Organic Modification of Inorganic Ions (Montmorillonite, Hydrotalcite) and its Application in Polylactic Acid-based Nanocomposites

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Abstract. In order to understand the organic modification of inorganic ions (montmorillonite, hydrotalcite) and its application in polylactic acid-based nanocomposites, and to explore the hot issues in this field, the mechanical properties, thermal stability, crystallization properties, ultraviolet shielding properties, rheological properties, flame retardancy and degradation properties of inorganic ions added to polylactic acid after organic modification were expounded. It will provide the development direction for the organic modification of inorganic ions and their application in polymers in the future.

Key words: Inorganic ions, modification, polylactic acid-based nanoparticles.

1. Overview of inorganic ions (montmorillonite, hydrotalcite)
Organic modification polylactic acid of inorganic ions (montmorillonite, hydrotalcite) is degradable. The storage of montmorillonite is abundant, with low price is low and excellent properties. At present, montmorillonite and hydrotalcite are two kinds of inorganic nanoparticles with pillar structure in modification, which have attracted a lot of attention in modifying the properties of polylactic acid.

1.1. Montmorillonite
Montmorillonite is a kind of clay mineral with flaky crystalline water-bearing silica-aluminate, whose main component is alumina-silica, which gives montmorillonite its unique surface activity, high cation exchange capacity and ability to strongly change the flow characteristics of liquids. However, due to the poor hydrophilicity of natural montmorillonite, the compatibility with polymer is poor, therefore, it is necessary to carry out organic modification and expand its application in the field.

1.2. Hydrotalcite
Hydrotalcite is a layered inorganic nano-material with two-dimensional space structure, whose surface contains a large number of hydroxyl groups. Water spray is the most prominent performance. It is the exchangeability of silver ions that makes it have broad application prospects in catalysts, absorbents, drug carriers and other fields. In addition, the synthesis method of hydrotalcite is relatively simple, and raw materials are readily available, and it is harmless to human body. At the same time, the thermal stability of hydrotalcite is relatively high. Therefore, it is of great value in the preparation of polymer
matrix and composite materials. Unfortunately, hydrotalcite also has its own shortcomings, because the charge density between the layers of hydrotalcite is relatively high, which is not conducive to the insertion of large polymer molecular chains. Therefore, it needs to be modified organically before processing

### 2. Modification of Inorganic Ions (Montmorillonite, Hydrotalcite)

Na-montmorillonite is organised by dimethyl diallyl ammonium chloride and the properties of organically modified bentonite are hydrophilic and oleophobic. Organically modified organic cations enter the bentonite layer through ion exchange, thus increasing the interlayer spacing to about 20 nm, to hydrophobic organically modified bentonite. Organic bentonite used more widely, it is organic compounds, surface modifier and natural bentonite was modified bentonite processing products, also is a kind of important fine chemical products development. This kind of after modification of bentonite, due to the long hydrocarbon chain surfactant coverage in bentonite on the surface of the wafer and form hydrophobic surface, at the same time because of the surfactant ions between the layers into the chip volume effect, increasing the chip layer spacing, to generate a new hydrophobic oleophilic complex organic bentonite, the strong expansion in the organic solvent, and can form good thixotropic gels. Al3+ in octahedral mechanism of bentonite can be replaced by Fe2+, Mg2+, etc., so that the surface of crystal is negatively charged. Excess negative charge is neutralized by cations such as Na+, K+, Ca2+ and Mg2+ adsorbed between layers, and organic cations are used as intercalation agents and intercalation cations. Cation is introduced into the interlayer of bentonite to make it organic.

#### 2.1. Organic Modification of Inorganic Ions (Montmorillonite, Hydrotalcite)

**2.1.1. Gel Organic Montmorillonite.** Gelatinous organic montmorillonite is prepared by single or mixed modification of quaternary ammonium salts, which can be classified as non-reactive organic montmorillonite according to type. Its properties are mainly influenced by montmorillonite purity, microstructure and charge characteristics of montmorillonite. The exchange of organic cation and montmorillonite is first carried out between layers. When the interlayer is nearly saturated, a small amount of organic cations are adsorbed to the edge. When used in suitable organic solvents, the dispersive organic montmorillonite flakes are combined with end to end ends to form a "Z" type pseudoplastic lattice structure which encapsulate a large number of solvents. The system has gel properties for low level charge type montmorillonite, because the modified bentonite has better gel properties, and the properties of bentonite containing such montmorillonite are good at home and abroad. Modification has been studied in depth.

The modified products have been widely used in paint, ink, grease, drilling, mud, daily chemical, glass fiber, resin, sealing, waterproofing materials and other fields. For the high level charge type montmorillonite, the commonly used modifiers are difficult to form stable high viscosity gel due to the electrostatic repulsion effect of cation exchange between layers. There are few reports on the preparation of high-viscosity organobentonite from montmorillonite raw materials. In addition to a few provinces such as Zhejiang, Xinjiang and so on, most of the available bentonite ores are calcium-based montmorillonite with high-level charge. Therefore, it is of great practical significance to study the organic modification and modification technology of high-level charge montmorillonite. According to the characteristics of raw materials and market demand in China, the author has developed high-level charge montmorillonite as raw material to prepare it. Medium viscosity gel type organo bentonite technology, the product performance is close to the effect of organic modification with low charge type montmorillonite raw material.

**2.1.2. Dispersed Organic Montmorillonite.** Dispersed organic montmorillonite can be divided into non-reactive and reactive organic montmorillonite according to the preparation process. For non-reactive organic montmorillonite, its dispersion performance is related to the total amount of cation exchange (CEC value) between layers of montmorillonite. The larger the CEC value is, the more organic cations
between layers can be exchanged, which is more conducive to the dispersion and coupling of montmorillonite crystal layer in organic phase. The interaction is enhanced until at least one dimension of the montmorillonite crystal layer is dispersed in the organic phase at nanoscale.

Non-reactive organic montmorillonite has limited dispersion compared with reactive montmorillonite, so it can only improve the thermomechanical properties of composites by about 20, but its advantages are low cost, wide application area, easy application, especially suitable for small-scale plastic processing enterprises. It is currently the main product to be popularized and applied. When treating montmorillonite with reactive organic substances, large size organic cations themselves not only enlarges the interlayer spacing of montmorillonite, but also extends the interlayer spacing by condensation or polymerization of organic cations under the action of initiator or heat until the montmorillonite lamellae are separated into nano-unit lamellae in one-dimensional direction and evenly dispersed in the matrix. The montmorillonite used is sodium-based montmorillonite, and its CEC value should be moderate (about 1.0 mmol/g). The reported intercalated polymerization type montmorillonite with better performance which is used by nylon 6 nanocomposites montmorillonite belongs to such kind. It is reported that the mechanical properties of composite materials can improve the 50~100, and the heat-resisting temperature nearly doubled, with good flame retardant and anisotropy. The intercalating agents are mainly used for a variety of long carbon chain of amino acids. But this method requires higher manufacturing costs and has the special requirement that intercalating organic structure must has the certain similarity with complex system, which limits its application. It can be seen from the information that when the content of montmorillonite clay is only 5(wt), the tensile strength and modulus of the montmorillonite/nylon 6 nano composite are significantly higher than that of pure nylon 6, especially the thermal variation temperature was more than doubled.

2.1.3. Adsorptive Organic Montmorillonite. Adsorptive organic montmorillonite is mainly used as environmental purification material, whose adsorption mechanism is mainly interlayer adsorption, which is different from that of other similar products (such as activated clay modified with montmorillonite). Therefore, it has special selectivity. The preparation process is to select appropriate amount of organic matter with long carbon chain (generally C12-18) to increase the interlayer spacing of montmorillonite first, and control the amount of organic matter to 20-60 of the exchange capacity of montmorillonite cation (CEC). The single-, double-, triple-chain cations used for modification can produce mixing bundles to make organic matter have synergistic effect, which makes the adsorption channels of modified organic montmorillonite more smooth than pure montmorillonite for specific organic matter, especially for benzene series, phenols, nitrobenzenes, anilines and polycyclic aromatic hydrocarbons, the adsorption rate can reach 90, while there is almost no benzene series on natural montmorillonite. Therefore, the preparation of organic montmorillonite for environmental purification is based on ion exchange between layers with appropriate amount of organic matter. The higher the CEC value, the better the modification effect of montmorillonite.

2.2. Inorganic/Organic Composite Modification of Nano Ions (Montmorillonite, Hydrotalcite)
Inorganic/organic composite modification is a reasonable combination of inorganic and organic modification methods. First, the inorganic modification of montmorillonite is carried out, then the organic modification is carried out. Finally, the organic composite montmorillonite is obtained. This method is widely used in sewage and wastewater treatment.

2.3. Synthesis Process of Inorganic Nano Ions (Montmorillonite, Hydrotalcite)
At present, the organic montmorillonite is mostly obtained through ionic exchange reaction of quaternary ammonium salt cationic with different structures or organic modified solvent with ion exchange capacity and sodium base bentonite. According to the characteristics of the different production technology, the synthesis method basically has 3 kinds: wet method, dry method, and pre-gel method. The wet synthetic process is: dispersion pulping of bentonite→purification→na-activated
modification→ organic cation covering modification→ washing filtering→ stoving→ grinding→ organobentonite powdery products

Whether high-quality organobentonite can be produced mainly depends on four factors: (1) whether the high-grade and high-quality montmorillonite concentrate can be obtained; (2) whether the montmorillonite mineral has high hydration performance and fully expands to form colloidal particles of 1-0.001μm; (3) whether the montmorillonite mineral has high cation exchange capacity and high reaction activity; (4) whether the organic coating agent has a higher adsorption and exchange capacity with the cation that can be exchanged with the montmorillonite layer and whether it has a macromolecular structure that can be fully expanded in the organic solvent.. High viscosity organobentonite is produced by wet processing, and the modified process conditions is that the bentonite slurry concentration is 30%, adding suitable amount of activator, after activation treatment, it will be heated to 50 ~ 80 ℃, and prearranged modifier is added for organic modification. And after the amount of organic surface active agent of 90~130 mmol/100g is added, with 1.5 hours of reaction and after filtration, drying, grinding, sieving, high viscosity organic bentonite products will be obtained.

3. Application of Inorganic Nano Ions (Montmorillonite, Hydrotalcite) in Polylactic Acid-based Nanocomposites

3.1. Application of Inorganic Nano-Ions and Polylactic Acid Composites
Inorganic nano-ion and polylactic acid composites are thermally and magnetically stable with stable. Size, therefore, the preparation of hydrotalcite, montmorillonite and poly lactic acid composites is an important method to obtain high performance materials. The melt blending method, hierarchical insertion and sol-gel method can be used. This paper describes in detail the theoretical basis for the future application of hydrotalcite montmorillonite in polymer.

3.2. Method
Melt blending method: The micro mixing rheometer reactor was used to prepare polylactic acid composites by melt blending under the shear action of the rotor. It has the following advantages: homogeneous mixing of raw materials, good dispersion of inorganic nano-fillers in the lactic acid mechanism, and the glass-like polylactic acid composites can be obtained, furthermore, the reaction process can be controlled artificially. Organic modification of montmorillonite, is mainly through cation exchange method, amino acid method, and organic acid salt method. Organic modification of hydrotalcite includes anion exchange method (introducing organic anions into the organic modification of hydrotalcite by using the intercalation of anions between layers of hydrotalcite). The pillar method is that the organic modification of hydrotalcite is carried out by increasing the interlayer distance of hydrotalcite by using pillar agent. After modification, it is advantageous to the insertion of mega-soft acid molecule. For example, amidation method and atom transfer radical polymerization (ATRP) method can introduce amide bonds and PMMI to modify the surface of water spray.

3.3. Property

3.3.1. Mechanical Properties. For polymer materials, improving their mechanical properties is conducive to expanding their application fields. Polylactic acid has poor toughness and high brittleness, so it is necessary to improve its mechanical properties. Dispersion and compatibility of organic modified hydrotalcite and montmorillonite in polylactic acid matrix have been significantly improved, and have good formation and effect, which is conducive to reducing the size of polylactic acid crystals and increasing the formation and density. The mechanical properties of PLA are improved by increasing the crystallization rate and crystallinity of PLA.
3.3.2. Crystallization Properties. The properties of polylactic acids depend largely on their crystallization properties. Organically modified hydrotalcite and montmorillonite can provide more formation points. In addition, these inorganic nanoparticles can make the arrangement of polylactic acid molecules more orderly, and can effectively reduce the semi-crystallization time and increase the crystallization temperature, resulting in the increase of the crystallization performance of polylactic acid.

3.3.3. Thermal Stability. Non-base transition nano ions have certain rigidity, which can effectively inhibit the movement of polylactic acid molecular chains, make the arrangement of polylactic acid molecular more orderly, so as to improve the thermal stability of materials. In addition, the existence of nanoparticles hinders the migration of small molecules generated by the pyrolysis of molecular chains in materials from inside to outside, and improves the thermal stability of composites. The thermal weight loss curve of polylactic acid/organic montmorillonite moves towards high temperature, which indicates that the thermal decomposition temperature of composites increases. Some scholars have studied the thermodynamic properties of polylactic acid/hydrotalcite nanocomposites by thermal degradation kinetics simulation. The results of DSC and TGA tests show that the initial thermal decomposition temperature of polylactic acid composites increases by 10.2 degrees. The presence of nanoparticles not only impedes the penetration and diffusion of polylactic acid thermal sorting products, but also restricts the movement of molecular chains so as to improve the thermal stability of the nanocomposites.

3.3.4. Rheological Property. According to the research, the addition of nano-filler has obvious influence on the rheological behavior of polymer. By measuring the rheological properties of polymer in melting state, the interaction force between polymer and nano-particles and the structural properties of nano-composites can be determined. The infiltration network structure is formed by friction between layers of montmorillonite, and polylactic acid presents Newtonian fluid at low shear frequency, while the polylactic acid/montmorillonite composites showed obvious shear thinning. The rheological properties can reflect the agglomeration phenomenon in the nanocomposites. The energy storage modulus of the composites is almost unaffected by the shear frequency at low frequency shear, and the increase of the rigidity of the composites indicates the improvement of the processing performance of the composites.

3.4. Emulsion Polymerization

Polyvinyl Acetate (PVAc), commonly known as white emulsion /latex, aggregates VAc through monomer in the presence of water, protective colloidal polyvinyl vinol and non-ionic emulsifiers and initiators. Polyvinyl acetate has the characteristics of Non-toxic, non-flammable, easy to produce, reliable, convenient application, saving resources, which can be widely used in wood processing, furniture assembly, bonding, building decoration, fabric printing and textile decoration and binding, bonding the components of porous materials and be considered as a green environment-friendly adhesive. However, the cost of VAc raw materials is high, and the cold resistance of PVAc, mechanical stability, heat resistance, water resistance and storage stability are poor. In the presence of organic montmorillonite, emulsifier-free copolymerization has a positive effect on the modification of PVAc.

The mole ratio of DMDAAC to Na-montmorillonite was 1.5: 1 with reaction time of 2 hours and reaction temperature of 60°C, and the organic montmorillonite will be prepared through ultrasonic heating. The IR atlas analysis of Na-montmorillonite and DMDAAC modified Na-montmorillonite shows that DMDAAC has been intercalated into montmorillonite, and the organic modification has been successful. The conditions for the emulsifier free emulsion polymerization of sodium montmorillonite and organic montmorillonite / vinyl acetate have been determined respectively: the polymerization temperature is 70°C, and the monomer drop speed is 1 drop /3 s, with the reaction time of 4 hours. The free radical copolymerization reaction appears in DMDAAC modified montmorillonite and white latex modified, and the modified montmorillonite/white emulsion was successfully prepared.
4. Conclusion

Inorganic nano-ions are deep-processed products of non-metallic minerals with special structure and properties, whose chemical composition and size of the laminates can be adjusted according to the need. With the help of different modifiers, treatment conditions or the recognition ability of the main laminates to molecule, the molecular assembly can be carried out by intercalation or ion exchange, and the products modified by montmorillonite with different properties can be prepared. The research and application of the modified organic montmorillonite are mainly concentrated in the interdisciplinary field of mineral-organic matter. In addition to its unique properties, the evaluation of the application effect of modified organic montmorillonite is greatly influenced by other auxiliary agents, equipment, technological conditions, etc. It is more convincing to characterize the physical and mechanical properties of the composite system after direct use, which is also currently used as the main evaluation methods.

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