Journal of Composites and Compounds 2 (2020) 85-91

Available online at www.jourcc.com

Journal homepage: www.JOURCC.com

Journal of Composites and Compounds

Clay-reinforced nanocomposites for the slow release of chemical fertilizers and water retention

Aliasghar Abouchenari [a], Khatereh Hardani [b], Somayeh Abazari [c], Fahimeh Naghdi [d], Mehdy Ahmady Keleshteri [e], Ata Jamavari [f], Amir Modarresi Chahardehi [g]*

[a] *Materials Engineering, Shahid Bahonar University, Kerman, Iran*
[b] *Department of Marine Chemistry, Faculty of Marine Science, Khorramshahr University of Marine Science and Technology, Khorramshahr, Iran*
[c] *Department on Materials and Metallurgical Engineering, Amirkabir University on Technology (Tehran Ploythechnic), Tehran, Iran*
[d] *Department of Materials and Industrial Engineering, Babol Noshirvani University of Technology, Mazandaran, Iran*
[e] *Advanced Materials Research Center, Materials Engineering Department, Najafabad Branch, Islamic Azad University (IAU), Najafabad, Isfahan, Iran*
[f] *Department of material science and engineering, Iran University of Science and Technology, Tehran, Iran*
[g] *Integrative Medicine Cluster, Advanced Medical and Dental Institute, University Sains Malaysia, Bertam, 13200, Kepala Batas, Pulau Pinang, Malaysia*

ABSTRACT

The present study includes an overview of the applications of clay-based nanocomposites from the past decade to date in various fields such as pharmaceuticals, water treatment, food packaging, electricity, automotive, and especially the production of chemical fertilizers with water retention and slow release. In the agricultural area, one of the promising materials that help green chemical engineering and green chemistry is slow-release fertilizer (SRF). Clay minerals and clay nanocomposites provide cost-effective and efficient material for this purpose. In this paper, the research and development of polymer nanocomposites based on clay in recent years with the focus on their application as novel fertilizers have been reviewed. Clay minerals are promising reinforcements to manufacture high-performance, lightweight, and low-cost nanocomposites because of their abundance, layered structure, low cost, and rich intercalation chemistry.

ARTICLE INFORMATION

Article history:
Received 4 June 2020
Received in revised form 14 June 2020
Accepted 26 June 2020

Keywords:
Clay nanocomposites
Slow release
Controlled release
Fertilizer

Table of contents

1. Introduction 85
2. Clay-reinforced nanocomposite 86
3. Applications of Clay-reinforced nanocomposite 86
3.1. Electro materials 86
3.2. Automotive Components 86
3.3. Coating and Pigments 87
3.4. Packaging Materials 87
3.5. Drug Delivery 87
3.6. Wastewater Treatment 88
3.7. Controlled- or Slow-Release Systems Applied to Fertilizers 88
4. Polymer/Clay Nanocomposites for Fertilizers 88
4.1. Chitosan/Clay Nanocomposites 88
4.2. Alginate/Clay Nanocomposites 88
4.3. Cellulose and their derivative 89
4.4. Acrylamide/clay nanocomposites 89
5. Conclusions and future insights 89

1. Introduction

The main factor in the agricultural area playing a very important role in plant growth is an appropriate distribution of fertilizer and water. However, around 50–70 % of potassium, 80–90 % of phosphorus, and 40–70 % of nitrogen incorporated in conventional fertilizers are wasted by volatilization or leaching, which leads to release of them into the environment rather than being absorbed by plants [1, 2]. Therefore, there

* Corresponding author: Aliasghar Abouchenari; E-mail: aliab596@yahoo.com
DOR: 20.1001.1.26765837.2020.2.3.4.4
https://doi.org/10.29252/jcc.2.2.4

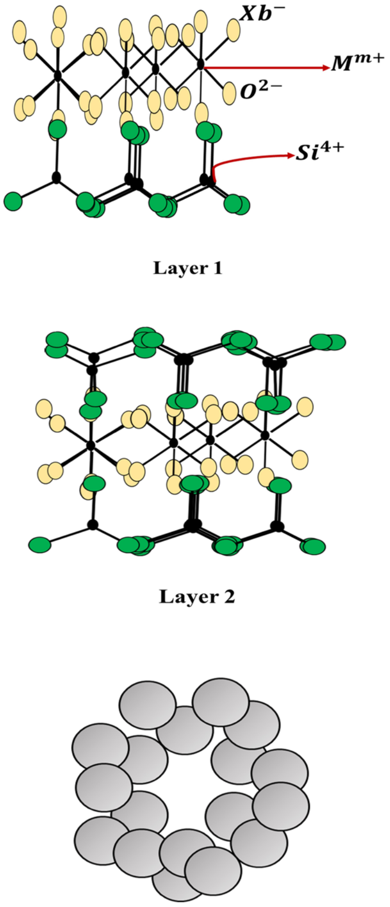

Fig. 1. (a) Crystal structure of clay minerals including 1:1 and 2:1-layer type, where M can be Fe, Mg, Al, etc. and X is mostly OH (b) Siloxane cavity in the basal plane of a tetrahedral sheet.

is a need for improvement and management of fertilizer nutrients and water resources utilization. The utilization of controlled- or slow-release fertilizers is one way to improve the fertilizer application. The first major category of this kind of fertilizer is matrix type formulations as a result of their facile fabrication. In this system, the active materials are distributed in the matrix and its diffusion occurs through intergranular (pores) or continuum openings (channels) in the matrix [3, 4]. Moreover, the aim of developing slow-release fertilizers is the gradual secretion of the nutrient to be regulated based on the nutrient requirement of plants. In order to control the release rate, the physical preparation of the fertilizers using engineered matrices could be used [5, 6]. As environmental protection issues are nowadays in the center of attention, the degradability of these systems is desired [7]. Clay-based nanocomposites have significantly attracted attentions among nanocomposites that are utilized in chemical fertilizers. Polymer nanocomposites are composed of a polymeric matrix filled with reinforcements with at least one dimension in the nanometer-scale [8]. One-dimensional nanofillers are in the form of layered minerals such as clay [9-12]. In the following sections, we have briefly mentioned the applications of clay-based nanocomposites, mainly in the field of chemical fertilizers for agricultural applications.

2. Clay-reinforced nanocomposite

Polymer nanocomposites have attracted much attention leading to investment in research and development around the world [8]. Clay platelets are one-dimensional disc-like nanoparticles that possess unique structure and characteristics [13]. These minerals are both synthesized clays such as magadiite, laponite, and fluorohectorite, and natural clays viz. saponite, hectorite, and montmorillonite [10]. Nowadays, the use

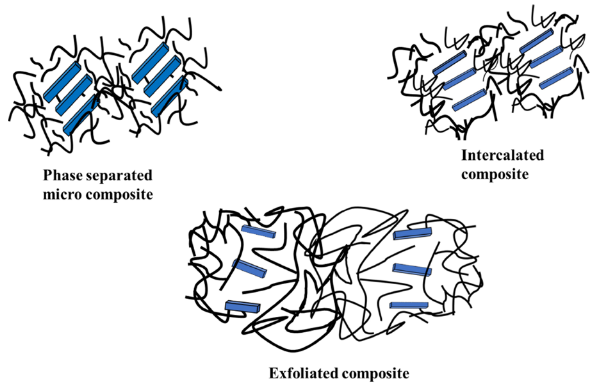

Fig. 2. Type of polymer clay nanocomposite.

of polymer/clay nanocomposites (PCNs) is one of the most applied modern technologies, since they can generate new polymer properties [14]. PCNs are widely used in modern technologies due to being able to introduce new properties to polymers [14]. PCNs possess unique characteristics including their capability to confine polymer chains at the nanometer scale and disperse in the matrix [15]. Properties of polymers such as gas barrier properties, toughness, heat distortion temperature, stiffness, modulus, strength, and chemical resistance could be significantly enhanced by adding a low amount of fillers [16-18].

Nanocomposites or conventional composites can be formed under the processing condition, components nature as well as the interfacial interactions of modified or unmodified layered silicates and polymer chains. The type of formed nanocomposites is illustrated in Fig. 2 [19].

3. Applications of Clay-reinforced nanocomposite

Clay-based polymer nanocomposites are promising alternatives to conventional micro composites as a result of the ability to disperse clay platelets in nanoscale in the matrix and improve physical, chemical, electrical, optical, thermal, mechanical, and barrier properties [10, 22].

3.1. Electro materials

New organic-inorganic hybrids with excellent electrical properties could be produced based on polymer nanocomposites. Conducting polymers reinforced with clay particles exhibit remarkable electrochemical properties, which have been employed for applications including smart windows, solid-state batteries, modified electrodes biosensors, and other electrochemical devices. PPR nanocomposites, for instance, could be developed to produce modified electrodes that are utilized as devices for electrocatalysis or sensors. Because PEO nanocomposites exhibit single ionic conduction behavior and relatively high conductivity at ambient temperature and they do not have significant dependence on temperature over conventional electrolytes based on $LiBF_4$/PEO, they could be offered as new electrolyte materials. Additionally, these nanocomposites are excellent models for investigation of the interfacial structure and dynamics [10, 23].

3.2. Automotive Components

Today, automotive industries are widely benefiting from polymer composites. Nevertheless, these composites are composed of polymers filled with a great number of microscale particles, flame resistant, chemical resistant, and thermal stabilizer additives. Hence, the enhanced performance often leads to the low fuel efficiency and increment of materials density. On the other hand, by using polymer nanocompos-

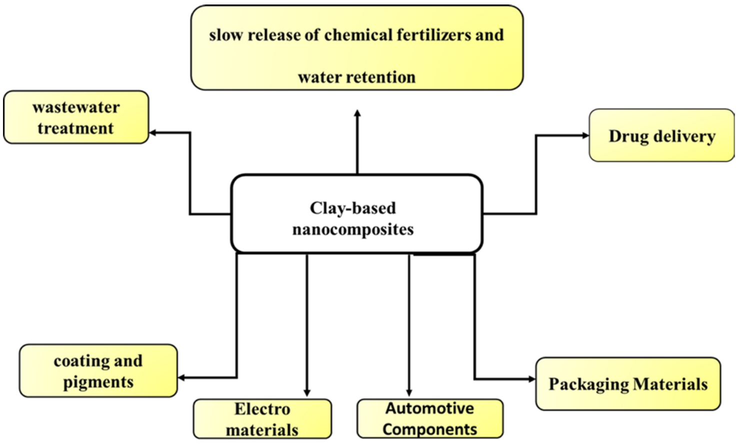

Fig. 3. Applications of clay-nanocomposite.

ites, transport industries such as aerospace and automotive can benefit from higher performance with affordable materials, and a significant reduction of weight. The commercial nylon 6/clay nanocomposites were first used by Toyota Motors in the timing-belt cover in the early 1990s. The manufactured timing-belt cover showed excellent thermal stability, enhanced rigidity with no wrap. As a result of the lower amount of clays, the weight also was saved by up to 25%. Besides, due to their remarkable enhancement of mechanical properties, barrier properties, and heat distortion temperature (HDT), nylon 6/clay nanocomposites have also been utilized as fuel hoses, oil reservoir tank, and engine cover in the automotive industry. In 2002, a thermoplastic olefin/clay nanocomposite with 2.5% reinforcement was also used by General Motors for step-assist on Chevrolet and Safari. Today, polymer nanocomposites are believed to have the potential to be used in different internal and external parts of vehicles including under-the-hood parts, door handles, and mirror housings. The polymer nanocomposites weight can benefit material recycling and environmental protection [10, 23]. The fundamental stages of nanocomposites' production for automotive applications are illustrated in Figure 4. In the production of competitive parts for a particular use, there might be some great challenges in each step that must be resolved. There exist different variations in the preparation process for a specific application that must be regulated according to the part specifications as well as the method of processing. Regarding these considerations, critical demands are imposed on the science and technology required for the processing of polymer-based composites [24].

3.3. Coating and Pigments

Nano pigments or PlanoColors® consisting of environment-friendly organic dyes and clays have been offered as potential substitutes for toxic palladium (Pd) and cadmium (Cd) pigments. The Plano Colors are easily dispersed in coatings and bulk polymers in the nanometer scale. By selecting suitable dyes from various organic dyes, different pigment colors are possibly synthesized. Additionally, materials that are dyed with Plano Colors completely keep their transparency due to the smaller size of these pigments in comparison with the light wavelength. Moreover, these nano pigments enhance temperature, ultraviolet (UV), and oxygen stability accompanied by high color efficiency and brilliance which is due to their improved interaction with light by their large surface area [10, 25].

3.4. Packaging Materials

Clay/polymer nanocomposites could exhibit remarkable improvement of shelf-life for various types of packaged food due to their excellent barrier properties. Furthermore, adding clay to polymers maintain the optical transparency of the nanocomposite films, which is not possible to achieve in conventional polymer micro composites. Hence, due to the above-mentioned characteristics, clay/polymer nanocomposites are widely acceptable in packaging industries including beverage containers, wrapping films, packaging of cereals, confectionery, cheese, processed meats, dairy products, fruit juice, and carbonated drinks bottles. Bayer, for example, has recently produced a novel food packaging plastic films made from nylon-6/clay nanocomposites with the exfoliated structure [26].

3.5. Drug Delivery

Recently, polymer/clay nanocomposites have attracted the attention of researchers in the field of controlled drug delivery. The number of published reports on these nanocomposites for drug delivery applica-

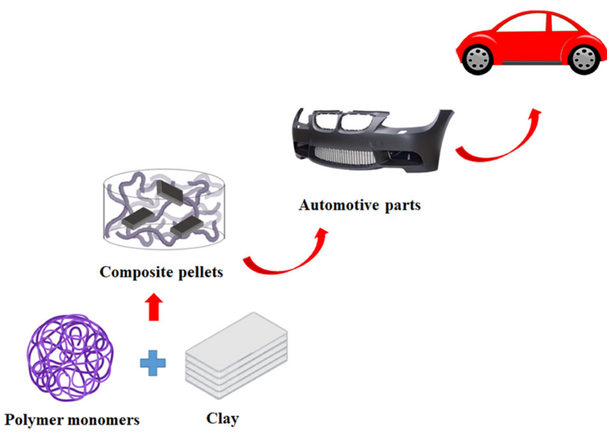

Fig. 4. Nanocomposites processing steps for automotive applications.

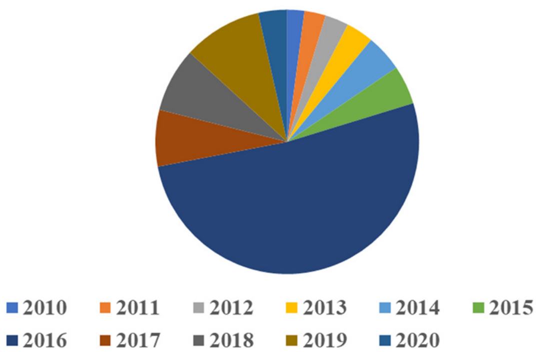

Fig. 5. Number of publication reporting clay-based nanocomposite for drug delivery.

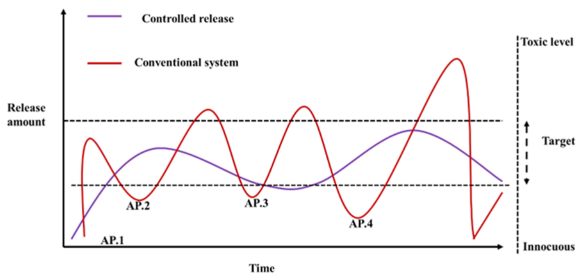

Fig. 6. Comparison between the controlled-release system and the conventional systems.

tions is illustrated in Fig. 5 [27, 28]. As a result of specific properties superior to pristine polymers such as increased thixotropy, enhanced mechanical strength, higher heat resistance, increased gaseous permeability, even with the addition of 5% or less content of clay, these nanocomposites have attracted considerable attention [29-34]. Due to the promising characteristics, polymer/clay nanocomposites have been proposed for applications in various fields such as pharmaceutical, biomedical, and biochemical fields [35-37].

3.6. Wastewater Treatment

One of the applications of polymer/clay is in the effective water treatment by adsorbing and flocculating of both organic and inorganic micro-sized pollutants from aqueous solutions. When some of these nanocomposites are modified with biocides, they show the ability of microorganisms removal including Escherichia coli, Staphylococcus aureus, Candida albicans, and Pseudomonas aeruginosa from wastewater. Compared to neat clay, polymer/clay nanocomposites could be easily recovered from aqueous solutions [38]. Furthermore, the treatment times of PCNs are reported to be better than that of either clay or polymer adsorbents. The nanocomposites also possess better life cycles and improved adsorption capacity in comparison with clay alone. Therefore, clay-reinforced nanocomposites exhibit a high potential of efficient wastewater treatment [39, 40].

3.7. Controlled- or Slow-Release Systems Applied to Fertilizers

Smart fertilizers that are fertilizers with controlled- and slow-release, can gradually release the containing nutrient with the possibility to regulate the release according to the nutritional requirements of plants. These systems make the nutrients available for a longer period compared to fertilizers with high solubility, which release their nutrients rapidly [41, 42]. The official distinction between slow-release and controlled-release of fertilizers does not exist. Reduction of environmental contamination, minimizing root damage and soil compaction, saving fuel, reducing the labor, elimination of parcels for covering, and prevention of physical damage to the crop due to application processes are the remarkable benefits of these systems [41]. Figure 6 compares a controlled release and conventional system for a specific active nutrient. Zhao et al. [43] studied the influence of fertilizer with controlled-release on the production, photosynthetic rate, nitrogen use efficiency, and ammonia volatilization in maize cultivation. According to their observation, the use of coated urea with sulfur or resin exhibited improved outcomes in all parameters compared to common fertilizers. Li et al. [44] utilized a slow-release fertilizer system based on treated coal ash for potassium sources. They tested the system directly in the soil and reported that the use of the slow-release system led to a positive effect on the development of crops. A new series of hydrogels consisting of methylcellulose, polyacrylamide, and montmorillonite were synthesized by Bortolin et al. [45]. They reported that the incorporation of clay led to some improvements in the properties of the materials. Adsorption–desorption investigation of urea demonstrated that the hydrogel composite that included montmorillonite released urea in a more controlled rate (around 200 times slower release rate compared to conventional pure urea) in comparison with the neat hydrogel. The results show the excellent potential of clay, especially montmorillonite, to produce novel fertilizers with controlled- or slower release.

4. Polymer/Clay Nanocomposites for Fertilizers

Due to being easily obtained, having higher efficiency, and resistance to environmental effects, systems based on polymers are more commonly used for various applications [46]. Besides, polymer-based products are used in different physical states as carriers such as melts, hydrogels, solutions, and powders. As biodegradable polymers can be degraded by microorganisms activity, they have some advantage over conventional polymeric systems leading to having greater control over the release of active component [47].

Nanocomposites based on polymer and low clay loading are new materials for the controlled release of materials [48, 49]. This group of nanocomposites consists of a polymeric matrix in which layered nano-scaled silicate is dispersed. The clay minerals are the general type of 2:1 layer- or phyllo-silicates including synthetic mica, saponite, montmorillonite, etc. In these minerals, silicate layers of 1 nm thickness and 10–2000 nm length are stacked [50-52]. It has been reported that the combination of polymer and clay could demonstrate greater control rate for the release of materials and could provide a firm network through strengthening the lattice structure [53].

4.1. Chitosan/Clay Nanocomposites

By partial deacetylation of chitin (abundantly found in the exoskeleton of water animals such as shrimp, crab, etc.), chitosan polysaccharide is derived [54]. Chitosan is considered as a naturally abundant material due to being naturally regenerating resource; moreover, it is degradable and non-toxic. Owing to the mentioned properties, this polysaccharide has gained considerable attention in various applications such as agricultural applications [54-59]. Chitosan has been used as a coating for compound fertilizers such as potassium, phosphorus, and nitrogen compounds [60]. Incorporation of layered silicates such as montmorillonite in the polymer could improve some properties such as the adsorption capacity for chemical compounds as well as water. Santos et al. [61] developed chitosan and montmorillonite clay microspheres containing potassium using a coagulation route. They reported that the incorporation of montmorillonite into chitosan resulted in enhanced sorption properties compared to the neat chitosan microspheres. Souza et al. [62] monitored the performance of microspheres based on chitosan/clay hybrid for the release of potassium nitrate in lettuce cultivation. Based on the obtained results, soils that were treated with the nanocomposites exhibited higher electrical conductivity and moisture. Additionally, in comparison with conventional fertilization, a gradual and homogenous release was observed. According to the statistical analysis, the nanocomposite microspheres exhibited an efficient, controlled release of nitrogen.

Messa et al. [63] developed microparticles of chitosan and montmorillonite for prolonged potassium nitrate release as an efficient fertilizer. The results indicated that the prepared microparticles could maintain higher potassium content in the soil for up to several weeks. They proposed that the chitosan/clay microparticles are good candidates for agricultural applications due to their release efficiency.

4.2. Alginate/Clay Nanocomposites

Alginate is a linear polysaccharide consisting of β-D mannuronic acid moieties and 1–4 linked α-L-guluronic in different compositions that is obtained from brown seaweed [64]. By incorporation of Ca^{2+} ions in an aqueous solution, alginate can be ionically crosslinked. As a result of this mild gelation capability, alginate is widely utilized as fertilizing systems with the controlled-release [64, 65]. On the other hand, the sodium alginate matrix is easily destructed by monovalent cations with poor mechanical properties. Moreover, controlled-release behavior is not always observed in sodium alginate hydrogels. A burst release of nutrients at the first stage is exhibited and then the remaining nutrients are released slowly [66]. He et al. [67] used sodium bentonite and alginate composites to encapsulate Raoultella planticola Rs-2 to prepare a slow-release biofertilizer with high efficiency and minimized production costs. After six months of storage, around 88.9% of Rs-2 in dried bentonite/alginate microcapsules survived. The efficient amount of alginate for the production of desirable composite microcapsules was remarkably lower compared to alginate alone. Release rate, biodegradability, and swelling decreased with increasing the content of bentonite and enhanced with the increment of NaAlg content. An initial burst in release curves of bacteria was observed for all the composite microcapsules; then a gradual increase occurred indicating that the release model was the first-order release. Therefore, the low-cost encapsulated microcapsules could be offered as promising slow-release fertilizers in farmlands. In another research, Singh et al. [68] synthesized starch–alginate beads by the incorporation of bentonite and kaolin for modification of the thiram fungicide release as well as minimizing the environmental contamination. Kaolin and bentonite were employed as adsorbent materials in the bead composition. According to the results, the addition of bentonite and kaolin to starch–alginate beads led to the controlled release of thiram. In comparison with the kaolin-based beads, the bentonite-based composition demonstrated a slower release rate.

4.3. Cellulose and their derivative

The most abundantly found biopolymer on earth is cellulose, which is the main constituent of plant-based materials such as hemp, wood, and cotton [69]. This linear polysaccharide is composed of β (1-4) linked D-glucose units (several hundred to thousands). There are multiple hydroxyl groups on the glucose units, which can react with different reagents either fully or partially to form other derivatives including cellulose esters and cellulose ethers [70].

As a result of film-forming ability, biodegradability, and renewability, the application of cellulose and its derivatives as carriers for fertilizing substances has attracted attention [45, 71-74]. The primarily used cellulose derivative for fertilizer coating is ethylene cellulose (EC), which is a biodegradable, hydrophobic, and inert material. Pérez et al. [75] sprayed EC ethanol solution (5%) onto urea-lignin particles in a Wurster fluidized bed at 60 °C. Different coating thicknesses of EC were applied on the particles and the nitrogen-release rates were measured by water leaching experiments. The observations showed that EC coating could inhibit water diffusion and decrease the nitrogen release rate.

Ni et al. [76] developed a slow-release nitrogen fertilizer system based on natural attapulgite clay, EC film, and sodium carboxymethylcellulose/hydroxyethylcellulose hydrogel. They reported that the prepared fertilizer system could effectively decrease the loss of nutrients, enhance the efficiency of water consumption, and increase the time of irrigation cycles in drought-prone environments.

4.4. Acrylamide/clay nanocomposites

Most superabsorbents are produced using synthetic hydrophilic polymers including polyacrylic acid or polyacrylic acid-poly acrylamide copolymer; however, they suffer from poor degradability in soil and accumulation over time [77].

Verma et al. [78] synthesized nanoclay/polymer composite based on in-situ polymerized acrylic acid-acrylamide and modified nanoclay for the availability of phosphorus for wheat as a test crop. They reported that the amount of phosphorus uptake enhanced from 3.32 mg kg^{-1} to 8.71 mg kg^{-1} for the treatment by conventional diammonium phosphate fertilizer and nanoclay/polymer composite treatment in Alfisol, respectively. The amount of increase in the case of Inceptisol was from 4.45 to 9.78 mg kg^{-1}. The percentage of soil phosphorus fixation at the flowering stage decreased from 50 to 0 and from 60 to 19 in Inceptisol and Alfisol, respectively. Moreover, fertilizer phosphorus use efficiency improved by loading phosphorus into the nanoclay-polymer composite. Thus, the modified nanoclay/polymer composite exhibited promising properties as a fertilizer carrier to decrease production cost and enhance nutrient use efficiency, particularly for phosphorus because its availability in soil is very low.

Rashidzadeh et al. [79] developed a slow-released system for nitrogen, phosphorus, and potassium (NPK) fertilizer encapsulated in a superabsorbent nanocomposite. NPK was encapsulated by in-situ polymerization of acrylamide, acrylic acid, and sodium alginate in the presence of montmorillonite clay. According to the results, the incorporation of montmorillonite led to the release of the nutrients in a more controlled way compared to neat superabsorbent. Because of good water retention capacity and good slow-release property, this system could be offered as a potential fertilizer carrier for agricultural applications.

5. Conclusions and future insights

It can be concluded that a significant part of the growing research fields is focused on polymer/clay nanocomposites for various challenging applications. More importantly, by the continuous increase in population, there is an ever-increasing food demand worldwide; therefore, it is necessary to increase crop productivity is to provide sufficient food for people. On the one hand, crop productivity could be achieved by using fertilizers. On the other hand, overusing fertilizers can cause some damage to environments and human health. Hence, to enhance the efficiency of fertilizing, slow-release fertilizers have attracted much attention. Polymer/clay nanocomposites exhibit promising properties to be used as superabsorbent and slow-release fertilizing systems [80].

In this regard, there will be further growth in the application of clays in different fields, especially in industrial and environmental applications. The significant technological importance of these composites is due to their tailoring characteristics including size, shape, hydrophilicity, and elementary building unit combinations. Various types of these minerals and their composites have not yet been widely investigated to develop new high-performance polymer composites. Therefore, the properties of these composites will be tailored to expand their potential applications.

Acknowledgments

The authors received no financial support for the research, authorship and/or publication of this article.

Conflict of Interest

All authors declare no conflicts of interest in this paper.

REFERENCES

[1] B. Ni, M. Liu, S. Lü, Multifunctional slow-release urea fertilizer from ethyl-cellulose and superabsorbent coated formulations, Chemical Engineering Journal 155(3) (2009) 892-898.
[2] W. Wang, A. Wang, Synthesis, swelling behaviors, and slow-release charac-teristics of a guar gum-g-poly (sodium acrylate)/sodium humate superabsorbent, Journal of Applied polymer science 112(4) (2009) 2102-2111.
[3] S. Al-Zahrani, Utilization of polyethylene and paraffin waxes as controlled

de-livery systems for different fertilizers, Industrial & engineering chemistry research 39(2) (2000) 367-371.
[4] R. Parish, Effect of coating thickness on spreader damage to encapsulated controlled-release fertilizer granules, Applied Engineering in Agriculture 17(4) (2001) 459.
[5] A. Pakseresht, A. Javadi, E. Ghasali, A. Shahbazkhan, S. Shakhesi, Evaluation of hot corrosion behavior of plasma sprayed thermal barrier coatings with graded intermediate layer and double ceramic top layer, Surface and Coatings Technology 288 (2016) 36-45.
90A. Abouchenari et al. / Journal of Composites and Compounds 2 (2020) 85-91
[6] A. Giroto, S. Fidélis, C. Ribeiro, Controlled release from hydroxyapatite nanoparticles incorporated into biodegradable, soluble host matrixes, Rsc Advanc-es 5(126) (2015) 104179-104186.
[7] U. Shavit, M. Reiss, A. Shaviv, Wetting mechanisms of gel-based controlled-re-lease fertilizers, Journal of Controlled Release 88(1) (2003) 71-83.
[8] S. Saadi, B. Nazari, Submission Title: Recent Developments and Applications of Nanocomposites in Solar Cells: a Review, Composites and Compounds 1(1) (2019).
[9] S.S. Ray, M. Okamoto, New polylactide/layered silicate nanocomposites, 6 melt rheology and foam processing, Macromolecular materials and engineering (288; NUMB 12) (2003) 936-944.
[10] Q. Zeng, A. Yu, G. Lu, D.R. Paul, Clay-based polymer nanocomposites: research and commercial development, Journal of nanoscience and nanotechnology 5(10) (2005) 1574-1592.
[11] P.C. LeBaron, Z. Wang, T.J. Pinnavaia, Polymer-layered silicate nanocompos-ites: an overview, Applied clay science 15(1-2) (1999) 11-29.
[12] T.J. Pinnavaia, G.W. Beall, Polymer-clay nanocomposites, John Wiley2000.
[13] C. Kannan, R. Ramanujam, Comparative study on the mechanical and micro-structural characterisation of AA 7075 nano and hybrid nanocomposites produced by stir and squeeze casting, Journal of advanced research 8(4) (2017) 309-319.
[14] R. Singh, V. Mahto, Synthesis, characterization and evaluation of polyacryl-amide graft starch/clay nanocomposite hydrogel system for enhanced oil recovery, Petroleum Science 14(4) (2017) 765-779.
[15] M. Mousa, N.D. Evans, R.O. Oreffo, J.I. Dawson, Clay nanoparticles for re-generative medicine and biomaterial design: a review of clay bioactivity, Bioma-terials 159 (2018) 204-214.
[16] S. Wu, A. Cheng, H. Hua, J. Shen, A study on structure and mechanical prop-erties of polyurethane/organic-montmorillonite nanocomposites, Polymer-Plastics Technology and Engineering 45(6) (2006) 685-689.
[17] W. Chow, J. Teoh, L. Lim, Mechanical and hygrothermal aging study on poly-styrene/organo-montmorillonite nanocomposites, Polymer-Plastics Technology and Engineering 47(10) (2008) 1040-1045.
[18] S.C. Tjong, Structural and mechanical properties of polymer nanocomposites, Materials Science and Engineering: R: Reports 53(3-4) (2006) 73-197.
[19] S. Pavlidou, C. Papaspyrides, A review on polymer–layered silicate nanocom-posites, Progress in polymer science 33(12) (2008) 1119-1198.
[20] G. Sposito, N.T. Skipper, R. Sutton, S.-h. Park, A.K. Soper, J.A. Greathouse, Surface geochemistry of the clay minerals, Proceedings of the National Academy of Sciences 96(7) (1999) 3358-3364.
[21] M. Alexandre, P. Dubois, Polymer-layered silicate nanocomposites: prepara-tion, properties and uses of a new class of materials, Materials Science and Engi-neering: R: Reports 28(1-2) (2000) 1-63.
[22] L. Bazli, A. Khavandi, M.A. Boutorabi, M. Karrabi, Correlation between vis-coelastic behavior and morphology of nanocomposites based on SR/EPDM blends compatibilized by maleic anhydride, Polymer 113 (2017) 156-166.
[23] G. Madhumitha, J. Fowsiya, S. Mohana Roopan, V.K. Thakur, Recent advanc-es in starch–clay nanocomposites, International Journal of Polymer Analysis and Characterization 23(4) (2018) 331-345.
[24] J.M. Garces, D.J. Moll, J. Bicerano, R. Fibiger, D.G. McLeod, Polymeric nanocomposites for automotive applications, Advanced Materials 12(23) (2000) 1835-1839.
[25] A.C. Lima, L.M. Jou, O.E. Barcia, I.C. Margarit-Mattos, Montmorillonite as corrosion protective pigment, Corrosion Science 141 (2018) 182-194.
[26] A.M. Youssef, S.M. El-Sayed, Bionanocomposites materials for food packag-ing applications: Concepts and future outlook, Carbohydrate polymers 193 (2018) 19-27.
[27] E. Asadi, A. Fassadi Chimeh, S. Hosseini, S. Rahimi, B. Sarkhosh, L. Bazli, R. Bashiri, A.H. Vakili Tahmorsati, A Review of Clinical Applications of Graphene Quantum Dot-based Composites, Composites and Compounds 1(1) (2019).
[28] W. Paul, C.P. Sharma, Inorganic nanoparticles for targeted drug delivery, Bio-integration of Medical Implant Materials, Elsevier2020, pp. 333-373.
[29] J.-H. Chang, Y.U. An, D. Cho, E.P. Giannelis, Poly (lactic acid) nanocompos-ites: comparison of their properties with montmorillonite and synthetic mica (II), Polymer 44(13) (2003) 3715-3720.
[30] S.H. Cypes, W.M. Saltzman, E.P. Giannelis, Organosilicate-polymer drug de-livery systems: controlled release and enhanced mechanical properties, Journal of controlled release 90(2) (2003) 163-169.
[31] A. Kiersnowski, J. Pigłowski, Polymer-layered silicate nanocomposites based on poly (ε-caprolactone), European polymer journal 40(6) (2004) 1199-1207.
[32] E. Günister, D. Pestreli, C.H. Ünlü, O. Atıcı, N. Güngör, Synthesis and charac-terization of chitosan-MMT biocomposite systems, Carbohydrate Polymers 67(3) (2007) 358-365.
[33] C. Pérez, V. Alvarez, A. Vazquez, Creep behaviour of layered silicate/starch–polycaprolactone blends nanocomposites, Materials Science and Engineering: A 480(1-2) (2008) 259-265.
[34] Y. Rao, Gelatin–clay nanocomposites of improved properties, Polymer 48(18) (2007) 5369-5375.
[35] M.-Y. Chang, R.-S. Juang, Stability and catalytic kinetics of acid phosphatase immobilized on composite beads of chitosan and activated clay, Process Biochem-istry 39(9) (2004) 1087-1091.
[36] M.-Y. Chang, R.-S. Juang, Use of chitosan–clay composite as immobilization support for improved activity and stability of β-glucosidase, Biochemical Engi-neering Journal 35(1) (2007) 93-98.
[37] M.-Y. Chang, H.-C. Kao, R.-S. Juang, Thermal inactivation and reactivity of β-glucosidase immobilized on chitosan–clay composite, International journal of biological macromolecules 43(1) (2008) 48-53.
[38] V.B. Yadav, R. Gadi, S. Kalra, Clay based nanocomposites for removal of heavy metals from water: A review, Journal of Environmental Management 232 (2019) 803-817.
[39] E.I. Unuabonah, A. Taubert, Clay–polymer nanocomposites (CPNs): Adsor-bents of the future for water treatment, Applied Clay Science 99 (2014) 83-92.
[40] S.A. Hosseini, M. Vossoughi, N.M. Mahmoodi, M. Sadrzadeh, Clay-based electrospun nanofibrous membranes for colored wastewater treatment, Applied Clay Science 168 (2019) 77-86.
[41] M.E. Trenkel, Slow-and controlled-release and stabilized fertilizers: An op-tion for enhancing nutrient use efficiency in agriculture, IFA, International fertiliz-er industry association2010.
[42] M. Sultan, A. Abdelhakim, M. Nassar, Cellulose-Based Hydrogels as Smart, Green and Controllable Nitrogenous Fertilizers Releasing Agents, Journal of Testing and Evaluation 49(4) (2019).
[43] B. Zhao, S. Dong, J. Zhang, P. Liu, Effects of controlled-release fertiliser on nitrogen use efficiency in summer maize, PloS one 8(8) (2013).
[44] J. Li, X. Zhuang, O. Font, N. Moreno, V.R. Vallejo, X. Querol, A. Tobias, Synthesis of merlinoite from Chinese coal fly ashes and its potential utilization as slow release K-fertilizer, Journal of hazardous materials 265 (2014) 242-252.
[45] A. Bortolin, F.A. Aouada, L.H. Mattoso, C. Ribeiro, Nanocomposite PAAm/methyl cellulose/montmorillonite hydrogel: evidence of synergistic effects for the slow release of fertilizers, Journal of agricultural and food chemistry 61(31) (2013) 7431-7439.
[46] L. Bazli, M.H. Bagherian, M. Karrabi, F. Abbassi-Sourki, H. Azizi, Effect of starch ratio and compatibilization on the viscoelastic behavior of POE/starch blends, Journal of Applied Polymer Science (2019) 48877.
[47] T.S. Daitx, M. Giovanela, L.N. Carli, R.S. Mauler, Biodegradable polymer/clay systems for highly controlled release of NPK fertilizer, Polymers for Ad-vanced Technologies 30(3) (2019) 631-639.
[48] K. Yano, A. Usuki, A. Okada, T. Kurauchi, O. Kamigaito, Polymer Science Part A, Polymer Chemistry 31 (1993) 2493.
[49] R. Bharadwaj, A. Mehrabi, C. Hamilton, C. Trujillo, M. Murga, R. Fan, A. Chavira, A. Thompson, Structure–property relationships in cross-linked polyester–clay nanocomposites, Polymer 43(13) (2002) 3699-3705.
[50] N. Sheng, M.C. Boyce, D.M. Parks, G. Rutledge, J. Abes, R. Cohen, Multiscale micromechanical modeling of polymer/clay nanocomposites and the effec-tive clay particle, Polymer 45(2) (2004) 487-506.
[51] C. Thellen, C. Orroth, D. Froio, D. Ziegler, J. Lucciarini, R. Farrell, N.A. D'Souza, J.A. Ratto, Influence of montmorillonite layered silicate on plasticized poly (l-lactide) blown films, Polymer 46(25) (2005) 11716-11727.
[52] L. Bazli, A. Khavandi, M.A. Boutorabi, M. Karrabi, Morphology and visco-elastic behavior of silicone rubber/EPDM/Cloisite 15A nanocomposites based on Maxwell model, Iranian Polymer Journal 25(11) (2016) 907-918.
[53] N. Xiaoyu, W. Yuejin, W. Zhengyan, W. Lin, Q. Guannan, Y. Lixiang, A novel slow-release urea fertiliser: Physical and chemical analysis of its structure and study of its release mechanism, Biosystems engineering 115(3) (2013) 274-282.
[54] M. Rinaudo, Chitin and chitosan: properties and applications, Progress

in polymer science 31(7) (2006) 603-632.
[55] Q. Li, E. Dunn, E. Grandmaison, M.F. Goosen, Applications and properties of chitosan, Journal of Bioactive and Compatible Polymers 7(4) (1992) 370-397.
[56] K. Haraguchi, Nanocomposite hydrogels, Current Opinion in Solid State and Materials Science 11(3-4) (2007) 47-54.
[57] X. Wang, S. Lü, C. Gao, X. Xu, Y. Wei, X. Bai, C. Feng, N. Gao, M. Liu, L. Wu, Biomass-based multifunctional fertilizer system featuring controlled-release nutrient, water-retention and amelioration of soil, RSC advances 4(35) (2014) 18382-18390.
[58] K. Xing, X. Zhu, X. Peng, S. Qin, Chitosan antimicrobial and eliciting prop-er-ties for pest control in agriculture: a review, Agronomy for Sustainable Develop-
[59] J.J. Perez, N.J. Francois, Chitosan-starch beads prepared by ionotropic ge-la-tion as potential matrices for controlled release of fertilizers, Carbohydrate po-ly-mers 148 (2016) 134-142.
[60] D.Y. Wu, S. Meure, D. Solomon, Self-healing polymeric materials: a review of recent developments, Progress in polymer science 33(5) (2008) 479-522.
[61] B.R. dos Santos, F.B. Bacalhau, T. dos Santos Pereira, C.F. Souza, R. Faez, Chitosan-montmorillonite microspheres: a sustainable fertilizer delivery sys-tem, Carbohydrate polymers 127 (2015) 340-346.
[62] C.F. Souza, R. Faez, F.B. Bacalhau, M.F. Bacarin, T.S. Pereira, In situ mon-itoring of a controlled release of fertilizers in lettuce crop, Engenharia Agrícola 37(4) (2017) 656-664.
[63] L.L. Messa, C.F. Souza, R. Faez, Spray-dried potassium nitrate-con-taining chitosan/montmorillonite microparticles as potential enhanced efficiency fertilizer, Polymer Testing 81 (2020) 106196.
[64] M. George, T.E. Abraham, Polyionic hydrocolloids for the intestinal delivery of protein drugs: alginate and chitosan—a review, Journal of controlled release 114(1) (2006) 1-14.
[65] Z. Wu, Y. Zhao, I. Kaleem, C. Li, Preparation of calcium–alginate micro-cap-suled microbial fertilizer coating Klebsiella oxytoca Rs-5 and its performance un-der salinity stress, European journal of soil biology 47(2) (2011) 152-159.
[66] A.L. Córdoba, L. Deladino, M. Martino, Effect of starch filler on calcium-al-gi-nate hydrogels loaded with yerba mate antioxidants, Carbohydrate polymers 95(1) (2013) 315-323.
[67] Y. He, Z. Wu, L. Tu, Y. Han, G. Zhang, C. Li, Encapsulation and character-iza-tion of slow-release microbial fertilizer from the composites of bentonite and alginate, Applied Clay Science 109 (2015) 68-75.
[68] B. Singh, D. Sharma, R. Kumar, A. Gupta, Controlled release of the fungicide thiram from starch–alginate–clay based formulation, Applied Clay Science 45(1-2) (2009) 76-82.
[69] D. Klemm, B. Heublein, H.P. Fink, A. Bohn, Cellulose: fascinating biopo-ly-mer and sustainable raw material, Angewandte chemie international edition 44(22) (2005) 3358-3393.
[70] I. Siró, D. Plackett, Microfibrillated cellulose and new nanocomposite ma-teri-als: a review, Cellulose 17(3) (2010) 459-494.
[71] D. Davidson, F.X. Gu, Materials for sustained and controlled release of nu-tri-ents and molecules to support plant growth, Journal of agricultural and food chemistry 60(4) (2012) 870-876.
[72] S. Bajpai, M. Swarnkar, S. Ahuja, On-demand release of urea from a cellu-los-ic hydrogel using a sprinkler based irrigation (SBI) model, Journal of Macro-mo-lecular Science, Part A 52(10) (2015) 779-785.
[73] H. Li, Y. Zhou, W. Tu, J. Ye, Z. Zou, State-of-the-art progress in diverse het-erostructured photocatalysts toward promoting photocatalytic performance, Ad-vanced Functional Materials 25(7) (2015) 998-1013.
[74] H.A. Essawy, M.B. Ghazy, F.A. El-Hai, M.F. Mohamed, Superabsorbent hy-drogels via graft polymerization of acrylic acid from chitosan-cellulose hybrid and their potential in controlled release of soil nutrients, International journal of bio-logical macromolecules 89 (2016) 144-151.
[75] M. Fernández-Pérez, F. Garrido-Herrera, E. González-Pradas, M. Villafranca-Sánchez, F. Flores-Céspedes, Lignin and ethylcellulose as polymers in controlled release formulations of urea, Journal of applied polymer science 108(6) (2008) 3796-3803.
[76] B. Ni, M. Liu, S. Lu, L. Xie, Y. Wang, Environmentally friendly slow-re-lease nitrogen fertilizer, Journal of agricultural and food chemistry 59(18) (2011) 10169-10175.
[77] B. Ni, M. Liu, S. Lü, L. Xie, Y. Wang, Multifunctional slow-release organic−inorganic compound fertilizer, Journal of agricultural and food chemistry 58(23) (2010) 12373-12378.
[78] Y. Verma, S. Datta, I.K. Mandal, D. Sarkar, Effect of phosphorus loaded or-ganically modified nanoclay-polymer composite on release and fixation of phos-phorus and its uptake by wheat (Triticum aestivum L.), Journal of Pure and Ap-plied Microbiology 10(3) (2016) 2299-2306.
[79] A. Rashidzadeh, A. Olad, Slow-released NPK fertilizer encapsulated by NaAlg-g-poly (AA-co-AAm)/MMT superabsorbent nanocomposite, Carbo-hy-drate polymers 114 (2014) 269-278.
[80] Y.D. Noh, S. Komarneni, M. Park, Mineral-based slow release fertilizers: a review, Korean Journal of Soil Science and Fertilizer 48(1) (2015) 1-7.