Am. J. Environ. Protect 2(6)*, 161-169 (2013).

[4]. Adak, B., Butola, B.S. and Joshi, M.: Effect of organoclay-type and clay-polyurethane interaction chemistry for tuning the morphology, gas barrier and mechanical properties of clay/polyurethane nanocomposites.*Appl. Clay Sci*. 161, 343–353 (**2018**).

[5]. Alhwaige, A.A., Ishida, H. and Qutubuddin, S.: Chitosan/polybenzoxazine/clay mixed matrix composite aerogels: preparation, physical properties, and water absorbency. *Appl Clay Sci.* 184, 105403 (2020).

[6]. Ali, F.; Ullah, H.; Ali, Z.; Rahim, F.; Khan, F.; Rehman, Z.U.: Polymer-clay Nanocomposites, Preparations and Current Applications: A Review. *Curr.Nanomater*. 1, 83–95 (**2016**).

[7]. Alix, S., Follain, N., Tenn, N., Alexandre, B., Bourbigot, S., Soulestin, J.and Marais, S.: Effect of highly exfoliated and orientedorganoclays on the barrier properties of polyamide 6 based nanocomposites. *J. Phys. Chem. C.* 116, 4937–4947 (**2012**).

[8]. Amari, A., Alzahrani, F.M., MohammedsalehKatubi, K., Alsaiari, N.S., Tahoon, M.A.andRebah, F.: Ben Clay-polymer nanocomposites: Preparations and utilization for pollutants removal.*Materials*. 14, 1365 (**2021**).

[9]. Bandyopadhyay, J. and Ray, S.S. : Applications of nanoclay-containing polymer nanocomposites. In Inorganic Nanosheets and Nanosheet-Based Materials; *Springer: Tokyo, Japan* 2017,501–521 (2017).

[10]. Baniasadi, H., Trifol, J., Ranta, A. and Seppälä, J.: Exfoliated clay nanocomposites of renewable long-chain aliphatic polyamide through in-situ polymerization.*Compos*. Part B Eng., 211, 108655 (**2021**).

[11]. Burmistr, M.V., Sukhyy, K.M., Shilov, V.V., Pissis, P., Spanoudaki, A., Sukha, I.V., Tomilo, V.I. and Gomza, Y.P.: Synthesis, structure,thermal and mechanical properties of nanocomposites based on linear polymers and layered silicates modified by polymericquaternary ammonium salts (ionenes). Polymer 46, 12226–12232 (**2005**).

[12]. Basak,B. B., Sharmistha P. and Datta, S. C.: Use of modified clays for retention and supply of water and nutrients.*Current Science* 102(9); 1272-1278 (2012).

[13]. Chaari, I., Medhioub, M. andJamoussi, F.: Use of clay to remove heavy metals

[14]. from Jebel Chakir landfill leachate. *J. Appl. Sci. Environ. Sanitation 6(2)*, 143-148 (2011).

[15]. Cherifi, Z., Boukoussa, B., Zaoui, A., Belbachir, M. and Meghabar, R.: Structural, morphological and thermal properties of nanocomposites poly (GMA)/clay prepared by ultrasound and in-situ polymerization.*Ultrason.Sonochem.* 48, 188–198 (**2018**).

[16]. Chrzanowski, W., Kim, S. Y. and Neel, E. A. A. Biomedical applications of clay.*Aust. J. Chem.* 66(11), 1315-1322 (2013).

[17]. Daramola, O.O., Oladele, I.O., Adewuyi, B.O., Olajide, J.L., Ogunbadejo A.S. and Adeyemi, P.: Tensile and hydrophilic properties of low-density polyethylene/titaniacomposites.*Leonardo J. Sci.* 29, 125–147 (2016).

[18]. Daitx, T.S., Carli, L.N. and Crespo, J.S.: Effects of the organic modification of different clay minerals and their application in biodegradable polymer nanocomposites of PHBV.*Appl Clay Sci.* 115, 157–164 (2015).

[19]. Derdar, H., Meghabar, R., Benachour, M., Mitchell, G.R.,Bachari, K., Belbachir, M.,Cherifi, Z., Baghdadli, M.C. and Harrane, A.: Polymer-Clay Nanocomposites: Exfoliation and Intercalation of OrganophilicMontmorilloniteNanofillers in Styrene–Limonene Copolymer.*Polym. Sci. Ser.A*. 63, 568–575 (**2021**).

[20]. Duan, Z., Thomas, N.L. and Huang, W.: Water vapour permeability of poly (lactic acid) nanocomposites.*J. Memb.Sci*. 445,112–118 (**2013**).

[21]. El-Korashy, S.A., Elwakeel, K.Z. and Abd El-Hafeiz, A.: Fabrication of bentonite/thiourea-formaldehyde composite material for Pb (II), Mn (VII) and Cr (VI) sorption: A combined basic study and industrial application. *J. Clean. Prod*. 137, 40–50 (**2016**).

[22]. Essomba, J.S., Jaya, P.A., Placide, D., Belibi, B., Ketcha, J.M. and Nishter, N.F.: Clay/polymer nanocomposites as filler materials for leather.*J. Clean. Prod.* 237, 117837 (**2019**).

[23]. Fekry, M.,Mazrouaa, A.M., Mohamed, M.G. and Abulyazied, D.E.: Properties of polyethylcyanoacrylate/modified Mt compositeswith highly exfoliated montmorillonite.*Polym. Bull*. 78, 5685–5711 (**2021**).

[24]. Fischer, H.; Polymer nanocomposites: From fundamental research to specific applications. *Mater. Sci. Eng. C*. 23, 763–772 (2003).

[25]. Galimberti, M., Cipolletti, V.R.and Coombs, M.: Applications of clay–polymer nanocomposites.Elsevier: Amsterdam, the Netherlands, *In Developments in Clay Science* 5,539–586 (2013).

[26]. Gelineau, P.; Stepie ´ n, M.; Weigand, S.; Cauvin, L. and Bédoui, F.: Elastic properties prediction of nano-clay reinforced polymer usingmulti-scale modeling based on a multi-scale characterization. *Mech. Mater*. 89,12–22 (**2015**).

[27]. Giannakas, A., Spanos, C.G., Kourkoumelis, N., Vaimakis, T. and Ladavos, A.: Preparation, characterization and water barrierproperties of PS/organo-montmorillonitenanocomposites. *Eur.Polym. J*. 44, 3915–3921 (**2008**).

[28]. Gong, X., Pan, L., Tang, C.Y., Chen, L., Hao, Z., Law,W.C., Wang, X., Tsui, C.P. and Wu, C.: Preparation, optical and thermal properties of CdSe–ZnS/poly (lactic acid)(PLA) nanocomposites. *Compos. Part B Eng*. 66, 494–499 (**2014**).

[29]. Gul, S., Kausar, A., Muhammad, B. and Jabeen, S.: Research progress on properties and applications of polymer/clay nanocomposite. *Polym.Plast. Technol. Eng*. 55, 684–703 (**2016**).

[30]. Guo, F., Aryana, S., Han, Y. and Jiao, Y.: A review of the synthesis and applications of polymer–nanoclaycomposites. *Appl.Sci*. 8, 1696 (**2018**).

[31]. Hiujian, L., Jinwei, Y. and Ling, X.: The synthesis and application of a high performance amino resin nanocomposite as a leather flameretardant.*J. Soc. Leather Technol. Chem.* 96, 5–10 (**2012**).

[32]. Jamshidian, M., Tehrany, E.A., Imran, M., Akhtar, M.J., Cleymand, F. and Desobry, S.: Structural, mechanical and barrier properties of active PLA–antioxidant films.*J. Food Eng.*110, 380–389 (**2012**).

[33]. Kabalan, L.; Zagho, M.M.; Al-Marri, M.J.; Khader, M.M.: Experimental and theoretical studies on the mechanical and structuralchanges imposed by the variation of clay loading on poly (vinyl alcohol)/cloisite® 93A nanocomposites. *J. Vinyl Addit. Technol*. 25, 172–181 (**2019**).

[34]. Kakarla, R.R., Venkata, R. and Bathula, B. (2019). Chapter 8—Recent advances in layered clays–intercalated polymer nanohybrids: synthesis strategies, properties, and their applications. In: Mariano M, Binoy S and Alessio L (eds.) Micro and nano technologies, modified clay and zeolite nanocomposite materials. *Amsterdam: Elsevier* 2019, 197–218.

[35]. Katti, K., Ambre, A. H., Peterka, N. andKatti, D. R.: Use of unnatural aminoacidsfor design of novel organomodified clays as components of nanocompositebiomaterials.*Phil. Trans. R. Soc. A. 368*, 1963–1980 (2010).

[36]. Kara, A., Tekin, N., Alan, A. and Safaklı, A.: Physicochemical parameters of Hg (II) ions adsorption from aqueous solution by sepiolite/poly (vinylimidazole).*J. Environ. Chem. Eng.* 4, 1642–1652 (**2016**).

[37]. Kausar, A.: Fundamental Principles and Applications of Polymer Nanocomposites Filled with both Nanoclay and Nano-Sized Carbon Allotropes–Graphene and Carbon Nanotubes: A review.*J. Plast.Film Sheeting* 36,209–228 (**2020).**

[38]. Kaushik, A.K., Podsiadlo, P., Qin, M., Shaw, C.M.,Waas, A.M., Kotov, N.A. and Arruda, E.M.: The role of nanoparticle layer separationin the finite deformation response of layered polyurethane-clay nanocomposites.*Macromolecules* 42, 6588–6595 (**2009**).

[39]. Kezia, B., Hocheol, S. and Jin, S.: A review on functional polymer-clay based nanocomposite membranes for treatment of water. *J Hazard Mater*. 379, 120584 (2019).

[40]. Kiliaris, P. and Papaspyrides, C.D.: Polymer/layered silicate (clay) nanocomposites: an overview of flame retardancy.*Progress in Polymer Science* 35 (7), 902-958 (2010).

[41]. Kim, D.H., Fasulo, P.D., Rodgers,W.R. and Paul, D.R.: Structure and properties of polypropylene-based nanocomposites: Effect ofPP-g-MA to organoclay ratio. *Polymer* 48, 5308–5323 (**2007**).

[42]. Koh, H.C., Park, J.S., Jeong, M.A., Hwang, H.Y., Hong, Y.T., Ha, S.Y. and Nam, S.Y.: Preparation and gas permeation properties ofbiodegradable polymer/layered silicate nanocomposite membranes. *Desalination* 233, 201–209 (**2008**).

[43]. Kornmann, X., Berglund, L.A., Sterte, J. andGiannelis, E.P.: Nanocomposites based on montmorillonite and unsaturated polyester.*Polym. Eng. Sci*. 38, 1351–1358 (2000).

[44]. Kumar, A., Zhang, R., Venkatesan, M., Stamenov, P. and Coey, J.M.D.: Exfoliation of hematite: Morphological, structural and magnetic investigations. *J. Magn.Magn.Mater.* 542, 168507 (**2022**).

[45]. Lee, Y.H., Lee, J.H., An, I.-G., Kim, C., Lee, D.S., Lee, Y.K. and Nam, J.D.: Electrospun dual-porosity structure and biodegradationmorphology of Montmorillonite reinforced PLLA nanocomposite scaffolds. *Biomaterials* 26, 3165–3172 (**2005**).

[46]. Liu, X., Cheng, C., Xiao, C., Shao, D., Xu, Z., Wang, J., Hu, S., Li, X. and Wang, W. Polyaniline (PANI) modified bentonite by plasma technique for U (VI) removal from aqueous solution. *Appl. Surf. Sci*. 411, 331–337 (**2017**).

[47]. Luo, J.J. and Daniel, I.M.: Characterization and modeling of mechanical behavior of polymer/clay nanocomposites.*Compos.Sci.Technol.* 63, 1607–1616 (**2003**).

[48]. Ma, P.X.:Scaffolds for tissue fabrication.*Mater. Today* 7, 30–40 (**2004**).

[49]. Mowla, D., Karimi, G. andSalehi, K.: Modeling of adsorption breakthrough behaviors of oil from salty waters in a fixed bed of commercial organoclay/sand mixture.*Chem. Eng. J*. 218, 116–125 (2013).

[50]. Morgan, A.B. and Gilman, J.W.: Characterization of polymer-layered silicate (clay) nanocomposites by transmission electron microscopy and X-ray diffraction: A comparative study. *J. Appl. Polym. Sci.* 87, 1329–1338 (**2003**).

[51]. Motawie, A.M.; Madani, M.; Esmail, E.A.; Dacrorry, A.Z.; Othman, H.M.; Badr, M.M.; Abulyazied, D.E.: Electrophysical characteristics of polyurethane/organo-bentonitenanocomposites. Egypt. *J. Pet*. 23, 379–387 (**2014**).

[52]. Naderi-Samani, H., Loghman-Estarki, M.R., Razavi, R.S.andRamazani, M.: The Effects of organoclay on the morphology, thermalstability, transparence and hydrophobicity properties of polyamide—Imide/nanoclaynanocompositecoatings.*Prog. Org. Coat*. 112, 162–168 (**2017**).

[53]. Oladele,I. O.,Adediran,A. A.,Akinwekomi,A. D.,Adegun, M. H.,Olumakinde,O. O.andDaramola,O. O.: Development of ecofriendly snail shell particulate-reinforced recycled waste plastic composites for automobile application, *The Scientific World Journal 2020* Article ID 7462758, 8 (2020).

[54]. Oladele, I.O., Omotosho, T.F. and Adediran, A.A.: Polymer-Based Composites: An Indispensable Material for Present and Future Applications: A Review. *International Journal of Polymer Science* 2020, Article ID 8834518, 12 (2020).

[55]. Oliveira, G. C., Mota, M. F., Silva, M. M., Rodrigues, M. G. F. and Laborde, H. M.: Performance of Natural Sodium Clay Treated with Ammonium Salt in The Separation of Emulsion Oil in Water. *Braz. J. Petrol. Gas 6(4)*, 171–183 (2012).

[56]. Owa,A. F.,Oladele, I. O.,Adediran,A. A. andOmotoyinbo, J. A.: Development of new polymers from Thevetiaperuviana oil," *International Journal of Engineering Research in Africa* 48, 9–23 (2020).

[57]. Panchuk, M., Kryshtopa, S., Sładkowski, A. and Panchuk, A.: Environmental aspects of the production and use of biofuels in transport.In Ecology in Transport: Problems and Solutions. Lecture Notes in Networks and Systems; *Springer Nature: Cham, Switzerland* 124, 115–168 (2020).

[58]. Pavlidou, S. and Papaspyrides, C.D.: Polymer–layered silicate nanocomposites: A review.*Prog.Polym. Sci.* 33, 1119–1198 (**2008**).

[59]. Penaloza, D.P., Jr.: Enhancedmechanical, Thermal and Barrier Properties of Clay-Based Polymer Nanocomposite Systems. *Építöanyag* (Online) 71, 74–79 (**2019**).

[60]. Pesetskii, S.S., Bogdanovich, S.P., Aderikha, V.N.: Polymer/clay nanocomposites produced by dispersing layered silicates in thermoplastic melts. In Research Anthology on Synthesis, Characterization, and Applications of Nanomaterials; IGI Global: *Hershey, PA, USA* 1002–1030 (2021).

[61]. Prabhakar, K., Debnath, S., Ganesan, R. and Kumar, P.: Mechanical and Tribological Behavior of Polymer Composite Materials: A Review, *IOP Conference Series. Material Scienceand Engineering* 344, Article ID 012015 (2018).

[62]. Prasanth, R., Shubha, N., Hng, H.H. and Srinivasan, M.: Effect of nano-clay on ionic conductivity and electrochemical properties of poly(vinylidene fluoride) based nanocomposite porous polymer membranes and their application as polymer electrolyte in lithium ion batteries. Elsevier: *Europe Polymer Journal, Macromolecular Nanotechnology* 49(2), 307-318 (2013).

[63]. Ramesh, P., Prasad, B.D. and Narayana, K.L.: Influence of montmorillonite clay content on thermal, mechanical, water absorption and biodegradability properties of treated kenaf fiber/PLA-hybrid biocomposites. *Silicon*. DOI: 10.1007/s12633-020-00401-9 (2020).

[64]. Ray, S.S.: Clay-Containing Polymer Nanocomposites: From Fundamentals to Real Applications; *Elsevier: Amsterdam, The Netherlands* 2013 ISBN 9780444594372 (2013).

[65]. Ray, S.S. and Okamoto, M.: Polymer/layered silicate nanocomposites: A review from preparation to processing. *Prog.Polym. Sci.* 28, 1539–1641 (**2003**).

[66]. Sanchez-Olivares, G., Sanchez-Solis, A., Calderas, F., Medina-Torres, L., Herrera-Valencia, E.E., Rivera-Gonzaga, A. and Manero,O.: Extrusion with ultrasound applied on intumescent flame-retardant polypropylene. *Polym. Eng. Sci*. 53, 2018–2026 (**2013**).

[67]. Sanchez-Olivares, G., Sanchez-Solis, A., Calderas, F., Medina-Torres, L., Manero, O., Di Blasio, A. and Alongi, J.: Sodium montmorilloniteeffect on the morphology, thermal, flame retardant and mechanical properties of semi-finished leather. *Appl. Clay Sci.*102, 254–260 (**2014**).

[68]. Shelley, J.S., Mather, P.T. and DeVries, K.L.: Reinforcement and environmental degradation of nylon-6/clay nanocomposites.*Polymer* 42, 5849–5858 (**2001**).

[69]. Shokrieh, M.M.; Kefayati, A.R.; Chitsazzadeh, M.: Fabrication and mechanical properties of clay/epoxy nanocomposite and itspolymerconcrete.*Mater.Des*. 40, 443–452 (**2012**).

[70]. Sudhakar, Y.N., Selvakumar, M.and Krishna, D.: Investigations on thermo-mechanical properties of organically modified polymer clay nanocomposites for packaging application*Polymers and Polymer Composites* 29(8), 1191– 1199 (2021).

[71]. Stojiljkovic, S., Stamenkovic, M., Kostic, D., Miljkovic, M., Arsic, B., Savic, I., Savic,
I. andMiljkovic, V.: The influence of organic modification on the structural and adsorptive properties of bentonite clay and its application for the removal of lead.*Sci. Sinter 45*, 363-376 (2013).

[72]. Tahir, S. S. andRauf, N.: Removal of a cationic dye from aqueous solutions by adsorption onto betonite clay.*Chemosphere 63*, 697-702 (2006).

[73]. Tan, B. and Thomas, N.L.: Water barrier properties of polymer/clay and polymer/graphenenanocomposites: A review.*J. Memb. Sci.* 514, 595–612 (**2016**).

[74]. Tawakkal, I.S.M.A., Cran, M.J. and Bigger, S.W.: Effect of kenaffibre loading and thymol concentration on the mechanical and thermal properties of PLA/kenaf/thymol composites.*Ind. Crops Prod.* 61, 74–83 (**2014**).

[75]. Tyan, H.;Wei, K. and Hsieh, T.: Mechanical properties of clay–polyimide (BTDA–ODA) nanocomposites via ODA-modified organoclay.*J.Polym.Sci.*Part B Polym.Phys. 38, 2873–2878 (**2000**).

[76]. Unuabonah, E.I. and Taubert, A.: Clay–polymer nanocomposites (CPNs): Adsorbents of the future for water treatment. *Appl. Clay Sci*. 99, 83–92 (**2014**).

[77]. Valapa, R.B., Loganathan, S., Pugazhenthi, G., Thomas, S. and Varghese, T.O.: Chapter 2—An Overview of Polymer–Clay Nanocomposites. In Clay-Polymer Nanocomposites; Jlassi, K., Chehimi, M.M., Thomas, S., Eds.; Elsevier: Amsterdam, The Netherlands 2017, 29–81 ISBN 9780323461535 (2017).

[78]. Vlasova, M., Dominguez-Patiño, G.,Kakazey, N., Dominguez-Patiño, M., Juarez-Romero,D. and MéndezEnríquez Y.: Structural-phase transformations in bentonite after acid treatment, Science of Sintering.*International journal of science and advanced materials* 35(3), 155-166 (2003).

[79]. Vyazovkin, S., Dranca, I., Fan, X. and Advincula, R.: Kinetics of the thermal and thermo-oxidative degradation of a polystyrene–clay nanocomposite. *Macromol. Rapid Commun*. 25, 498–503 (**2004**).

[80]. Wang, R., Li, H., Ge, G., Dai, N., Rao, J., Ran, H. and Zhang, Y.: Montmorillonite-Based Two-Dimensional Nanocomposites: Preparation and Applications. *Molecules* 26, 2521 (2021).

[81]. Yang, J., Li, H., Zuo, J. andAn, Y.: Effect of copolymer structure on micellar behavior of acrylamide-octylphenylpoly (oxyethylene) acrylate surfactant.ColloidPolym. Sci. 279, 279–282 (**2001**).

[82]. Yang, Z., Wu, M. and Chen, G. The effect of montmorillonite modification on crystallization behaviour of polypropylene/montmorillonite composites. *PolymPolym Compos*. 24(5), 331–340 (2016).

[83]. Yas, M.H., ShahraniKorani, H. and ZareJouneghani, F.: Studying the Mechanical and Thermal Properties of Polymer NanocompositesReinforced with Montmorillonite Nanoparticles Using Micromechanics Method. *J. Solid Mech*. 12, 90–101 (**2020**).

[84]. Yeh, J.M. and Chang, K.C.: Polymer/layered silicate nanocomposite anticorrosive coatings.*J. Ind. Eng. Chem.* 14, 275–291 (**2008**).

[85]. Yildiz, G.; Senkal, B.F.: Formation of composites between polyvinylimidazole and bentonites and their use for removal of remazol black B from water. *Sep. Sci. Technol.* 51, 2596–2603 (**2016**).

[86]. Zapata, P. A., Belver, C., Quijada, R., Aranda, P. and Ruiz-Hitzky, E.: Silica/clay organo-heterostructures to promote polyethylene–clay nanocomposites by *in situ* polymerization. General:*Appl. Catal. A. 453*, 142–150 (2013).

[87]. Z˙ enkiewicz, M., Richert, J. and Róz˙an´ ski, A.: Effect of blow moulding ratio on barrier properties of polylactidenanocompositefilms. *Polym. Test*. 29, 251–257 (**2010**).
[88]. Zeng, Q.H.; Yu, A.B.; Lu, G.Q.; Paul, D.R.: Clay-based polymer nanocomposites: Research and commercial development. *J.Nanosci. Nanotechnol*. 5, 1574–1592 (**2005**).
[89]. Zwane, R., Sadiku, E. and Ray, S.: Thermal and rheological properties of polyamide 6/layered double hydroxide clay composites. *PolymPolym Compos*. 27(9), 567–581 (2019).