Review

A Brief Review of the Latest Advances of Attapulgite as a Reinforcing Agent in Polymer Matrix Nanocomposites

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Abstract: The development of polymeric nanocomposites using clay minerals as a Nano filler is of great interest to researchers and industry. Many clay minerals are used to modify the properties of the polymers; this strategy improves the thermal and mechanical performance and changes the surface finishing and the processing characteristics. The Attapulgite (ATP), which is a clay mineral of the hydrated magnesium silicates family, has gained prominence in recent years because it combines low cost and high performance. It has a large surface area, strong absorption capacity superior to any other natural mineral, good mechanical resistance and thermal stability. These properties make ATP an ideal candidate for reinforcing polymeric materials. Different approaches and emerging technologies have been applied to improve the thermal and mechanical properties of polymer/ATP nanocomposites which can extend the different chemical treatments used in ATP. Therefore, this review article presents the latest advances related to the use of ATP in the development of polymeric nanocomposites, showing future perspectives for new trends in ATP applications. In general, ATP modifies the mechanical properties of polymers, either in the natural or modified state. And is a good alternative for the replacement of lamellar clays such as montmorillonites with the advantage of having a lower cost and a wide world market to be explored, which drive new trends in applications for ATP, such as flame retardant of cotton fabrics, dye adsorption, hydrogel membranes for wound dressing, sustainable packaging and fuel cell applications.

Keywords: Attapulgite, Nanocomposite, Clay Mineral, Polymers, Thermal and Mechanical Properties

Introduction

The addition of clay mineral fillers in polymeric materials is a great industrial strategy and has become frequent in the polymer industry. This strategy improves the thermal, mechanical and thermo-mechanical properties, changing the surface appearance and processing characteristics and mainly reducing the final cost of the products (Liu et al., 2020; Gill et al., 2020; Abbasian et al., 2020; Adak et al., 2018; Rapacz-Kmita et al., 2015).

The development of nanocomposites with good cost-benefit resulted in the study of the feasibility and convenience of using a large number of mineral fillers (Rapacz-Kmita et al., 2015). Polymeric nanocomposites are a composite materials class where a dispersed phase has at least one of its dimensions less than 100 nanometers (nm). Thus, the dispersed phase has a large surface area, which allows a greater transfer of tension between the polymer matrix and the dispersed phase. This great transfer of tension results in a high reinforcement notably for the improvement in the mechanical properties,
processability, permeability and thermal stability of the nanocomposite. Another great advantage in the use of nanofillers is the small amount of clay mineral that is used in the composition, contributing for the production of parts with low density and high performance (Bogue, 2011; Hussain et al., 2006; Rane et al., 2018; Thostenson et al., 2005).

Three main methods can be used to obtain nanocomposites with the addition of clay minerals.

In Situ Polymerization (ISP): This method involves the addition of the clay filler in the mixture of monomers and polymerization reagents. The nanofillers are swollen by the liquid monomers, followed by the polymerization process. The particles are then surrounded by the polymeric chain that is forming, ensuring the dispersion of the inorganic content. The process is initiated by radiation or heat, in addition to the diffusion of a suitable initiator for the monomer in question. However, very strict control of the polymerization process is required to achieve a good exfoliation of nanofiller (Rane et al., 2018; Alexandre and Dubois, 2000; Liu et al., 2017; Powell and Beall, 2007; Wang et al., 2014; Xie et al., 2014; Zhang et al., 2016).

Solution Intercalation (SI): In this method, the clay and the polymer are added to an organic solvent. The solvent is chosen so that the fillers can be easily swollen by it and the polymer dissolves in it as well. The polymer solution will adsorb the clay and disperse it. After that, the solvent is evaporated and the clay particles are well dispersed in the nanocomposite structure (Rane et al., 2018; Alexandre and Dubois, 2000; Giannellis, 1996; Lee et al., 2018; Xiang et al., 2017; Yin et al., 2010a; 2010b).

Melt Intercalation (MI): This method consists of increasing the system temperature to melt the polymer and disperse the clay in it. The high shear levels that the polymer chains will exert on the nanofillers cause the clay mineral particles to break and disperse. This way of dispersion of the filler in the polymer is ideal for the properties to be applied in an anisotropic manner, that is, without a specific direction for the stress application. During this process, the melted polymer chains tend to diffuse in between nanofillers to produce the nanocomposite system. This process can be considered eco-friendly, as it does not involve the use of high amounts of solvents. Also, it is the cheapest process because it manages to produce nanocomposites on a large scale (Rane et al., 2018; Zhang et al., 2016; Fornes et al., 2001; Liu et al., 1999; Qi et al., 2013; Zhao et al., 2012).

Polymeric nanocomposites using clay usually have very attractive mechanical and thermal properties and are superior to conventional composites, as well as reduced permeability values, better chemical resistance to solvents and greater flame retardancy. Polymeric composites reinforced with clays are of great interest due to their applications in the packaging and automotive industries. There are studies on clay reinforced with rubber and silt as well. It is becoming quite common to mix clay and rubber particles processed in different civil and geotechnical constructions such as light landfill, road substrate, fill with embankment, embankments, asphalt construction, sound barrier, railway construction and reinforcement of foundation. However, the use of these mixtures in full-scale projects requires a better understanding of the mechanical performance of the mixtures (Rouhanifar et al., 2020; Majedi et al., 2020; 2021; Yazdani et al., 2018; Rouhanifar and Afrazi, 2019).

Several clay minerals have been widely studied to improve the mechanical properties of polymeric matrices, such as montmorillonite (Rodrigues Passos Severino et al., 2019; Passer et al., 2013a; 2013b; Barbalho, 2012; Bai et al., 2018), halloysite (Bertolino et al., 2020; Lisuzzo et al., 2020; Alam et al., 2020), sepiolite (Ferrari et al., 2017; Kim et al., 2020; Fernández-Barranco et al., 2020; Wang et al., 2020; Sun et al., 2020; Di Credico et al., 2019) and attapulgite (palygorskite) (da Silva et al., 2020; Tian et al., 2020; Yang et al., 2020; Elbassyoni et al., 2020).

Among the existing clay minerals, some have remarkable characteristics like the Palygorskite (Pal) or Attagulgite (ATP). Pal is the term recommended by International Mineralogical Association (IMA) for nomenclature, but the most used trade name for many producers is ATP. In this study, the ATP denomination will be used. This clay has a fibrous morphology with a 2:1 crystalline structure, which consists of two layers of periodically inverted silica tetrahedral connected by an octahedral layer. Each tetrahedral layer presents 180° inversion for each sequence of four or six SiO4 tetrahedrons. This structure leads to the formation of channels that extend throughout the longitudinal direction of the fiber (Murray, 2020; Frost et al., 2001; López-Galindo et al., 2007).

Bradley (1940) proposed the first structural pattern for ATP and suggested that the clay mineral has the chemical formula [(Mg, Al)3Si2O10(OH)4]·4H2O. The ATP contains three forms of water in its structure: (a) Coordinated water, with cations of the octahedral leaf, (b) zeolitic water, presents in the channels in which it interacts with both the coordinated H2O molecule and the leaf tetrahedral and (c) hydroxyl water, linked to the clay structure in the center of the leaf octahedron (Xavier et al., 2012). Figure 1 shows the chemical structure of the ATP proposed by Bradley (1940).

Due to these structural aspects, ATP has interesting properties such as high specific surface area, high sorption, low surface charges, bleaching power and thixotropic properties in the presence of electrolytes (Haden and Schwint, 1967; Galán, 1996). Some of its properties are listed in Table 1. In addition to these good properties, ATP has a low-cost with a price of 0.2-0.5
US$/Kg (as a comparison, the price of montmorillonite is on average 10-15 US$/Kg). A rough cost estimation was made based on the price of materials from the platform (Alibaba.com-09/05/2020).

The largest deposits of ATP group minerals around the world were formed either by chemical sedimentation in island seas and lakes, hydrothermal alteration of clays, basaltic glass, or volcanic sediments in the open oceans or by direct crystallization in calcareous soils (Singer and Galan, 2000). These aspects of geological formation are associated with the Mediterranean to semi-arid climate, which reflects in the distribution of these minerals in low latitudes, mainly in arid and semiarid areas of the world (Singer et al., 2011). The location of the main reported deposits of ATP is shown in Fig. 2.

Table 2 shows the chemical composition of ATP from various sources around the world. All the ATPs in the municipality of Guadalupe-PI have clay minerals: Attapulgite, kaolinite, smectite, illite and chlorite, with a predominance of ATP followed by kaolinite. Brazilian ATP has a lower CaO and higher K2O content when compared to ATPs from other countries. These differences can be attributed to the content and nature of the Guadalupe ATPs and/or the types and content of contaminants (Baltar and Luz, 2003). The ATP geological formation process allows the association with a large number of accessory minerals, such as quartz, mica, calcite, dolomite, among others, associated with the occurrence of clay minerals; in addition to the presence of organic matter. Often depending on the desired application, it is necessary to separate the main clay mineral from all these impurities (accessory minerals and organic matter) in a process called acid activation (Luz and Lins, 2008).

| Table 1: Properties of attapulgite (Singer et al., 2011) |
|-----------------|-------------------|
| Melting point (°C) | 1.550             |
| Length (μm)       | 0.2-2.0           |
| Width (Å)         | 100-300            |
| Thickness (Å)     | 50-100             |
| Channels dimensions (Å) | 3.7×6.4       |
| Specific surface area (m²/g) | 150              |
| Cation Exchange capacity (meqiv/100g) | <25            |
| Brookfield viscosity, suspension | 10.000-12.000 (cP) |
| Specific gravity (g/cm³) | 2.0-2.3          |

Fig. 1: The chemical structure of ATP

Fig. 2: Attapulgite reported deposits
separation methods, non-ATP particles can be removed that settle in the background. From this, through physical agents aims to break up clusters, leaving ATP mixing process combined with the action of dispersing between the density and/or particle size of minerals to sedimentation method is based on the difference towards these forces (Stempkowska 2001; Xavier et al., 2003; Grim, 1969; Van Olphen and Fripiat, 1979). Sodium silicate acts in the opposite way to destabilize the suspensions, forming clusters, ceramic powders when in a liquid medium. Van der Waals forces act to destabilize the suspensions, forming clusters, in this way, sodium silicate acts in the opposite way towards these forces (Stempkowska et al., 2017). The sedimentation method is based on the difference between the density and/or particle size of minerals to promote separation between them. In this way, a mixing process combined with the action of dispersing agents aims to break up clusters, leaving ATP suspended particles while quartz and other impurities settle in the background. From this, through physical separation methods, non-ATP particles can be removed (Murray, 2000; Purcell and Parker, 2012).

However, only the sieving and the sedimentation technique are not effective to remove the total quartz content, these techniques only reduce the amount of quartz. Many authors have reported the difficulty of completely removing quartz. Neto et al. (1993) when analyzing the ATP from Guadalupe (Brazil), submitted the samples to physical processing to reduce the quartz content. Luz et al. (1988) through granulometric analysis and X-Ray Diffraction (XRD) found a reduction in the percentage of quartz the finer the granulometry. In addition to physical separation methods, to minimize other impurities like carbonates and organic matter, a chemical and/or thermal treatment can be used. These treatments also result in an improvement of some properties, such as absorption, adsorption, specific surface area, cation exchange capacity, among others. Chemical treatment can be done by washing or immersing the clay in acid or oxidizing substances. And heat treatment occurs when the sample is heated to a certain temperature and then remains for a certain period (Souza Santos, 1989).

Chemical treatment, also known as acid activation, is very effective for the removal of organic matter and carbonates (limestone and dolomite). It is carried out using oxidizing reagents, such as Hydrogen peroxide ($\text{H}_2\text{O}_2$) and strong acids, such as Hydrochloric Acid ($\text{HCl}$) and Sulfuric Acid ($\text{H}_2\text{SO}_4$). $\text{H}_2\text{O}_2$ oxidizes organic matter and depending on the amount of organic matter and the oxidant content the sample to physical processing to reduce the quartz content. Luz et al. (1988) through granulometric analysis and X-Ray Diffraction (XRD) found a reduction in the percentage of quartz the finer the granulometry.

Using strong acids, the acid activation in the clay occurs as follows: The soluble salts are partially dissolved, resulting in a reduction of iron and aluminum content; sodium and potassium ions go in solution unless they are present into the silicate structure. The calcium ion content; sodium and potassium ions go in solution unless they are present into the silicate structure. The calcium ion present is totally or partially solubilized, while the magnesium ion can remain almost entirely in the clay. It is important to note that acid activation allows the improvement of the physical-chemical properties of ATP without destroying its crystalline structure, such as increasing the adsorption capacity, bleaching power and mainly increasing the surface area (Frost et al., 2001).

### Table 2: Chemical composition of several samples of ATP from different locations (Baltar and Luz, 2003; Grim, 1969; Van Olphen and Fripiat, 1979)

| Content (%) | São Pedro Clear Guadalupe Brazil | São Pedro Dark Guadalupe Brazil | Boa Vista Guadalupe Brazil | Nizhni-Novgorod Russia | Taodeni Saara Algeria | Attapulgus Georgia USA |
|------------|---------------------------------|---------------------------------|--------------------------|-----------------------|----------------------|-----------------------|
| SiO$_2$    | 68.50                           | 66.70                           | 57.90                    | 51.17                 | 54.71                | 55.03                 |
| Al$_2$O$_3$| 10.30                           | 9.10                            | 12.10                    | 13.73                 | 13.48                | 10.24                 |
| Fe$_2$O$_3$| 4.00                            | 3.70                            | 7.20                     | 1.55                  | 2.10                 | 3.53                  |
| FeO        | -                               | -                               | -                        | 0.31                  | -                    | -                     |
| MgO        | 5.60                            | 7.40                            | 4.90                     | 6.40                  | 5.44                 | 0.49                  |
| CaO        | 0.17                            | 0.17                            | 0.10                     | 2.89                  | 2.79                 | -                     |
| K$_2$O     | 1.20                            | 0.83                            | 2.20                     | -                     | -                    | 0.47                  |
| Na$_2$O    | 0.10                            | 0.11                            | 0.14                     | -                     | -                    | -                     |
| H$_2$O     | -                               | -                               | -                        | 10.29                 | 8.65                 | 9.73                  |
| MnO        | 0.12                            | 1.10                            | 0.50                     | -                     | -                    | -                     |
| P$_2$O$_5$ | 0.03                            | 0.03                            | 0.05                     | -                     | -                    | -                     |
| TiO$_2$    | 0.70                            | 0.60                            | 0.61                     | -                     | -                    | -                     |
| L.F.*      | 9.50                            | 11.06                           | 13.37                    | 13.24                 | 12.63                | 10.13                 |

* L.F.- Loss to fire
An example of the effectiveness of acid treatment in ATP is shown in the study that prepares nanocomposites of Polyurethane (PU)/epoxy blends with natural ATP and ATP-acid (Xu et al., 2019). The results showed that the activation in ATP did not alter the crystalline structures, it improved the glass transition Temperature ($T_g$) of the composites, however, the addition of activated ATP had a significant reinforcing effect on the nanocomposite.

Figure 3a shows the diffractogram of raw ATP and ATP after Acid Treatment (ATP-acid). Analyzing the diffractogram, it is possible to identify four main phases: Attapulgite (orthorhombic structure), calcite, dolomite and quartz. The main ATP diffraction peaks occur at approximately 8.6° and 19.9°. For quartz, the most significant peak is found at 26.7° and for calcite around 29.3°. It is possible to observe that with the acid treatment there was a reduction in the intensity of the peaks of calcite and dolomite, indicating that these impurities are partially removed from the ATP. In addition, the ATP related peaks do not undergo significant changes, which indicates that the acid treatment does not destroy its crystalline structure (Fig. 3b) (Kim et al., 2020; Elbassyoni et al., 2020).

**Modification of ATP**

In order to improve the interaction of ATP with polymeric materials, in addition to acid activation, it is desirable to perform a superficial modification of ATP. As this clay mineral has a great capacity for cation exchange, it is possible to perform organophilization by cation exchange. Thus, ATP can be modified through two different processes, silanization with the addition of aminosilane and organophilization with the addition of an organic compound.

The silanization reactions occur due to the interaction by covalent bonding of the silylating agent with the silanol groups that are on the surface of the clay minerals, as shown in Fig. 4. Silylating agents are compounds that have the general formula, $(X)_3Si(R)Y$, in which X is an alkoxide group (RO–), R is called a spacer group which is usually $(CH_2)_3$ and Y determines the reactivity and applicability of the compound, it assumes several formulas, the most common being NH$_2$, CI, CN, NCO and SH (Xue et al., 2010).

Another technique for the organophilization of clays is by adding organic compounds. The organophilization of clays is usually carried out using the ion exchange technique, or better, with the replacement of cations present in the clay, usually Na$^+$. These cations are easily exchangeable because they are monovalent and they facilitate the exchange for organic cations of quaternary ammonium salts (cationic surfactants) or even other types of salts, in an aqueous solution. The salts used in the modification have one or two groups of long-chain hydrocarbons linked directly to a nitrogen atom where the cationic part of the molecule is located (Kakegawa and Ogawa, 2002).

These modifiers allow reducing the surface energy of the clay, improving its wettability with the polymeric matrix. This contributes to the increase in adhesion between the inorganic phase and the polymeric matrix, in addition to facilitating the penetration of the polymeric chains between the clay agglomerates, enabling dispersion and distribution in the polymeric matrix (Xue et al., 2010).
Polymer/ATP Nanocomposites

For an overview of the scientific works related to the use of ATP, an extensive search of the articles and patents was realized on Web of Science and Espacenet databases, respectively. To highlight the most recent works and new trends, the research was limited to the period from 2010 to 2020. Also, to suit the scope of this review, the articles and patents were researched with the specific filters of the use of ATP in nanocomposites of the polymeric matrix. Figure 5a shows the number of articles and patents produced per year and Fig. 5b shows the different processing methods of the polymer/ATP nanocomposites.

Studies on obtaining nanocomposites with the addition of small clay minerals contents to the thermoplastic matrix have shown significant improvement in mechanical properties, water vapor barrier and flammability resistance concerning neat polymer (Gao et al., 2005).

Table 3 summarizes the developments of polymeric nanocomposites based on a thermoplastic matrix with the addition of ATP, showing the type of ATP treatment, processing method and the highlighted properties.

Thiré et al. (2011) developed nanocomposites of PHBV/ATP organically modified with hexadecyltrimethylammonium chloride. The addition of 3 and 5 wt% organophilic ATP led to significant changes in the properties of PHBV like a reduction in the degree of crystallinity and a decrease in the crystalline melting Temperature (T_m) and T_g.

The effect of surface modification of ATP on the morphology and thermal properties of PA6 ATP nanocomposites was studied by Cisneros-Rosado et al. (2018). The nanocomposites were prepared by melt intercalation and the ATP was modified with 3-aminopropyl trimethoxysilane bromide and tributylhexadecyl phosphonium. Experimental evidence confirmed the grafting of surface agents into ATP and, as expected, nanocomposites exhibited high thermal stability and less surface energy. The ATP particles favored the formation of the gamma crystalline form and increased the decomposition temperature of PA6.

da Silva et al. (2020) prepared PA12/ATP nanocomposites by high-speed mixing using a thermokinetic homogenizer. The addition of ATP increased the modulus of elasticity, hardness, degree of crystallinity and the apparent size of the crystallites. The addition of up to 5% by mass of ATP increased the tensile strength and deformation at rupture, after this amount, the concentration increased significantly and there was no good dispersion.

Wang et al. (2014a) prepared PBT/ATP nanocomposites by in situ polymerization. The results show that PBT/ATP nanocomposites have greater thermal stability than neat PBT. The PBT/ATP nanocomposite with a higher ATP content can delay the transport of polymer chains to the growing crystals compared to the nanocomposite PBT/ATP with a lower ATP content. According to dynamic results from the mechanical analysis, the nanocomposite PBT/ATP storage module has been significantly improved and the addition of ATP particles promotes the crystallization of PBT.

In addition to these improvements in mechanical and thermal properties, some recent studies have also studied the influence of ATP on the flammability of nanocomposites. Besides the direct influence of ATP on the flammability of materials, this clay mineral can also be used as a synergic agent in combination with flame retardants. Hou et al. (2020) prepared PA6/Melamine Cyanurate (MCA)/ATP nanocomposites by two-step-melt polymerization. For the composition with 6.2% of ATP and 11.5% of MCA, the mechanical properties of the nanocomposites were up to 44.81 MPa and the samples passed the UL-94 V-0 flammability rating, with the Limited Oxygen Index (LOI) reaching 27.9%. Thus, the authors concluded that the combination of MCA and ATP provided a marked improvement in the flame retardancy of PA6, in addition to maintaining its mechanical properties.

In general, ATP modifies the mechanical properties of polymers, either in the natural or modified state and has been shown to be a good alternative for the replacement of lamellar clays such as montmorillonites with the advantage of having a lower cost and a wide world market to be explored.
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Fig. 5: (a) number of articles and patents produced per year from 2010 to 2020 and; (b) processing methods of the polymer/ATP nanocomposites

Table 3: Summaries the developments of polymeric nanocomposites-based thermoplastic matrix with the addition of ATP, showing the type of ATP treatment, processing method and highlighted properties.

| ATP                  | Polymer Matrix | ATP content                  | Processing Method* | Highlighted Properties                                                                 | Reference |
|----------------------|----------------|------------------------------|-------------------|----------------------------------------------------------------------------------------|-----------|
| Sieved (320 mesh)    | Carboxymethyl cellulose | 5, 10, 20 and 25 wt%       | ISP               | The incorporation of ATP enhanced the swelling capability                                | Wang and Wang (2010) |
| Acide activation (HCl)| Polyurethane-urea| Non specified                | ISP               | This work opens up a possibility for the preparation of infrared low-loss emissive materials | Wang et al. (2010a) |
| Sieved (320 mesh)    | Hydroxethyl Cellulose-PAA1 | 5-10, 20, 30 and 35 wt%  | ISP               | The introduction of ATP into polymeric network can improve the water absorption rate     | Wang et al. (2011) |
| Pretreated with H2O2 and acid activated (HCl) | PAN2 | 1-7 wt% | SI | A small amount of results in a homogeneously stress transfer and energy dissipation, increasing the mechanical properties | Yin et al. (2010a) |
| Dispersed into ethanol and silane | PP1 | 2-10 wt% | MI | The steady shear viscosities of the nanocomposites are much higher than those of pure PP at lower shear rates | Zhang et al. (2010) |
| Sieved (200 mesh)    | Guar Gum-poly(Sodium Acrylate-co-Styrene) | Fixed                     | ISP               | The composites exhibited improved swelling capacity and rate, pH-resistance, sub-resistance and solvent-responsive properties | Shi et al. (2011) |
| Pretreated with H2O2 and acid activated (HCl) | PAN2 | 0.5, 1, 3 and 5 wt% | SI | The analysis on the steady shear rheology results showed that elevating temperature promote the orientation effect of ATP nanorods on the PAN1 chains | Yin et al. (2010b) |
| Sieved (200 mesh)    | Methyicellulose | 5, 10, 20 30 and 35 wt%   | ISP               | The nanocomposite shows excellent on-off switching swelling characteristics between pH 2.0 and 7.4 | Wang et al. (2010b) |
| Treated with surfactant | PIBV1 | 1-5 wt% | ISP | The morphology can be adjusted in a wide range by controlling the content of the ATP | Thir et al. (2011) |
| Treated with surfactant | PMMA1 | Non specified               | ISP               | The different morphologies of ATP/PMMA1 composite particles can be adjusted in a wide range by simply controlling the introduction of the ATP | Zhang et al. (2012) |
| Sieved (320 mesh)    | Poly(ethylene glycol)-based hydrogel | 1, 3, 5 and 7 wt% | ISP | The incorporation of ATP can improve the oil absorbency of PBMA1 | Wang et al. (2013) |
| Dispersed in ethanol solution | P(MEO2MA-co-OEGMA-co-ACs) | Non specified | ISP | The tensile strength, tensile modulus and an effective cross-linked chain density increased with the increasing content of ATP | Wang and Chen (2012) |
| Purified (not specified) and doped with Fe3O4 | Poly (ethylene glycol)-based hydrogel | 1, 3, 5 and 7 wt% | ISP | The hydrogel can continue to swell in an alternating magnetic field after equilibrium swelling in deionized water | Wang et al. (2012) |
| Sieved (320 mesh)    | PBMA1 | Non specified               | ISP               | The polymer nanocomposites possess excellent water absorption in distilled water or saline solutions | An et al. (2012) |
| Silane coupling in acid conditions | PPA1 | 5, 10, 15 and 30 wt% | MI | The modulus, fracture strength and tensile strength enhanced | Tang et al. (2013) |
| Grinded | Sodium carboxymethyl cellulose-PAA1 | 1-10 wt% | ISP | Excellent pH-responsive behavior and good regeneration ability | Liu et al. (2013) |
| Natural              | PBMA1 | 1, 3, 5 and 7 wt%           | MI | Nanocomposites revealed significant improvement in mechanical properties, Especially the break elongation of PBMA1/ATP nanocomposite with 1 wt% ATP | Qi et al. (2013) |
| Natural              | palmitic acid | Non specified               | MI | The composite showed well-connected open nanoscale channels and pores in its structure | Chen et al. (2013) |
| Washed with distilled water | PnPDE | Non specified               | ISP | Pul-PnPD sensor displays excellent analytical performances for glucose determination | Luo et al. (2013) |
| Washed with distilled water | PuPDE1 | Non specified               | ISP | The PuPDE1/PnPD nanocomposite showed high uptake toward a cationic dye | Xie et al. (2014) |
| Baked, ground and acid activated (HCl) | PAA1 | Non specified               | ISP | The micogel had a high adsorption capacity towards heavy metal ions, especially to Pb2+ | Liu et al. (2014a) |
| Natural | Epoxy | 3% | MM | The simulation result revealed that nanoparticle can indeed change the crack initiation and propagation pattern | Zhu et al. (2014) |
| Already purified | PBMA1 | 1 and 3 wt% | ISP | ATP acts as a heterogenous nucleating agent in PBMA1 crystallization and accelerated the crystallization rate | Zhang et al. (2014) |
| Received doped with Fe3O4 | Poly (ethylene glycol)-based microgel | 1 and 3 wt% | ISP | The microgel possess increasing pH response and excellent temperature-responsive characteristics | Wang et al. (2014a) |
| Material                        | Crosslinker                     | Method        | Properties                                                                 |
|--------------------------------|---------------------------------|---------------|-----------------------------------------------------------------------------|
| Natural                        | PAMPS (17)                      | Non specified | ISP                                                                         |
|                                |                                 |               | The addition of appropriate amount of APT can effectively improve the water absorption and salt water performance of the superabsorbent composite Xu et al. (2014) |
| Baked, graded and acid-activated (HCl) Silane treatment PP and LLDPE (12) 3,5 and 7 phr MI | ISP | The ATPE/PAAs hydrogen showed good adsorption selectivity toward the Pb (II) ion Lui et al. (2014b) |
| Baked, graded and acid-activated (HCl)  | PAA (3)                        | Non specified | ISP                                                                         |
| Acid activated                  | Treated with HCl and H2O (4)    | PEI (14)      | 5,10,15 and 20 wt% MI                                                      Lin et al. (2014c) |
| Modified with a silane coupling agent | PU (11)                       | Non specified | ISP                                                                         |
| Natural                        | Chitosan/PVA (18)               | 1-6 wt%       | SI                                                                          Liu et al. (2015) |
| Natural                        | Chitosan/PAA (co-Am) (11)       | Non specified | ISP                                                                         Liu et al. (2015) |
| ATP firstly                     | Baked at 140°C; acid activation (HCl) Natural | PANI (18)     | Non specified                                                              PLA et al. (2015a) |
| Milled and sanded (320 mesh)    | Hydroyxyl cellulose -based hydrogel | Non specified | ISP                                                                         |
| Milled and sanded (320 mesh)    | Epoxy resin                     | Non specified | Thermoset                                                                  Yang et al. (2015) |
| ATP modified with [3+2-aminomethylaminoxy] trimethoxysilane (Z-6020) | PP-g-MA (18)     | 0.5-5 wt%      | MI                                                                          Chen et al. (2016) |
| Natural                        | PVC (33)                       | 5 phr         | MI                                                                          Wang et al. (2015) |
| Washed in HCl and introduction of a silane coupling agent KH-570 Centrifugation (1500 rpm) and acid activation (HCl) | PS (32)          | 0.5-2 wt%       | ISP                                                                         Zhu et al. (2016a) |
| Acid activation (HCl) Natural   | Chitosan                        | 1-4 wt%       | ISP                                                                         |
| Dispersed in H2O/ Ethanol solution | PEBA (22) | Non specified | SI                                                                          |
| Natural                        | PP (39)                        | Non specified | SI                                                                          |
| Natural                        | PP-g-co-PVA (13)               | Non specified | ISP                                                                         |
| Natural                        | Chitosan                       | Non specified | SI                                                                          |
| Dispersed into 250 mL of 0.5 mol L-1 H2SO4 | EVA (26) | 3-7 Phr       | MI                                                                          Shao et al. (2017) |
| Dispersed into a solution of γ-Aminomoprophyli- ethyleneoxide in isopropyl Alcohol | EVA (26) | Non specified | SI                                                                          |
| Natural                        | PEBA (22)                      | Non specified | SI                                                                          |
| Natural                        | PLA-PPAT (10)                  | 1-7.5 wt%     | MI                                                                          Xiang et al. (2017) |
| Thermally-Treated Attapulgite (TAT) | PEI (13) | 0.5-2.5 wt%  | SI                                                                          Zhu et al. (2017) |
| Dispersed in silane coupling agent and organic acid solution Natural | PASA (29) | Non specified | SI                                                                          |
| Natural                        | PDMS (50)                      | 0.5-5 wt%     | SI                                                                          Liu et al. (2018) |
| Natural                        | Cellulose                      | Non specified | SI                                                                          |
| Natural                        | Epoxy resin                    | Non specified | Thermostat                                                                 |
| Natural                        | PP (33) and PS (17)            | 2.3-3 wt%     | ISP                                                                         Lin et al. (2019) |
| Acid activation (HCl) Chitosan  | Chitosan                       | 1-8 wt%       | ISP                                                                         Hu et al. (2020a) |
| Acid activation (H2SO4) Chitosan | PA2 (11)                      | 2-10 wt%      | SI                                                                          Liu et al. (2020b) |
| Sieded (200 mesh) PEI (11)      | PA2 (11)                       | 1-10 wt%      | MI                                                                          Kim et al. (2020) |
| Acid activation (HCl) PAA (3)   | Non specified                  | ISP                                                                         |
| Acid activation (HCl) Cellulose | Chitosan                       | Non specified | SI                                                                          Chen et al. (2020a) |
| NH2 and PMMA grafting PDMA (19)| 1 and 2 wt%                    | SI                                                                          Tuan et al. (2020) |
| Dispersed in H2O/ Ethanol solution | HDPE (13) | 2, 4, 6 and 8 wt % | MI                                                                          Chen et al. (2020b) |
| Co-Nihydroxides grafting       | UHMWPE (14)                    | 2 wt%          | MI                                                                          Meng et al. (2021) |
| Dispersion in 20% N2O solution  | 4 and 12 wt%                   | ISP                                                                         Ma et al. (2021) |

1 ISP: In Situ Polymerization, SI: Solution Intercalation and MI: Melt Intercalation
Future Perspectives

The era of nanotechnology has reached several sectors in recent years, encompassing more and more specific materials for different applications. The polymer/ATP nanocomposites listed here highlight the growing search for these materials with excellent properties. In the past three years (2018-2020), some specific applications have been studied, which drive new trends in applications for ATP, such as flame retardant of cotton fabrics (Gao et al., 2019), dye adsorption (Chen et al., 2019; Chen and Zhu, 2019), hydrogel membranes for wound dressing (Sun et al., 2020), sustainable packaging (Wang et al., 2018) and fuel cell applications (Hu et al., 2020a; 2020b).

Chen et al. (2019; Chen and Zhu, 2019) prepared a nanocomposite hydrogel based on cellulose and ATP by a facile method. The SEM micrographs showed that nanocomposite hydrogel exhibited a porous structure and rough inner surface and ATP was incorporated inside. The addition of ATP reduced the swelling degree of nanocomposite hydrogel and enhanced its adsorption capacity. Through the results, the authors concluded that the nanocomposite hydrogel prepared could be used in removing dyes from wastewater.

Hu et al. (2020a; 2020b) prepared proton exchange membranes composed of chitosan/modified organic ATP for fuel cell applications. The composite membranes exhibited better mechanical property, dimensional and thermal stability compared to the neat chitosan membrane. The proton conductivity of the composite membrane is also increased, the composite membrane with 4% by weight of ATP content exhibited the highest proton conductivity of 26.2 mS cm$^{-1}$ at 80°C with 100% relative humidity, which is 25.1% larger than the pure chitosan membrane. These results can explore a simple and green strategy for preparing chitosan-based proton exchange membranes, which have great potential in the application of proton exchange membrane fuel cells.

In addition to this trend of applications observed in the last three years (2018-2020) and limited for the use in nanocomposites, the specific properties of ATP also allow for other promising advanced uses such as support of nanoparticles for sensor devices and high-performing catalysts, new adjuvants for vaccines, clay-biological interfaces for tissue engineering and bioreactor devices (López-Galindo et al., 2007).

Conclusion

ATP has interesting properties such as high specific surface area, high sorption, low surface charges, bleaching power and thixotropic properties in the presence of electrolytes. These properties make ATP an ideal candidate for reinforcing polymeric materials. Different approaches and emerging technologies have been applied to improve the thermal and mechanical properties of polymer/ATP nanocomposites which can extend the different chemical treatments used in ATP. ATP mainly modifies the mechanical properties of polymers, increasing the elastic modulus and tensile strength either in the natural or modified state and with low filler contents (even less than 6%). Regarding thermal properties, ATP acts as a nucleating agent, increasing the degree of crystallinity and the $T_g$ of the polymeric matrices. In this way, ATP is a good alternative for the replacement of lamellar clays such as montmorillonites with the advantage of having a lower cost (0.2-0.5 US$/Kg) and a wide world market to be explored, which drives new trends in ATP applications, such as flame retardant on cotton fabrics, dye adsorption, hydrogel membranes for dressings, sustainable packaging and fuel cell applications.

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Author’s Contributions

All authors equally contributed in this work.

Ethics

This article is original and contains unpublished material. The corresponding author confirms that all of the other authors have read and approved the manuscript and no ethical issues involved.

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