Nanotechnology and its Applications

Chapter 2

Preparation of Nanolayered Silicate and its Applications in Rubber Composites

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1. Structure and Properties of Nanolayered Silicates

As a type of nanolayered silicates, montmorillonite (MMT) belongs to monoclinic system, which is generally irregular flake. Its color is white with light gray, sometimes with light blue or light red, and the luster is dim. It has strong adsorption capacity and ion exchange capacity, as well as high colloid, plasticity and adhesion. Its Mohs hardness is $2 \sim 2.5$, specific gravity is $2 \sim 2.7 \mathrm{g/cm^3}$, and bulk density is $1 \sim 1.1 \mathrm{g/ml}$. Its chemical composition is $Na_{0.7}(Al_{3.3}Mg_{0.7})Si_8O_{20}(OH)_4 \cdot nH_2O$.
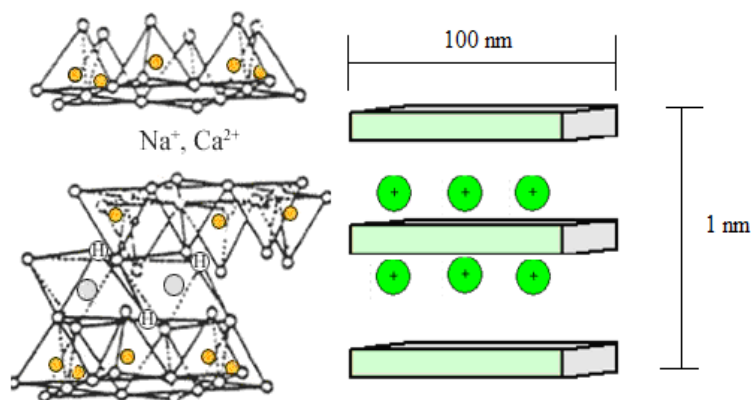

Figure 1: Structural diagram of MMT (2:1 nanolayered silicate).

Natural MMT is a lamellar structure, which belongs to 2:1 layered silicate. The lamellar thickness is about 1 nm, and the length and width is about 100 nm. The molecular structure contains three sublayers, and an aluminum oxygen octahedral sublayer is added between the

two silicon oxygen tetrahedral sublayers. The sublayers are covalently connected by sharing oxygen atoms. The close packing structure of tetrahedron and octahedron makes it have a highly ordered lattice arrangement. MMT has high stiffness and is not easy to slip between layers. The interlayer contains hydrated Na^+, Ca^{2+}, etc., and they can exchange inorganic cations. If it is used as a reinforcing agent for organic substances such as polymers, ion exchange is required. Organic cations (i.e. intercalation agents) are usually used to change the polarity of MMT lamellae and reduce the surface energy of silicate lamellae, so as to increase the affinity between the two phases [1-3].
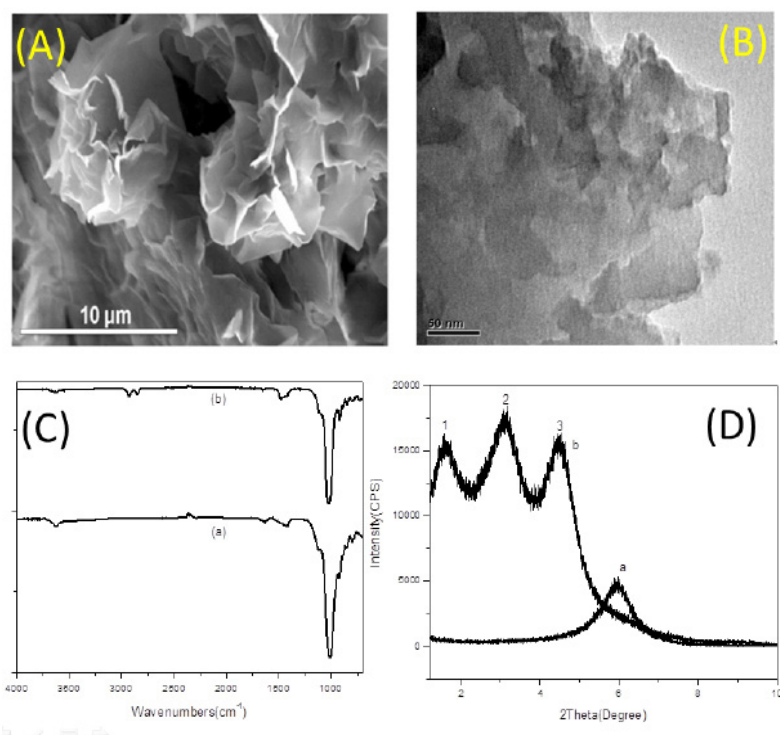
Figure 2: Characterization of MMT (A) SEM, (B) TEM, (C) FTIR (a) before and (b) after organic modification, (D) XRD (a) before and (b) after organic modification.
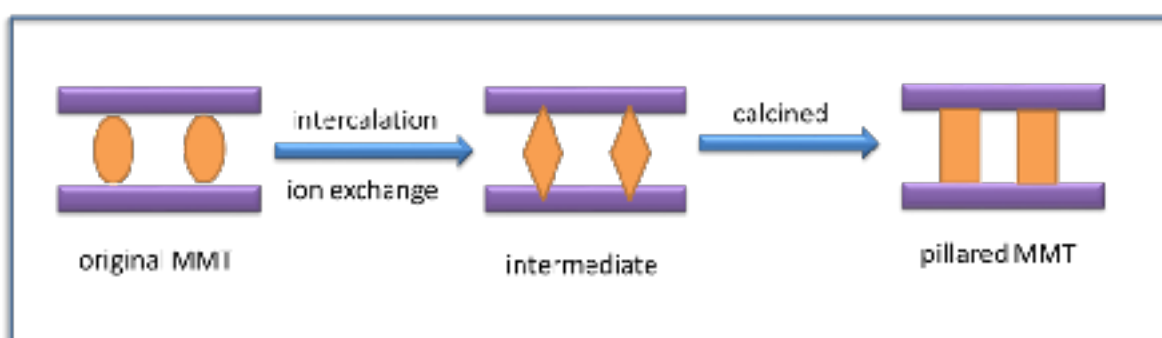
Figure 3: Preparation process of pillared MMT.

Inorganic salt modification is carried out by adding one or more inorganic metal hydrate cations to exchange with exchangeable cations between MMT. These ions act as the role of balancing the negative charge on silica tetrahedron. At the same time, due to the action of interlayer solvent, MMT can be stripped and dispersed into thinner single crystals [13]. The salts used for MMT modification mainly include aluminum salt, magnesium salt, zinc salt, copper salt, etc. The preparation process of pillared MMT was shown in Fig.3. Cooper *et al.*

[14] modified the surface of MMT with polymerized Fe^{3+} and Al^{3+}. In the study on the selective adsorption and adsorption capacity of Cd, Cu, Ni, Pb and Zn in water, it was found that the adsorption performance of MMT for sewage has been significantly improved, and the effect of modified MMT is significantly better than that of original one.

2.2. Organic Modification

MMT is hydrophilic and oleophobic due to a large number of inorganic ions between layers, which is not conducive to its dispersion in organic phase and adsorption of organic substances. When MMT is used in organic system, it must be organically modified, that is, organic cations are used to replace the inorganic cations in MMT (generally sodium MMT). This is to change the form of interlayer ions in MMT crystal layer, and thus to make its surface hydrophobic and have good expansion performance. The organic synthesis of MMT is one of the key steps for the preparation of nanocomposites [15-18]. Through organic modification, the interfacial polarity and chemical microenvironment of inorganic materials are improved, and the affinity between two phases is increased. The hydrophilicity of the surface of MMT is not conducive to its dispersion in the organic phase and adsorption of organic substances, and it often needs to be organically modified to make the surface of MMT hydrophobic. Common organic modifiers mainly include amino acids, alkyl ammonium salts, polymer monomers and coupling agents [19, 20]. This organic modification is only carried out between crystal layers to increase the interlayer domain and does not affect the structure of MMT, as shown in **(Figure 4).**
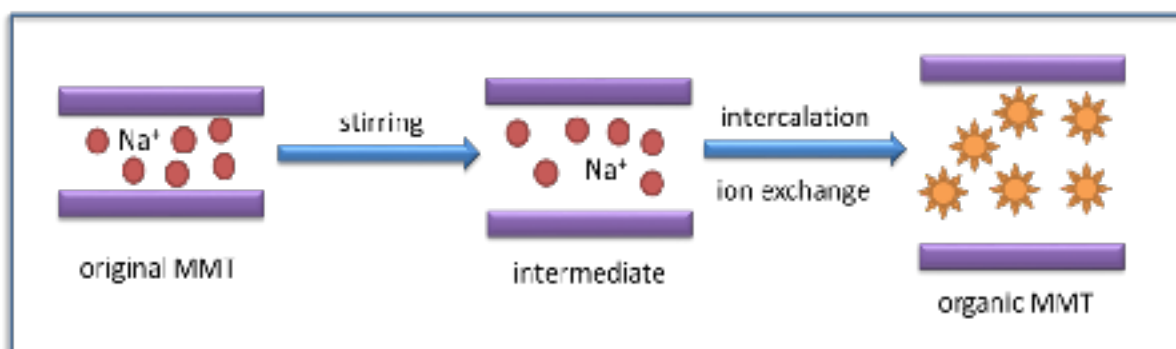

Figure 4: The ion exchange diagram between MMT interlayers.

2.2.1. Amino Acid Modification

Amino acid molecules contain an amino group ($-NH_2$) and a carboxylic acid group ($-COOH$). Under the condition of acidic medium, a proton in the carboxylic acid group of the amino acid molecule is transferred to the amino group to form an ammonium ion (NH_3^+). This newly formed ammonium ion enables the amino acid to have the ability of cation exchange with the cations between the MMT layers. After the cation exchange between ammonium ions in amino acids and MMT lamellae, organic MMT with organic amino acids can be prepared [21-25]. Liu *et al.* [26] put amino acids or their methyl esters and long-chain cetyltrimethyl ammonium bromide between the layers of MMT through exchange method to realize the

functionalization of MMT, and was used to load metallocene catalysts and dilute the original polymerization. Zhou *et al.* [27] used a new gemini cationic surfactant containing amino acids to modify the surface of MMT through particle exchange reaction, and used TGA to study the thermal stability of modified MMT, as shown in **(Figure 5). (Figure 5a)** showed that the residual amount of OMMT after modification was less than that of MMT, indicating that the decomposition amount of OMMT was more than that of MMT. Fig.5b showed that the decomposition temperature of MMT was about 640°C, while that of OMMT was lower, which may be due to the thermal decomposition of the modified organic components.
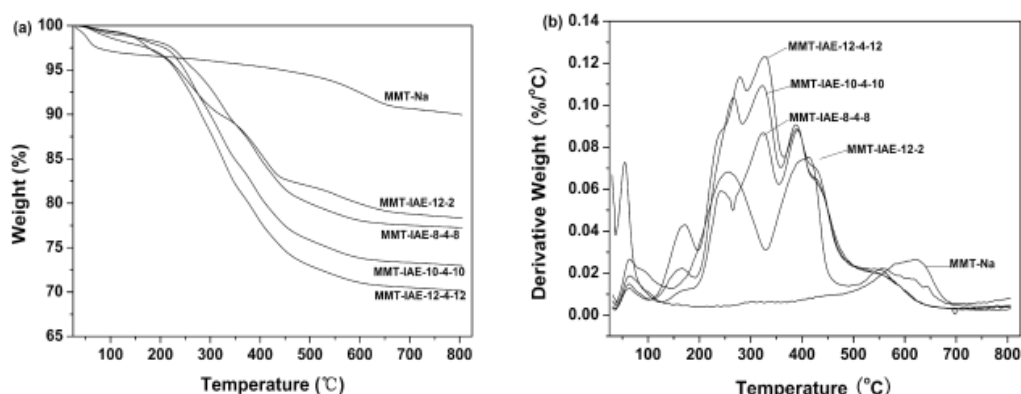

Figure 5: TGA (a) and DTG (b) of MMT and OMMT.

2.2.2. Coupling agent modification

The surface active organic functional groups are used for chemical adsorption or reaction with the surface of MMT, so as to cover the particle surface with surfactants (usually silane, titanate coupling agent, stearic acid, silicone, *etc.*) to increase its wettability. Zhao *et al.* [28] modified MMT with chlorosilane, stirred and refluxed chlorosilane and MMT, washed and filtered with acetone, dried under vacuum, and finally obtained silylated OMMT after grinding. The results showed that there was no obvious difference in the dispersion results regardless of the amount of silane intercalated between the layers of MMT. It also showed that under the experimental conditions, the main factors affecting the dispersion were the interaction between particles and layers together with the hydrophilicity and hydrophobicity of MMT.

2.2.3. Organic quaternary ammonium salt modification

This method is related to long carbon alkyl quaternary ammonium salt. The organic cations of it can enter the MMT layer through ion exchange reaction. The surface of the nanolayer is covered with the alkyl long carbon chains, and thus its surface changes from hydrophilicity to lipophilicity, increasing the affinity between organic MMT and polymers. Meanwhile, the longer alkyl molecular chains are arranged in a certain way between the layers, which can increase the layer spacing [29-31]. This is conducive to the intercalation of polymeric monomers or macromolecules into the layers. Yoon *et al.* [32] preliminarily modified MMT (M0) with mononuclear octadecylamine to obtain S1, then further modified it with polyoxyethylene octadecylamine to obtain S2, and finally treated it with octadecyl

dimethyl ammonium chloride to obtain modified OMMT (S3). This process was carried out under the protection of nitrogen. The modification results were analyzed by XRD diffraction, as shown in Fig.6. It can be seen from Fig.6 that the diffraction angles of S1, S2 and S3 obtained in the modification process were smaller than those of M0, and the reflected layer spacing was larger than that of MMT, realizing the intercalation effect.
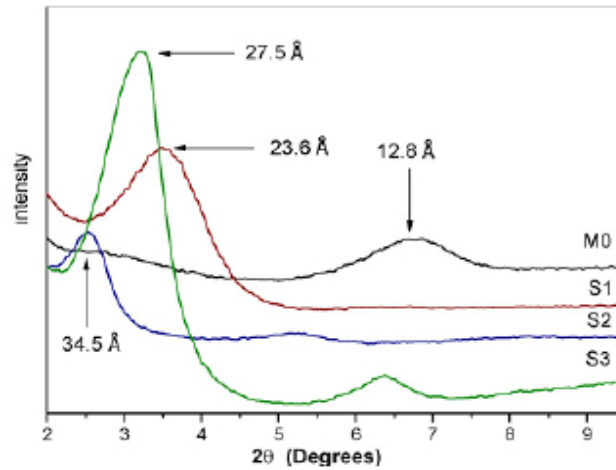

Figure 6: XRD diffraction patterns of MMT and OMMT.

2.2.4. Monomers modification

The monomers of polymer can be directly intercalated into the interlayer of MMT as modifier, and then the nanocomposites were obtained by in-situ addition polymerization. The process has low cost, high efficiency and good development prospects, but there are not many monomers meeting this structure [33-37]. At present, aniline is more studied in this kind of modifier, and the prepared hybrid material has high conductivity and thermal stability [38]. Zhao *et al.* [39] modified Na^+-MMT with amino polyhedral oligomeric silsesquioxane (POSS). As shown in Fig.7, the interlayer spacing of the modified MMT increased obviously, which was conducive to the next step of forming larger interlayer space and corresponding composites with polymers. In addition, it can significantly improve its heat resistance.
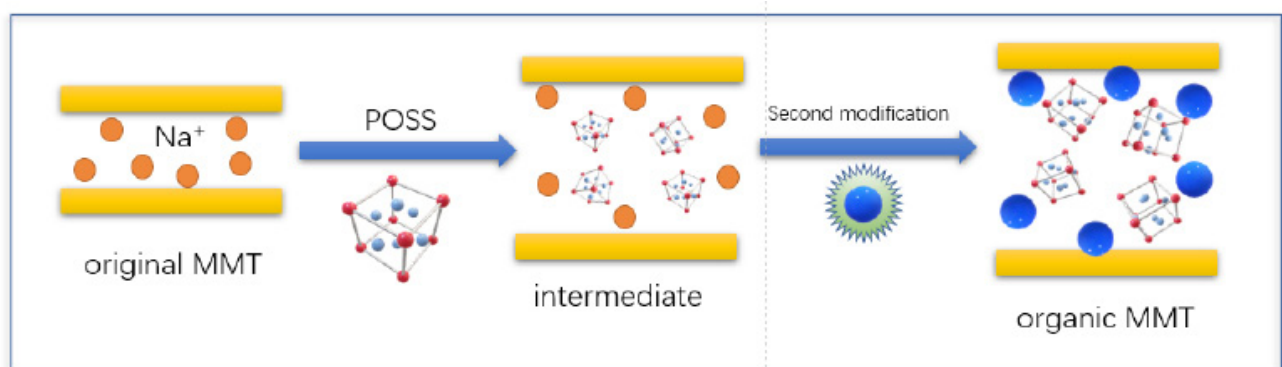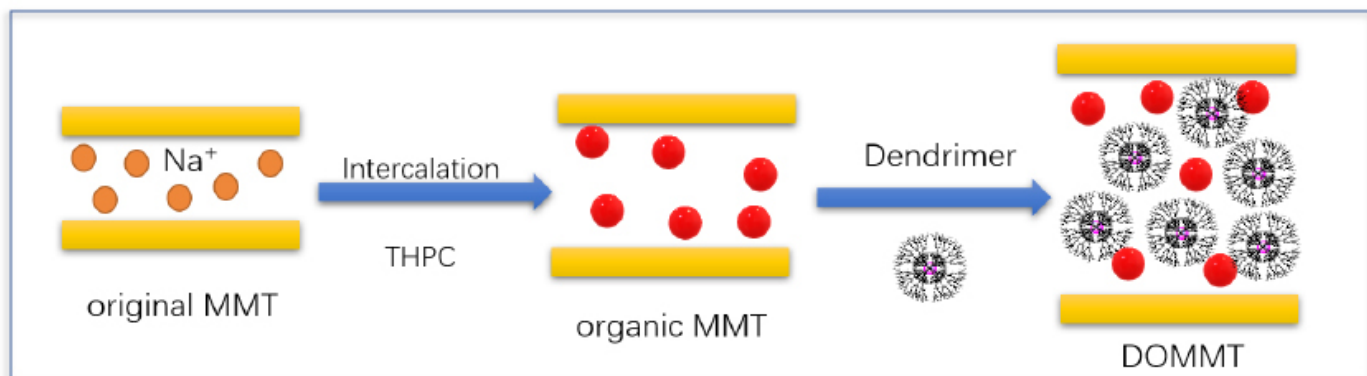

Figure 7: Schematic preparation diagram of POSS modified MMT.

2.2.5. Dendrimer modification

Dendrimer is a linear polymer with dendron on each repeating unit. It has been applied in biomedical fields from simple drug delivery carriers to complex medical imaging, including nano biosensors and nano catalysts. It has precise nano structure, and its synthesis methods include divergence method and convergence method. It has the following characteristics: First, a large number of end groups are enriched on the surface; Second, it is highly branched and contains a large number of holes and cavities. Thus, it is difficult to crystallize and has no winding chains; Third, the proportion of molecular composition is controllable. Special synthetic methods, unique molecular structure and excellent physical and chemical properties provide an opportunity for the application of dendrimers in many fields [40-43]. Zhao and Wang [44] used quaternary phosphonium salt THPC to modify inorganic MMT, and organic MMT was obtained. Results showed that THPC can effectively intercalate MMT in acid conditions (pH=1.46), and the interlayer spacing was increased from 1.43 nm to 1.58 nm. Then, they prepared dendritic organoclay flame retardant by in-situ polymerization. The layer spacing of DOMMT was 2.1 nm, which was 47% higher than that of origin MMT, and the thermal stability was also improved.

Figure 8: Schematic preparation diagram of dendrimer modified MMT.

3. Preparation Technology of Nanolayered Silicates Reinforced Rubber Composites

The preparation methods of rubber/organic MMT (OMMT) nanocomposites mainly include monomer intercalation in situ polymerization, macromolecule direct intercalation and small molecule intercalation with macromolecules. Among them, direct intercalation of macromolecules includes rubber solution intercalation, liquid rubber intercalation, rubber latex intercalation and rubber melt intercalation.

3.1. Monomer intercalation in situ polymerization method

Monomer intercalation in-situ polymerization means that the rubber monomer is first inserted into the interlayer of MMT (generally, the monomer and MMT are dissolved in a solvent respectively). And then the monomer is polymerized in situ under external conditions, such as oxidant, light, heat, initiator or electron. The large amount of heat released during polymerization is used to overcome the Coulomb force between MMT sheets and expand

the MMT sheets, so that the nanoscale sheets are combined with the rubber matrix in the form of chemical bond to obtain nanocomposites. According to the different polymerization mechanism of monomers, it can be divided into addition polymerization and polycondensation. The rubber nanocomposites prepared by monomer intercalation in-situ polymerization have uniform dispersion of MMT layers and strong adhesion between MMT and rubber interface. They belong to chemical bonding and have excellent properties. However, the polymerization reaction is complex, the reaction conditions are harsh, and it is not easy to control and it is difficult to realize industrial production [45-48].
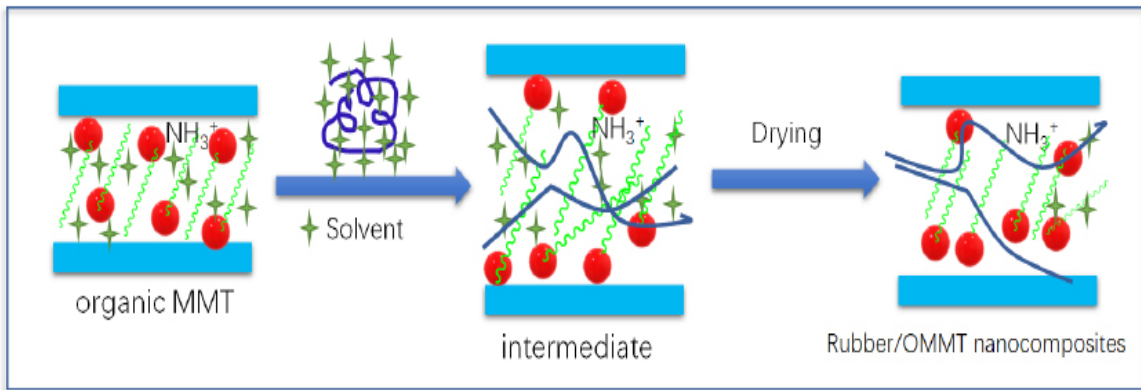
3.2. Solution intercalation method

The rubber solution intercalation method is to organically modify the surface of MMT, disperse it in a suitable solvent, and then add it into the rubber solution. After stirring and removing the solvent, rubber/OMMT nanocomposites can be obtained [49-53]. This method has the advantages of simple process, physical interaction between MMT and rubber, and endows the composites with excellent mechabnical properties. However, suitable solvents must be found for different rubbers, and a large number of solvents are difficult to recover, which is unfavorable to the environment and causes high cost. Gu *et al.* [54] prepared polybutadiene rubber/OMMT nanocomposites by solution intercalation method, and the structure of the composites was analyzed by transmission electron microscope and X-ray diffractometer, and their physical, mechanical and thermal properties were studied. Results showed that these nanocomposites owned better tensile performance and thermal stability.
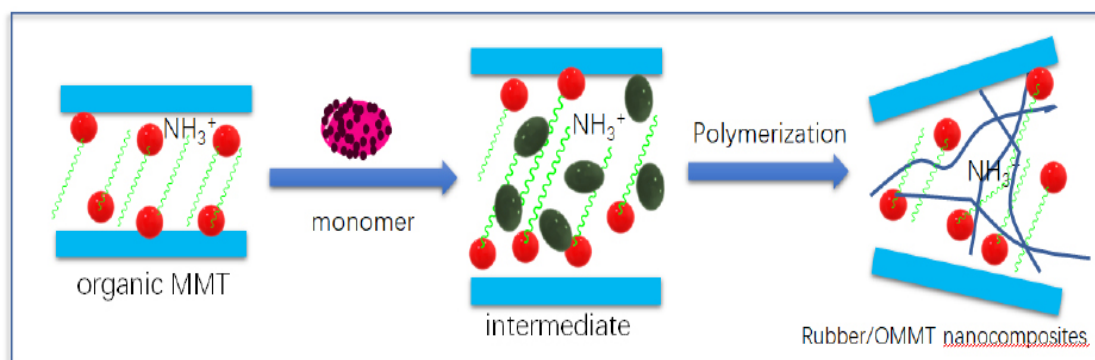
Figure 9: Schematic preparation diagram of rubber nanocomposites by monomer intercalation in-situ polymerization method.

3.3. Liquid intercalation method

Intercalation of liquid rubber to prepare rubber nanocomposites is a novel method. Low viscosity of liquid rubber is a favorable condition for the nano dispersion of intercalation materials. The preparation process of this method is relatively simple. The interface of the composite belongs to chemical bonding, with strong adhesion and excellent material properties. However, the type of liquid rubber is limited, the price is high and its own performance is poor. It usually has practical value to be used together with other rubber. Therefore, the application of liquid rubber intercalation method is limited [55-57].

Figure 10: Schematic preparation diagram of rubber nanocomposites by solution intercalation method.

3.4. Emulsion intercalation method

The principle of emulsion intercalation is to isolate and intercalate latex particles and MMT in aqueous phase by using the hydrophilic characteristics of MMT. After the flocculation, the dispersion of MMT in the aqueous phase is solidified in the polymer matrix, and thus the composite material is prepared. The MMT and water suspension were mixed with rubber latex at a strong stirring to form a homogeneous mixture. After a period of time, the coagulant was added to flocculate, then the flocculant was dehydrated and dried to prepare rubber/ MMT nanocomposite [58-60]. Since most rubber has their own emulsion form and has no special requirements for rubber latex, the technology is simple, easy to control, and low in cost. Moreover, the nanocomposite has excellent properties, so it is expected to be the first method to realize rubber/MMT nanocomposites in industrial production. Gu and Hong [61-63] prepared styrene butadiene rubber (SBR)/MMT nanocomposites by emulsion intercalation method.
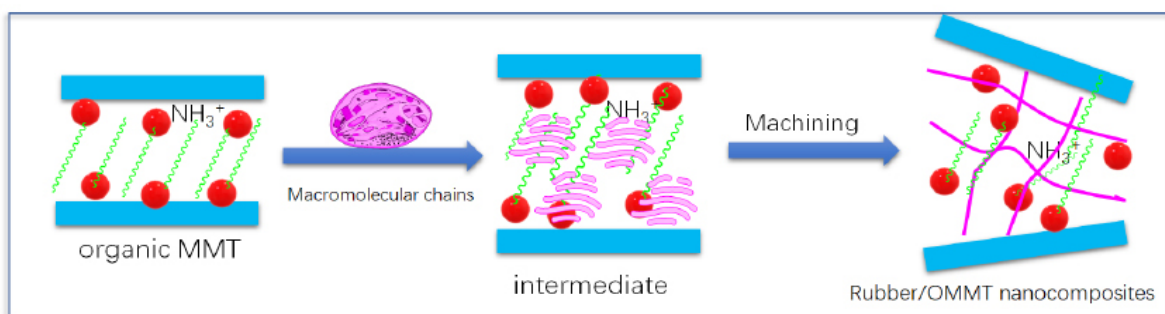
Figure 11: Schematic diagram of preparation of rubber nanocomposites by rubber melt intercalation method.

3.5. Melt intercalation method

The melt intercalation method is to heat the organically modified MMT and rubber to the molten state, and directly insert them into the interlayer under the action of static or shear force to prepare polymer matrix nanocomposites. This technology is simple, easy to control and easy to realize industrial production. However, the high melt viscosity is not conducive to intercalation, the dispersion effect is not ideal, and the performance improvement of the nanocomposites is not obvious. If strong intercalation driving force can be obtained

by this method, its application prospect will be broader [64-66]. Wang *et al.* [67] prepared polybutadiene rubber (BR)/OMMT nanocomposites by melt intercalation method.

4. Conclusions

Facing the traditional situation that carbon black and white carbon black are dominant in the reinforcement of rubber materials, developing new nano reinforcement agents with low price to obtain the best reinforcement is an important research direction of rubber industry. Due to the special lamellar structure of MMT and its nano size effect, the interfacial force of MMT in the rubber matrix is strong. To improve the quality of MMT and better meet the application requirements, it is necessary to modify the surface of MMT. The modification methods include inorganic modification, organic modification and organic-inorganic composite modification. Rubber/organic MMT nanocomposites have special structure and excellent properties, showing attractive application prospects. There are many methods for developing special and functional rubber nanocomposites, such as monomer intercalation in situ polymerization, solution intercalation and melt intercalation methods, and so on. The new rubber nanocomposites with high performance and multi-function can be designed and produced according to the requirements and they have good application prospects.

5. Acknowledgements

6. References

1. Calvert P. Rough guide to the nanoworld.Nature, 1996,383(26):300-301.

2. Karaborni S., Smit B., Heidug W., Urai J., Vanoort E. The swelling of clays: molecular simulations of the hydration of montmorillonite. Science, 1996, 271(5252):1102-1104.

3. Cases J.M. Mechanism of adsorption and desorption of water vapor by homoionic montmorillonite: 3. the Mg2+, Ca2+, Sr2+ and Ba2+ exchanged forms [J]. Clays and Clay Minerals, 1997, 45(1):8-22.

4. Wang J.C., Chen Y.H., Jin Q.Q. Organic montmorillonite as a substitute for aerosilica in addition-type liquid silicone rubber systems[J]. Macromolecular Chemistry & Physics, 2005, 206(24):2512-2520.

5. Wang J.C., Chen Y.H., Wang Y.Q. Preparation and characterization of novel organic montmorillonite-reinforce blocked polyurethane nanocomposites[J]. Polymers and Polymer Composites, 2006, 14(6): 591-601.

6. Wang J.C., Zheng X.Y., Hao W.L, Nan X., Pan X. Synthesis of hyper-branched quaternary ammonium salt and its application into montmorillonite. Powder Technology, 2012, 221(1):80-89.

7. Yang K., Wang J.C., Zheng X.Y. Research status of structure, properties and modification of montmorillonite. Journal of Shanghai University of Engineering and Technology, 2011, 25(1): 65-70.

8. Funes I., Peralta M.E., Pettinari G.R., Carlos L., Parolo M.E. Facile modification of montmorillonite by intercalation and grafting: The study of the binding mechanisms of a quaternary alkylammonium surfactant. Applied Clay Science, 2020, 195(5):105738.

9. Khar'Kova E.M., Mendeleev D.I., Levin I.S., Sorokin S.E., Gerasin V.A. Influence of small amounts of water and ethanol on Na+-montmorillonite solid-state modification by inorganic and organic intercalants. Applied Clay Science, 2020, 195(5):105734.

10. Zhu L.Z., Chen B.L. Application and progress of organic montmorillonite in wastewater treatment. Environmental Pollution Control Technology and Equipment, 1998, 6 (3): 53-61.

11. Yu Z.G., Jia C.X. Research progress of montmorillonite modification. Progress in Fine Petrochemical Industry, 2005, 6 (8): 5-8.

12. Wang X.L., Zhao S.L. Synthesis of ethylene glycol ether catalyzed by modified montmorillonite solid acid. Journal of Liaoning University of Petrochemical Technology, 2008, 28 (4): 4-8.

13. Huang F.C., Lee J.F., Lee C.K., Chao H.P. Effects of cation exchange on the pore and surface structure and adsorption characteristics of montmorillonite. Colloids and Surfaces, 2004, 239(3):41-47.

14. Cooper C., Jiang J.Q., Ouki S. Preliminary evaluation of polyeric Fe and Al modified clays as adsorbents for heavy metal removal in water treatment. Journal of Chemical Technology and Biotechnology, 2002, 77(5): 546-551.

15. Li N., Ma J.Z., Bao Y. Research progress of montmorillonite modification. Chemical Research, 2009, 20 (1): 98-103.

16. Xie Y., Zhang M., Zhou, Y. Progress in the organic modification of montmorillonite. Chemical Industry and Engineering Progress, 2012.

17. Ren Z., Zhu Y., Wu Q., Zhu M., Yu J. Enhanced storage stability of different polymer modified asphalt binders through nano-montmorillonite modification. Nanomaterials, 2020, 10(4): 641.

18. Soliman M.A., Rashad G.M., Mahmoud M.R. Organo-modification of montmorillonite for enhancing the adsorption efficiency of cobalt radio nuclides from aqueous solutions. Environmental science and pollution research international, 2020, 26(10): 10398-10413.

19. Nagendrappa G., Chowreddy R.R. Organic reactions using clay and clay-supported catalysts: a survey of recent literature. Catalysis Surveys from Asia, 2021, 25:231-278.

20. Ran Y.H., Sun S.Y., Shen K.X., Tan D.Y., Ren Y.Q. Investigation on the synergistic effect of surfactants for silylation of montmorillonite. Materials Science Forum, 2020, 999: 155-163.

21. Mallakpour S., Khani M. Characterization of nanocomposite laminates fabricated from aqueous dispersion of polyvinylpyrrolidone and l-leucine amino acid modified-montmorillonite. Polymer Bulletin, 2016, 73(10): 1-12.

22. Costa T., Melo J., Paskocimas C.A. Thermal and chemical treatments of montmorillonite clay. Ceramics International, 2013, 39(5):5063-5067.

23. Valera-Zaragoza M., Agüero-Valdez D., Lopez-Medina M., Dehesa-Blas S., Juarez-Arellano, E. A. Controlled modification of sodium montmorillonite clay by a planetary ball-mill as a versatile tool to tune its properties. Advanced Powder Technology, 2021, 32(2): 591-599.

24. Czonka S., Kairyt A., Miedzińska K., Strkowska A., Adamus-Wodarczyk A. Mechanically strong polyurethane composites reinforced with montmorillonite-modified sage filler. International Journal of Molecular Sciences, 2021, 22(7): 3744.

25. Zhang M., Peiyang H.E., Yanmei L.I. Contemporary approaches toα,β-dehydroamino acid chemical modifications. Chemical Research in Chinese Universities (English Edition), 2021, 37(5): 11.

26. Liu C.B., Wang D., Wei L.M., Tang T., Huang B.T. Ethylene intercalation in situ polymerization catalyzed by functionalized montmorillonite supported metallocene catalyst. National Polymer Academic Conference, Chinese Chemical Society, 2003.

27. Zhou L.M., Chen H., Jiang X.H., Fang L., Zhou Y.F., Yin W.M., Ji X.Y. Modification of montmorillonite surfaces using a novel class of cationic gemini surfactants. Journal of Colloid and Interface Science, 2009, 332(1): 16-21.

28. Zhao C.G., Yang M.S., Feng M. Preparation and properties of chlorosilane modified montmorillonite. Chemical Journal of Chinese Universities, 2003, 24 (5): 928-931.

29. Xie Y., Zhou Y., Yang, X. Preparation and characterization of organic montmorillonite intercalated with stearic ester quaternary ammonium salt surfactant. Non-Metallic Mines, 2012, 35(6):74-76.

30. Yang Y., Zhu Z.K., Yin J., Wang X.Y., Qi Z.E. Preparation and properties of hybrids of organo-soluble polyimide and montmorillonite with various chemical surface modification methods. Polymer, 1999, 40(15):4407-4414.

31. Xie W., Gao Z., Pan W.P., Hunter D., Singh A., Vaia, R. Thermal degradation chemistry of alkyl quaternary ammonium

montmorillonite. Chemistry of Materials, 2001, 13(9): 2979-2990.

32. Yoon K.B., Sung H.D., Hwang Y.Y., Noh S.K., Lee D.H. Modification of montmorillonite with oligomeric amine derivatives for polymer nanocomposite preparation. Applied Clay Science, 2007, 38: 1-8.

33. Kheiralla Z., Rushdy A.A., Betiha M.A., Yakob N. High-performance antibacterial of montmorillonite decorated with silver nanoparticles using microwave-assisted method. Journal of Nanoparticle Research, 2014, 16(8): 2560.

34. Gianni A.D., Amerio E., Monticelli O., Bongiovanni R. Preparation of polymer/clay mineral nanocomposites via dispersion of silylated montmorillonite in a uv curable epoxy matrix. Applied Clay Science, 2008, 42(1-2): 116-124.

35. Bongiovanni R., Mazza D., Ronchetti S., Turcato E.A. The influence of water on the intercalation of epoxy monomers in Na-montmorillonite. J Colloid Interface, 2006, 296(2): 515-519.

36. Yoshimoto S., Ohashi F., Ohnishi Y., Nonami T. Synthesis of polyaniline–montmorillonite nanocomposites by the mechanochemical intercalation method. Synthetic Metals, 2004, 145(2-3):265-270.

37. Kim B.H., Jung J.H., Kim J.W., Choi H.J., Joo J. Effect of dopant and clay on nanocomposites of polyaniline (pan) intercalated into Na+-montmorillonite (Na+-MMT). Synthetic Metals, 2001, 121(1-3):1311-1312.

38. Huskić M., Žagar E., Žigon M, Brnardić I., Macan J., Ivanković M. Modification of montmorillonite by cationic polyesters. Applied Clay Science, 2009, 43: 420-424.

39. Zhao F., Wan C.Y., Bao XJ, Kandasubramanian B. Modification of montmorillonite with aminopropylisooctyl polyhedral oligomeric silsequioxane. Journal of Colloid and Interface Science, 2009, 333: 164-170.

40. Mignani S., Shi X., Zablocka M., Majoral J.P. Dendritic macromolecular architectures: dendrimer-based polyion complex micelles. Biomacromolecules, 2021, 22(2):262-274.

41. Lr A., Yang G.B., Yc A. A manganese (II)-based coordinative dendrimer with robust efficiency in intracellular peptide delivery. Bioactive Materials, 2021, 9:44-53.

42. Li Y., Zhou Y., Wang T., Long K., Zhang Y., Wang W. Photoenhanced cytosolic protein delivery based on a photocleavable group-modified dendrimer. Nanoscale, 2021, 13: 17784-17792.

43. Wang J., Qu G., Liu X., Yu Q., Zhang N. Preparation and swelling behavior of end-linked hydrogels prepared from linear poly (ethylene glycol) and dendrimer-star polymers. Journal of Polymer Engineering, 2021, 41(3):202-210.

44. Wang J.C., Sun K., Hao W.L., Du Y.C., Pan C. Structure and properties research on montmorillonite modified by flame-retardant dendrimer. Applied Clay Science, 2014, 90: 109-121.

45. Guo C.Y., Ma Z., Zhang M.G., He A.H., Ke Y.C. Preparation of PE/MMT nanocomposite by monomer intercalation and in situ compolymerization. Chinese Science Bulletin, 2002, 47:1267-1270.

46. Guptam B., Rakesh A., Ambrose A., Avinash M., Pandey C. In-situ synthesis of polyaniline coated montmorillonite (Mt) clay using Fe+3 intercalated Mt as oxidizing agent. Applied Clay Science, 2014, 95:50-54.

47. Feng L., Yang M., Wang G. In situ polymerization of ammonium ion monomers intercalated in the montmorillonite template. Chemical Journal of Chinese Universities, 2006, 27(11): 2213-2216.

48. Zehhaf A., Morallon E., Benyoucef A. Polyaniline/montmorillonite nanocomposites obtained by in situ intercalation and oxidative polymerization in cationic modified-clay (sodium, copper and iron). Journal of Inorganic and Organometallic Polymers and Materials, 2013, 23(6): 1485-1491.

49. Mu Q., Feng S. Thermal conductivity of graphite/silicone rubber prepared by solution intercalation. Thermochimica Acta, 2007, 462(1-2):70-75.

50. Gu Z. Cis-1,4-polybutadiene rubber/organic montmorilionite nanocomposites prepared by solution intercalation method. China Synthetic Rubber Industry, 2008, 31(4):273-277.

51. Zheng G., Song G., Liu W., Wang B., Jin L. Preparation and properties of organo-montmorillonite/cis-1,4-polybutadiene rubber nanocomposites by solution intercalation. Applied Clay Science, 2009, 45(1-2):50-53.

52. Shi X., Gan Z. Preparation and characterization of poly (propylene carbonate)/montmorillonite nanocomposites by solution intercalation. European Polymer Journal, 2011, 43(12): 4852-4858.

53. Wang J.C., Yang K., Xu N. Effect of intercalation agent on the structure and properties of OMMT and RTV/OMMT composites. Journal of Applied Polymer Science, 2012, 123(3):1293-1301.

54. Gu Z., Song G.J., Li P.Y., Wang L., Wang H.L. CIS polybutadiene rubber/organic montmorillonite nanocomposites were prepared by solution intercalation method. Synthetic Rubber Industry, 2008, 31 (4):4.

55. Ouyang X., Luo Y.F., Jia D.M. Natural rubber/montmorillonite nanocomposites prepared by mixing intercalation method. Journal of South China University of Technology, 2006, (9):80-85.

56. Wang X., Jia D., Chen Y. Structure and properties of natural rubber/montmorillonite nanocomposites prepared by mixing intercalation method. Synthetic Rubber Industry, 2005, 28(2):145.

57. Takahashi C., Shirai T., Fuji M. Study on intercalation of ionic liquid into montmorillonite and its property evaluation. Materials Chemistry & Physics, 2012, 135(2-3):681-686.

58. Lu J., Zhao X. A new approach of enhancing the shear stress of electrorheological fluids of montmorillonite nanocomposite by emulsion intercalation of poly-N-methaniline. Journal of Colloid & Interface Science, 2004, 273(2):651-657.

59. Choi H.J., Kim J.W., Joo J., Kim B.H. Synthesis and electrorheology of emulsion intercalated PANI-clay nanocomposite. Synthetic Metals, 2001, 121(1-3):1325-1326.

60. Nodehi A., Moosavian M.A., Haghighi M.N., Sadr A. A comparative study on the properties of ABS/clay nanocomposites prepared by direct melt intercalation and in-situ emulsion polymerization techniques. Iranian Polymer Journal, 2007, 16(3):49-55.

61. Gu Z., Song G.J., Li P.Y., Wang L., Wang H.L., Qi F. The structure and properties of styrene butadiene rubber/ montmorillonite nanocomposites prepared by emulsion intercalation. Special Rubber Products, 2007, 28(3): 22-25.

62. Gu Z., Song G.J., Li P.Y., Wang L., Wang H.L., Wang B.J. Styrene butadiene rubber /organic montmorillonite nanocomposites were prepared by emulsion intercalation. Synthetic Rubber Industry, 2008, 31(3): 214-217

63. Hong X.B., Chen Y.M, Xie K. Improvement of organic montmorillonite/SBR nanocomposite technology by emulsion method. Rubber Industry, 2004, 51 (9): 524-526.

64. Wang S., Yuan H., Qu Z., Wang Z., Chen Z., Fan W. Preparation and flammability properties of polyethylene/clay nanocomposites by melt intercalation method from Na+ montmorillonite. Materials Letters, 2003, 57(18):2675-2678.

65. Unnikrishnan L., Mohanty S., Nayak S.K., Ali A. Preparation and characterization of poly (methyl methacrylate)– clay nanocomposites via melt intercalation: effect of organoclay on thermal, mechanical and flammability properties. Materials Science and Engineering: A, 2011, 528(12):3943-3951.

66. Daniel D.J., Panneerselvam K. Mechanical and thermal behavior of polypropylene/cloisite 30b/elvaloy ac 3427 nanocomposites processed by melt intercalation method. Transactions of the Indian Institute of Metals, 2016, 70(4):1131-1138.

67. Wang S.H., Zhang Y.X., Zhang Y., Peng Z.L. Tensile stress-strain behavior of CIS polybutadiene rubber/organic montmorillonite nanocomposites II Stress softening effect and stress relaxation Synthetic Rubber Industry, 2005, 28 (5): 378-383.