Reviews on Application of Self-healing Microcapsules in Armor Protection

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Abstract

For the problem that cracks existed when advanced composites such as fiber reinforced composites or ceremic-fiber composites were attacked or shocked, the cracks were difficult to heal immediately. Self-healing microcapsules which could heal cracks to some extents had aroused scienststs' great interests in armor protection. The corresponding manufacturing methods, including Matrix Polymerization, In-situ Polymerization, In-situ Cross-linking, Solvent Evaporation and its applications in fabric clothing, military camouflage and defense, energy storage for armor protection were reviewed in this paper and the corresponding technical problems and future devepments were prospected finally.

Keywords

Reviews, Application,Self-healing Microcapsules.

1. Introduction

Numerous researches on self-healing technology are underway for microcapsule-based coating systems over the last decades[1–6]. Under the directions of this technique, microcapsules rupture upon damage inducing cracks in the coating layer, releasing their encapsulated liquid healing agent into the crack planes. The organic and inorganic self-healing materials, surrounded by urea-formaldehyde (UF) thermosetting shell were microencapsulated, and the microcapsules were embedded into different polymer coating materials, showing protective ability on steel plate (e.g., effective inhibition from metal corrosion and rusting)[1, 2].

A norbornene-based ring opening metathesis polymerization (ROMP) healing agent, endo-dicyclopentadiene (endo-DCPD), as self healing agent was also microencapsulated with UF shell[7–12]. UF capsules filled with endo-DCPD were developed in nano-size, which is important in fabricating thin coating applications[3].

The microcapsules, including the healing agent and capsule shell, are divided into different kinds, simple sphere, double-wall, multi-walled , multi-core and so on . The corresponding diagrams are shown as follows. And its corresponding diameter is from 0.1 to1000um.

2. Another section of your paper

Several micro-capsules manufacturing methods including Matrix Polymerization, In-situ Polymerization, Solvent Evaporation, In-situ Cross-linking and so on. The former two methods are the most common, low-cost, convenient and easy-doing methods.

2.1 Matrix Polymerization

Emma[13] employs dicyclopentadiene (DCPD) as the monomer and a microcapsule outer shell composed of poly(urea-formaldehyde) and inner shell of ethylene maleic anhydride copolymer (EMA).

Microencapsulated epoxy and mercaptan-derivative healing agents were incorporated into an epoxy matrix to produce a polymer composite capable of self-healing by Lee[14]. Maximum fracture loads were measured using the double-torsion method. Thermal aging at 55°C and 110°C for 17hours was applied to heal the pre-cracked samples. The results show that the healing temperature has a significant effect on recovery of load transferring capability after fracture.

Hollow poly(urea-formaldehyde) microcapsules were vacuum infiltrated with a reactive amine curing agent. They were used in dual capsule epoxy-amine healing chemistry to produce thermally stable self-healing epoxy polymers by Henghua Jin and his co-workers[15]. Autonomic healing in excess of 90% is achieved in a high Tg (152–213°C) structural polymer cured at high temperature (121–177°C). It shows that the self-healing materials begin to work efficiently and heal the cracks at the lower temperature.

The method matrix polymerization is similar to in-situ crossing polymerization. However, the most different point is that by usage of the former method, the two different composites can mix physically and in the latter method, the chemical bonds of composites can cross each other.

2.2 In-situ Polymerization

Mary[16] combined the interfacial polymerization of PU and the in situ polymerization of UF to prepare liquid-filled microcapsules with two distinct shell walls. The polyurethane was dissolved in the EPA core liquid prior to adding this mixture to the aqueous phase during the encapsulation procedure. The results showed that these double-walled microcapsules improved stability at high temperatures compared to single-walled microcapsules with the same core liquid. Additionally, the second inner shell wall leads to PU/UF EPA microcapsules with improved mechanical properties as evidenced by capsule compression studies.

Then Song[17] filled PUF microcapsules with DCPD were successfully prepared by in situ-condensation polymerization. The results showed that with the formaldehyde content increasing, the outer shell wall can be extended. The rough porous outer layer can promote the adhesion of the capsules to the matrix resin when embedded in a polymeric host material.

Li[18] filled Polymeric microcapsules (MCs) with catalyst to release the catalyst to initiate the polymerization reaction. Poly(urea–formaldehyde) (PUF) MCs filled with DBTDL (PUF/DBTDL MCs) were prepared using urea (U) and formaldehyde (F) as the wall shell materials by in situ polymerization. The U-F resins could easily polymerize in the presence of the core material DBTDL to produce PUF polymers, then they deposited on the surface of the DBTDL droplets, forming PUF/DBTDL MCs. The application of PUF/DBTDL MCs to cyanate ester resins preliminarily showed the reaction control capability of the MCs due to the slow release of DBTDL through the wall shell.

Song[19] prepared Hexadecane microcapsule phase change materials by the in-situ polymerization method using hexadecane as core materials, urea-formaldehyde resin and urea-formaldehyde resin modified with melamine as shell materials respectively. The results indicated that hexadecane was successfully coated by the two types of shell materials.

Self-healing microcapsules were synthesized by in-situ polymerization by Yan Ying[21] with urea-formaldehyde resin as shell materials and dicyclopentadiene as core material. The encapsulation process of microcapsules was observed by using optical microscopy. The results shows that the effects of different emulsifier concentrations and emulsifying rotation speed on the particle size distribution of microcapsules were investigated. The experimental results showed that microcapsules were prepared with smooth surface by adding DBS of 5% as emulsifier with the rotation speed of

6000r·min-1. Encapsulation ratio of microcapsules can be increased from 73% to 89.2% by adding 4% NaCl solution.

The in-situ polymerization is the most common method we have used to manufacture the composites. And the procedure is simple and the controlling elements are not so many.

2.3 Solvent Evaporation Method

2-Phenylimidazole (2-PZ) and polymethyl acrylic glycidyl ester (PGMA) were performed by Aijie et al[23] to fabricate a novel microcapsule latent curing agent of 2-PZ/PGMA by solvent evaporation method with 2-PZ as the core material and PGMA as the shell material. A novel single-component 2-PZ/PGMA/epoxy adhesive is also prepared by mixing 2-PZ/PGMA with epoxy resin matrix. Results showed that 2-PZ/PGMA had good sphericity and narrow diameter distribution.

In this method, temperature controlling is the very important point.

2.4 In-situ Cross-linking

Yoshinari et al[24] prepared Hybrid microcapsules of porous inorganic particles and epoxy resin shell to apply to the self-healing agent. A water soluble imidazole of gelation promoting agent as the core material was microencapsulated in the porous inorganic particles, which were coated with epoxy resin. The porous inorganic particles were prepared with the interfacial reaction between sodium silicate and calcium ion in the (W/O) dispersion. The corn oil dissolving epoxy resin to be microencapsulated with gelated epoxy resin.

In this method, the important point is that the formation of the W/O dispersion. This method has the advantages that the working condition is not as strict and high as what we think and it operates simply.

3. Organization of the Text

3.1 Micro-capsules in Fabric Clothing

With the expansion of the activity or application field, it couldnt satisfy the compositive requirements of highly effective，Warm, comfortable and convenient for thermal protective textile through traditionally increasing the thickness of the fabric to improve thermal retardancy． As the phasechange materials(PCMs)，which could absorb or release latent heat during the phase change procedure at proper temperature，was introduced in the application to textile，the temperature of the enclothing ‘micro environment’ can be regulated． Most of the PCMs with a phase change temperature around room temperature are solid-liquid PCMs, so that they must be encapsulated in order to prevent the lost of PCMs during the phase change procedure．

Pang[25] manufactured one kind of microcapsule containing phase change material of n-octadecane was successfully prepared by in-situ polymerization using melamine-formaldehyde-urea(MFU)resin as the wall material. It was found that micro-encapsulated phase change materials could be finished onto the fabric surface uniformly for using foam coating weft plain fabric． The fabric had a certain delay time of temperature variation． The air permeability and mechanical properties of the fabric before and after finishing had slight change and met the requirement of clothing．

When working under high or low temperature enviroment, human body must stand corresponding extreme-hot or extreme-cold, so as to prevent high-temperature energy into body inside. So micro-capsules have been popularly researched by researchers in applications of kinds of protective clothings or equipments. Simulatanously, micro-capsules are used in kinds of military clothings or equipments, for example, pilot warm glove, military cold or hot combat boots, military submersible suit and so on[26-27].

Chen[28] studied low temperature resistance of the finished fabrics by phase change micro-capsules，low-cost microcapsules was prepared． Phase change microcapsules were finished by plain，twill，plain knit fabrics and low temperature resistance of the finished fabric were tested and evaluated． Microcapsules containing n-octadecane(MicroCl8)with various compositions of urea and melamine-formaldehyde(MUF)copolymer as shells were fabricated through in-sit u polymerization and therreal performance of microcapsules was analyzed. The microcapsules were coated to plain, twill, plain knit fabrics' surface in intumescent coating, and the finished fabrics' multiple sets of performance were tested respectively. Results showed that the low temperature resistance of the plain weave fabric is the Best.

3.2 Micro-capsules in Military Camouflage and Defense

Adjusting the temperature by increasing or decreasing the thickness of clothing solely already couldn't satisfy the requirements of functionality and comfort of clothing，especially applying for the field ofprotecting low temperature. Phase change materlals can absorb or release a large number of latent heat during phase transition[29-30]. Making phase change material into microcapsule can not only improve the specific Surface aera，increase the heat transfer, but also avoid the leakage of the phase change materials. Compounding the microcapsule onto the fabrics can adjust the temperature of the fabric micro-environment，relieve the discomfort because of the temperture mutations effectively,and reduce the thickness ofthe fabric to increase wear-comfort. This study prepared phase change microcapsule with excellent pe—brmaJlce by using the microcapsule technology to clad n-octadecane. Then the microcapsules were commpounded on the fabric in order to make thermal control fabrics which have thermal control performance and wear-comfort.

Shi[31] prepared the phase change microcapsules using n-octadecane as core by

In-situ polymerization. Thermoregulation fabrics were prepared by fabrics which were treated by phase change microcapsules by a pad—dry-cure method. The appearance，thermal storage performances，permeability and mechanical properties of thermoregulation fabrics were characterized. Besides，the impact of the mass fractions of phase change microcapsules and the types of binder on the properties of thermoregulation fabrics were discussed. The results indicated that the finishing effect of thermoregulation fabrics were best when the content of phase change microcapsules was 30％and polyacrylate Was used as binder.

Huang[32] researched microenca psulated phase change materials (MPCM) which is based on improving safety factor and thermal insulation, reducing the thickness of metallic thermal protection system(MTPS) for vehicle. Microenca psulated phase change materials as surface coating filler of multi-layer efficient thermal insulation structure or sealing material filler in unit protection system play a role in heat sink; Phase change materials coating protect vehicle as ablating cover when the ceramic tiles of thermal protection system fell off, or crackle and heat leak occured. Transient heat transfer mechanism of ceramic tiles thermal protection added phase change materials coating in the reentry process is investigated by theoretics, design thetransfer thermal analysis model, one-dimension transient heat transfer model is established as to analyze the influence of microenca psulated phase change materials for thermal protection system. The count indicate that on the one hand the phase change materials coating could effectively reduce the undersurface temperature of thermal protection system, on the other hand could reduce the thick ness of thermal protection system as the same thermal insulation. Urea-formaldehyde resin microcapsules containing phase change material, para ffin, are synthesized by in-situ polymerization. The result indicate that the microcapsules are round, have smooth and dense surface, kind encapsulation.

3.3 Micro-capsules in Energy Storage

Chen[33] fabricated inorganic hierarchically porous micro-/nanostructures with designed sizes, shapes, compositions, and functionalities. suitable synthetic methods, new functionalities, the integrated particle size, tap density, and interfacial properties between the electrode material and electrolyte, strategies to control and optimize the morphologies of electrode materials remain to be systematically established. Additionally, the favorable interface at the operating voltage should be further investigated.

Zhang[34] selected he porous materials and organic phase-changing materials to fabricate a granulated phase-changing composite for energy storage . The energy-storing performance durability and heat insulation of this composite were studied. The results showed that organic phase-changing materials can penetrate into the porous space of pore diameters from sub- micrometers to several hundreds micrometers and occupy major part of the porous space . The resulting composite exhibits outstanding energy-storing performance and good durability .

As a new technology， microcapsules was applyedin military camounage and defence， solid propellant fields by foms of color change microcapsules， MCPCMs and energy contained microcapsules.

4. Conclusion

The manufacturing methods and its applications were introduced in this paper. However, there are still some limitations. On one hand, the processing of manufacturing the microcapsules are complex to some extends and some affiliated products can produce during the working time that could affect the manufacturing effiency. On the other hand, through the microcapsules can make the healing effects but it can not heal the cracks completely and some deep researches will need to be done.

(1) In the healing system, materials choosing of wall (shell) material and core material, the healing temperature are the greatest affecting elements and at the same time the glass transition temperature is considerable.

(2) In the manufacturing procedure, the encapsulation ratio, particle size, diameter distribution make great effects in the active self-healing effects.

(3) Most microcapsules researched are about 150um and new kinds will be needed to make breakthrough.

(4) The road to make micro-capsules into products still needs a long road to go and many researches require to be done. Whether micro-capsules are suitable for fabric clothing, military camouflage and energy storage, experiments are needed to be testified.

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