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Study on Surface coating of halogen-free Flame retardant MCA

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Abstract：The advantages of MCA-coated microcapsules are summarized. Four common preparation methods for microcapsules are listed, and the in situ polymerization or emulsion polymerization for MCA-coated flame retardants is proposed.

Keywords：melamine cyanurate; Microencapsulation; capsule wall material

INTRODUCTION

Melamine Cyanurate (MCA) is a green and environmental friendly nitrogen-based halogen-free flame retardant with excellent performance, its nitrogen content is close to 50%, which is widely used in nylon, rubber, resin and other polymer materials, etc. The flame retardant mechanism of MCA is to change the thermal degradation process of plastic, so that the polymer material decomposes at high temperature and produces a large amount of inert gas, which will make the carbonized layer expand and foam and play a role in the external oxygen. At the same time, MCA can enhance the fluidity of polymer materials, increase the molten drop during combustion, thus taking away a large amount of combustion heat, and play a flame retardant effect. However, due to the lack of active groups in MCA prepared by the traditional method (its molecular structure is shown in Figure 1), the compatibility between MCA particles and various polymer materials is poor, and the obvious clustering phenomenon often occurs during the use of MCA, thus reducing its flame retardant effect. Therefore, MCA needs to undergo surface treatment before it can be used more effectively(Yakshibaeva 2001) .

Activation modification of MCA surfaces using microencapsulation coating technique is a proven method to improve MCA dispersion(2020). Microencapsulation is a technique that uses various types of film-forming materials to encapsulate the core material of the capsule to make a miniature container with a diameter of 1-1000μm (Chung, Chang et al. 2018, Aslam, Belazi et al. 2019, Almekhlafi, Ospel et al. 2020). The microencapsulation technology retains the original physicochemical properties of the capsule core material, and at the same time isolates the MCA from the polymer material to achieve a better dispersion effect, when the polymer material combusts, the capsule wall material is destroyed and the coated MCA is quickly released to play a flame retardant role. At present, some researchers have explored the coating modification of traditional flame retardants such as red phosphorus, ammonium polyphosphate, aluminum hypophosphite, etc. and achieved some results, but the coating modification of MCA flame retardants is relatively little studied.

PREPARATION OF MCA-COATED PARTICLES

At present, the common preparation methods for the modification of flame retardants at home and abroad are in situ polymerization, interfacial polymerization, coalescence and emulsion polymerization.

In situ polymerization

In situ polymerization is the initiator and polymerization monomer directly into the dispersed phase, in this reaction system, the dispersed phase as the core material, so that all the anti-initiator and polymerization monomer is located in the external core material particles, and the wall monomer can be soluble in the system solvent, the resulting polymer is insoluble in the system solvent, by controlling the wall monomer in the core material particles on the surface of the deposition to form a package, the method is more suitable for MCA The particles were modified by coating (Demerath, Bonati et al. 2020). (Dhali and Biswas 2019) used in situ polymerization to coat melamine-formaldehyde resin on the outer layer of solid-liquid mixed paraffin to prepare microcapsules of phase change material for dehumidification of self-cooled solutions. The

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characterization results showed that when the emulsifier accounted for 60% of the core material mass and the emulsification speed was 1000 r/min, the latent heat of phase change of the microcapsules reached 52.48J/g and the embedding rate reached 58.44%. A microencapsulated flame retardant coated with magnesium hydroxide was prepared by in situ polymerization using 4,4-diphenylmethane diisocyanate (MDI) and melamine (MEL) as coating materials, and its structure and properties were characterized (Ducci, Lange et al. 2018), who demonstrated that the thermal stability and dispersion properties of the microencapsulated flame retardants were significantly improved with a decrease in hydrophilicity.

Interface Aggregation

Interface polymerization uses two solvents to dissolve two monomers with high reaction performance respectively, and requires that the two solvents are not mutually soluble, the reaction site is located at the interface of the two solvents, the two monomers for irreversible monopolization reaction. The advantage of this method is that it allows smooth polycondensation reactions of reactive monomers that are unstable at high temperatures, thus expanding the range of polycondensed monomers for the synthesis of polyamide, polyarylate, polyurethane and other materials. (Friedrich, Ponce et al. 2020)] used stearyl butyrate emulsified by styrene-maleic anhydride copolymer (SMA) as the core material, toluene 2,4-diisocyanate (TDI), isoflurane diisocyanate (IPDI), and three monomers of polyether poly methoxide as the coating material, and prepared micro-urethane shell microcapsules by interfacial polymerization, which were then arranged onto the surface of the fabric by dip rolling to achieve heat storage of textiles Temperature control function..

Cohesion method

The coalescence method can be divided into mono-coalescence method and recondensation method. The mono-coalescence method is to add a suitable coagulant to the reaction system, by reducing the solubility of the polymer in the solution, so that coalescence and polymerization can occur, using the mono-coalescence method of preparation process is simple, easy to operate and can be wrapped into the capsule multiple times (Gao, Wen et al. 2020). By the interaction between the polymers with different charges, the monomer material can form a uniform polymer layer around the core material, which is characterized by high coating rate and mild processing conditions. The effects of core-to-wall ratio, wall material concentration, emulsifier concentration, stirring speed, and homogenization speed on the formation of chitosan-arabinoglu linalool microcapsules were investigated, and the effects of core-to-wall ratio, wall material concentration, emulsifier concentration, stirring speed, and homogenization speed on the formation of chitosan-arabinoglu linalool microcapsules were investigated by Griffin (Griffin, Mariano et al. 2020)], who treated flavors and fragrances by microencapsulation technique, using chitosan (CS) and gum arabic (GA) as the coating wall materials and linalool as the core material. Hong (Hong, Jeong et al. 2018) used urea-formaldehyde resin, honey-amine resin and melamine-formaldehyde-urea copolymer resin as the capsule wall materials respectively, and the recoalescence method was used to treat the heat-storing, heat-storing and heat-absorbing materials. The function of octanoic acid was coated, and the effect of reaction conditions and other factors on the thermal properties of the coated particles was investigated. The results show that when the emulsification time is 120 min and the system temperature is 50-70 ℃, the coated particles have the highest latent heat of phase change value.

Emulsion polymerization

Emulsion polymerization refers to the mechanical stirring or vibration, by adding emulsifiers to make the monomer in solution to form an emulsion and polymerization, the reaction products can be either latex, or after washing and drying to get powder or needle polymer (Kamran, Salam et al. 2018). The emulsion polymerization method has the advantages of easy control of production, large degree of polymerization, and easy removal of residual monomers (Kawamura, Fujimura et al. 2020), but the addition of emulsifiers may affect the performance of the final polymerized product, which requires post-treatment. In order to improve the dispersion of organic pigments in water, Lemke (Lemke 2020) wrapped pigment particles by fine emulsion polymerization to produce pigment sub-microcapsules, and studied their film-forming properties. The results showed that when the pigment content in the monomer dispersion was 12% and the mass ratio between the soft and hard monomer butyl acrylate and styrene was 3:2, the emulsification system was more stable, and the sub microcapsules were well dispersed and could be directly used for paint printing and dyeing. (Liebeskind, Zhang et al. 2018) used melamine-formaldehyde resin (PMF) as the wall material and trimethylolpropane tris(3-mercaptopropionate) (TMPMP) as the core material, and prepared the composite microcapsules curing agent of thiol@ melamine-formaldehyde resin by emulsion polymerization method: When the core material accounted for 2% of the emulsion mass and the core-wall ratio was 2: 1, the product had stable structure, good heat resistance and showed closed-cell structure, and the applicable temperature range was 0-200℃.

According to the characteristics of various polymerization methods and the molecular characteristics of MCA, interfacial polymerization is not suitable for the use of MCA coating due to the need for two solvents in the system; coalescence method of operation more steps, and the operation of each step requires high precision, in order to ensure the success rate of the experiment, the experiment in the MCA coating modified in situ polymerization or emulsion polymerization alone, can also be considered a combination of the two methods.

COVERING MATERIAL SELECTION

The wall material is modified by wrapping on the surface of MCA, so the choice of the cyst wall material is particularly important. The selected cyst wall material should meet the following conditions: (1) good compatibility with the encapsulated material MCA, the polymerization process can be deposited on the surface of the MCA to form the cyst wall; (2) raw materials must be readily available and inexpensive.

(3) non-toxic and non-irritating to the human body; (4) need to have a certain degree of thermal stability to facilitate preservation, but at high temperatures, the wall material will rupture or decomposition of the flame retardant released. In practical applications, the selection of the wall material is also related to the use of the product and the characteristics of the core material, such as phase change materials as the core material of the coating microcapsules require the wall material to have a certain degree of density to prevent liquid leakage, the fragrance as the core material of the fragrance microcapsules require the wall material to have a certain degree of permeability to play fragrance slow release properties. At present, various types of polymer materials are widely used at home and abroad as coating materials (Lee, Cheon et al. 2018), which can be divided into natural polymer materials and synthetic polymer materials.

Due to the characteristics of halogen-free flame retardant MCA, we prefer to use synthetic polymers to modify its coating. In recent years, researchers have used a variety of synthetic polymers to modify the flame retardants, and have obtained good results. (Minarik, Langhammer et al. 2019). prepared co-microencapsulated flame retardants (M (A&M)) by coating two substances, ammonium polyphosphate (APP) and melamine pyrophosphate (MPP), with polyurethane (PU) as the wall material, and melted and blended them with polypropylene (PP) to prepare flame retardant polypropylene composites. The test results showed that the flame retardant performance of the composites was best when the APP/MPP was 3/1. The flame retardant aluminum hypophosphite (AHP) was coated by (Lu, Xie et al. 2019), and the modified aluminum hypophosphite (MAHP) flame retardant was successfully prepared. The finished products were characterized by a series of tests including infrared spectroscopy, X-ray diffraction and thermogravimetric analysis, and the results showed that the highest heat loss temperature of MAHP was 358 ℃, which was 7 ℃ higher than that of AHP, and the complete decomposition temperature was 500 ℃, which was 70 ℃ higher than that of AHP, with improved thermal stability and flame retardant effect. The thermal stability and flame retardant effect were improved. Pentaerythritol, 4,4-diphenyl diisocyanate and melamine were used as raw materials to surface coat ammonium polyphosphate by in situ polymerization, which effectively improved the water resistance and combustion residue rate of ammonium polyphosphate; (Mizuno, Saito et al. 2019). used triphenyl phosphate (TPP) as a capsule wall material to coat diatomaceous earth/ammonium polyphosphate (DIA/APP) and prepared a double-layer The microcapsules structure DIA-APP-TPP, which greatly improved the flame retardancy and thermal stability of the composites .Bin (Morales, Lu et al. 2017)synthesized high efficient flame retardant aluminum phosphate (ALP) microcapsules with ammonium phosphomolybdate trihydrate as raw material and applied them to polyurethane foam, which resulted in an LOI value of 28.5%; (Nicholas, Fischbein et al. 2019) used honeyamine resins to pair phosphoric acid respectively Diammonium and 1,6-hexamethylene-hexanedioate were embedded, and the resulting microcapsules were fused and mixed with polypropylene matrix using a twin-screw extruder, and when the microcapsules were added at 5%, the mechanical properties and flame retardant properties of the material achieved the expected results.

In summary, urea-formaldehyde resin and honey-amine resin are the more widely used capsule wall materials and can be the first choice for MCA coating. In addition, the researchers of this research group had previously used acrylic resins as the wall materials to cover the phase change materials of paraffin wax and successfully prepared three different wall materials of microcapsules (Nehai, Guettouche et al. 2020), so acrylic resins can also be chosen to cover the use of MCA.

CONCLUSION

Microencapsulation is a practical and widely used technology . The use of microencapsulation to modify MCA can not only enhance the dispersion in the polymer, but also provide a synergistic flame retardant effect if MCA is coated with a material with flame retardant properties. In addition, if the MCA particles are further surface treated, such as recoating, surface alkylation, etc., the application performance will be further increased, so the microencapsulation modification of MCA and other environmentally friendly flame retardants requires further research and development

REFERENCES

Almekhlafi, M., et al. (2020). "Endovascular Treatment Decisions in Patients with M2 Segment MCA

Occlusions." American Journal of Neuroradiology **41**(2): 280-285.

Aslam, M. N., et al. (2019). "Fourth Order MCA and Chaos-Based Image Encryption Scheme." Ieee Access 7: 66395-66409.

Chung, S. Y., et al. (2018). "The efficiency of FLAIR images for hemodynamic change after STA-MCA bypass with Moyamoya disease and symptomatic steno-occlusive disease." Cerebrovascular Diseases 45: 263-263.

Demerath, T., et al. (2020). "High-resolution compressed-sensing time-of-flight MRA in a case of acute ICA/MCA dissection." Neuroradiology 62(6): 753-756.

Dhali, M. K. and M. Biswas (2019). "MCA on mechanism of river bed potholes growth: a study of middle Subarnarekha River basin, South East Asia." Environment Development and Sustainability 21(2): 935-959.

Ducci, R. D., et al. (2018). "Predictors of dependence after MCA ischemic stroke submitted to thrombolysis." Neurological Research 40(2): 97-101.

Friedrich, S., et al. (2020). "Non-linearities in Superconducting Tunnel Junction Radiation Detectors and Their MCA Readout." Journal of Low Temperature Physics 200(5-6): 200-205.

Gao, D. D., et al. (2020). "Flame retardant effect and mechanism of nanosized NiO as synergist in PLA/APP/CSi-MCA composites." Composites Communications 17: 170-176.

Griffin, A. S., et al. (2020). "Inferolateral thalamic ischemia secondary to PCA P2 perforator occlusion mimics MCA stroke syndrome." Neurosurgical Review 43(1): 339-342.

Hong, H. J., et al. (2018). "Preparation of Mesalazine-Clay Composite Encapsulated Alginate (MCA) Bead for Targeted Drug Delivery: Effect of Composite Content and CaCl2 Concentration." Macromolecular Research 26(11): 1019-1025.

Kamran, S., et al. (2018). "Factors that Can Help Select the Timing for Decompressive Hemicraniectomy for Malignant MCA Stroke." Translational Stroke Research 9(6): 600-607.

Kawamura, K., et al. (2020). "Persistent Local Vasogenic Edema with Dynamic Change in the Regional Cerebral Blood Flow after STA-MCA Bypass for Adult Moyamoya Disease." Journal of Stroke & Cerebrovascular Diseases 29(4).

Lee, K. Y., et al. (2018). "Analysis of FLAIR Hyperintense Vessels by the Different Phase of Multiphase CTA in Acute MCA Occlusion." Stroke 49.

Lemke, J. (2020). "Introduction to MCA symposium on Halliday & Vygotsky." Mind Culture and Activity 27(3): 210-215.

Lu, Y. F., et al. (2019). "Extraction of weak fault using combined dual-tree wavelet and improved MCA for rolling bearings." International Journal of Advanced Manufacturing Technology 104(5-8): 2389-2400.

Minarik, R., et al. (2019). "Radiometric and Atmospheric Corrections of Multispectral mu MCA Camera for UAV Spectroscopy." Remote Sensing 11(20).

Mizuno, A., et al. (2019). "You can never be too prepared: ECMO for MCA." American Journal of Obstetrics and Gynecology 220(1): 122-123.

Morales, H., et al. (2017). "Variable MR and pathologic patterns of hemorrhage after iodinated contrast infusion in MCA occlusion/reperfusion model." Journal of Neurointerventional Surgery 9(12): 1248-1252.

Nehai, S. A., et al. (2020). "Regional modeling of soil sensitivity to water erosion in JIJEL region (Algeria) using MCA and GIS." Applied Geomatics.

Nicholas, L., et al. (2019). "Dispelling Myths about Antenatal TAPS: A Call for Action for Routine MCA-PSV Doppler Screening in the United States." Journal of Clinical Medicine 8(7).

Yakshibaeva, Y. R. (2001). "Carbohydrate receptor expression on melanoma B16 and MCA sarcoma cell surface and effect of mono- and disaccharides on adhesion and homotypic aggregation of cells in vitro." Experimental Oncology 23(4): 274-277.