Research on Functional Modification of Waterborne Polyurethane Coatings

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Abstract—**This paper provides an overview of characteristics and applications of functional waterborne polyurethane coatings, summarizes the functional modification of waterborne polyurethane coatings, including flame retardant, waterproof, corrosion protection, mildewproof and sterilization, anti-graffiti, as well as transparency and heat insulation, describes future development trend of nanomaterials applied to functional modification of waterborne polyurethane coatings .**

Keywords—**waterborne polyurethane,coatings,functional modification,research progress**

I. INTRODUCTION

With the increasing awareness of environmental protection, people paid more attention to their own living environment. Environment protection was held in high regard.Traditional solvent based coatings have quiet a few of organic solvents which not only caused damage to the environment, but also caused harm to people's health.To reduce solvent based coatings' negative effects on the environment and people's health, states enacted laws to limit the emissions of volatile organic compounds(VOC) and the contents of organic solvents, which made traditional solvent based coatings face serious challenges. The volatile organic compounds(VOC) of Waterborne coatings are extremely low compared to conventional solvent based coatings. Such features as non-toxicity,no stimulation and no pollution have made waterborne coatings a research focus in recent years.The actions taken around the world to reduce organic solvents contents and volatile organic compounds(VOC) emissions not only made transition from traditional solvent based coatings to waterborne coatings a necessity, but also made green environmental protection coatings the development trend of coating industry.Waterborne polyurethane(WPU) coatings as one of the green environmental protection coatings are in line with the development of coating industry, known as"three premises"of resource, energy and pollution-free as well as "four principles of E" of economy, efficiency,ecology and energy[1]. A growing number of scholars committed to the development of waterborne polyurethane(WPU) coatings. The exceptional mechanical properties with which waterborne polyurethane(WPU) coatings provide the material have irreplaceable advantages over traditional solvent based coatings.

II. WATERBORNE POLYURETHANE COATINGS

Waterborne polyurethane is a binary colloid system with water as its disperse medium in which polyurethane resin dissolves.Waterborne polyurethane(WPU) coatings contain a small number of organic solvents. Compared to traditional solvent-based polyurethane coatings, waterborne polyurethane(WPU) coatings not only have the advantages of corrosion resistance and abrasion resistance which are inherent in solvent-based polyurethane coatings, but also own the properties of non-toxicity, pollution-free and nonflammable to which solvent-based polyurethane coatings are not available.So there are a wide range of applications of leather coatings, textile coatings, wood coatings,automotive coatings, architectural coatings and so on for waterborne polyurethane(WPU) coatings[2]. However, the hydrophilic groups contained in the molecules of waterborne polyurethane limit the scope of application to some extent, making waterborne polyurethane(WPU) coatings have shortcomings in terms of water resistance and weather resistance.In order to improve the functionality and enlarge the applying scope, people have developed waterborne polyurethane(WPU) coatings with special physical and chemical properties by functional modification of waterborne polyurethane(WPU) coatings in recent years to meet the demand of functional waterborne polyurethane(WPU) coatings in people's

production and daily life.

III. Functional Waterborne Polyurethane Coatings

A. Types of Functional Waterborne Polyurethane Coatings

Functional waterborne polyurethane (WPU) coatings possess characters which common waterborne polyurethane (WPU) coatings are not available to , such as flame retardant, waterproof, corrosion protection, mildew proofing and sterilization , anti-graffiti, transparency and heat insulation and so on.The author will make a brief introduction of flame retardant waterborne polyurethane (WPU) coatings, waterproof waterborne polyurethane (WPU) coatings, corrosion protection waterborne polyurethane (WPU) coatings, mildew proofing and sterilization waterborne polyurethane (WPU) coatings, anti-graffiti waterborne polyurethane (WPU) coatings, as well as transparency and heat insulation waterborne polyurethane(WPU) coatings in the following text.

B. Characteristics and Applications of Functional Waterborne Polyurethane Coatings

There are two types of flame retardant waterborne polyurethane(WPU) coatings. One is halogen-containing and the other is halogen-free. Halogen-free flame retardant coatings used widely at present are intumescent flame retardant, which have the characteristics of halogen-free, low smoke and low toxicity,etc.Waterproof waterborne polyurethane(WPU) coatings are not only widely used in outside waterproofing layer on account of high bonding strength and high mechanical strength but also widely used for coating agents preparing waterproof and moisture permeable fabric in virtue of non-toxicity, no stimulation and no pollution.Corrosion protection waterborne polyurethane(WPU)coatings take corrosion-proof waterborne polyurethane as coatings binder.Single component polyurethane comprise the majority of corrosion-proof waterborne polyurethane. They are the most promising owing to superior performances of low temperature curing,salt tolerance,abrasion resistance,high deformability and impact resistance.Organic anti-bacterial and inorganic microbicide are included as the two types of mildew proofing and sterilization waterborne polyurethane(WPU) coatings. Waterborne polyurethane(WPU)coatings are vulnerable to microbial contamination.Polluted waterborne polyurethane(WPU) coatings would produce mildew. The polymer resin, pigments and fillers, additives and water contained in waterborne polyurethane(WPU) coatings are the main factor of mildew, which provide the necessary nutrition for microbial survival. To inhibit microbial growth and reproduction, people added mould fungicidal to waterborne polyurethane(WPU) coatings to protect coating which protect the substrate from destruction. Anti-graffiti waterborne polyurethane(WPU) coatings are aimed at removing graffiti.There shall be characteristics of hydrophobic,oil-repellent, stain resistance and abrasion resistance for the film.The two key factors of anti-graffiti are the surface properties and compactness of coating.Transparency and heat insulation waterborne polyurethane(WPU) coatings are designed to reduce energy consumption for glass. The visible light transmittance and ultraviolet rejection of coating film are both very high. Transparency and heat insulation waterborne polyurethane(WPU) coatings show promising application prospect in the areas of automotive and architectural glass for transparency and heat insulation .

IV. Functional Modification of Waterborne Polyurethane Coatings

A.Flame Retardant Waterborne Polyurethane (WPU) Coatings

Materials involved in application of waterborne polyurethane(WPU) coatings mostly belong to flammables.Those materials without flame retardant treatment are extremely easy to cause fire disaster.Therefore, flame-retardation of waterborne polyurethane(WPU) coatings has been one of the focuses of scientific research worker. The preparation for flame retardant waterborne polyurethane(WPU) coatings depends on what kind of flame retardant additives are chosen. The premise of preparing flame retardant waterborne polyurethane(WPU) coatings successfully is adding suitable flame retardant additives in resin.

Sun Jiachen [3] selected APP-PER-MEL composite intumescent flame retardant system to prepare flame retardant waterborne polyurethane(WPU) coating,the flame retardant effect of which was obvious.Xu Xiaoguang [4] chose Pentaerythritol / melamine as flame retardant to prepare

acrylate modified waterborne polyurethane(WPU) flame retardant coating, the flame retardant properties of which were improved obviously.

B.Waterproof Waterborne Polyurethane (WPU) Coatings

The water resistance of waterproof waterborne polyurethane(WPU) coatings is better than waterborne polyurethane(WPU) coatings.The effective method for the preparation of waterproof waterborne polyurethane(WPU) coatings is composite modification of waterborne polyurethane(WPU) and other resins. The commonly used modified resins include epoxy resin, acrylic resin and silicone resin etc.

Luo Jianguang [5] prepared the epoxy resin modified waterborne polyurethane(WPU), which had cross-linked structure with improved water resistance and solvent resistance.Williams N [6] prepared the core-shell no cross-linking acrylic-polyurethane hybrid dispersion by means of adding acrylic monomer,chain extenders and catalysts in hydrophilic polyurethane prepolymer via the reaction of free radical polymerization,the water resistance of which was improved to some extent. The organic silane modified waterborne polyurethane(WPU) prepared by Wu Ningjing [7], compared to unmodified one, the water absorption of which was only 5.5%, 1/6 of unmodified waterborne polyurethane(WPU) when the content of added organic silane was 0.6%.

C.Corrosion Protection Waterborne Polyurethane (WPU) Coatings

Anti-corrosion modification of waterborne polyurethane(WPU) coatings possesses very important significance for the corrosion protection of metals and other materials. The role in anti-corrosion coating is to cover the surface of the metal, slow down the passivation and electrochemical corrosion of the metal as well.Corrosion resistance of waterborne polyurethane(WPU)coatings could be improved by modification of epoxy resin, silicone and nano materials.

Wang Chunyan [8] prepared waterborne epoxy polyurethane with epoxy resin modification,and then took it as the base material for preparing zinc rich coating. In the testing process of electrochemical impedance spectroscopy (EIS) and corrosion potential,they made a contrast between zinc rich coatings with a small amount of aluminum powder and traditional ones to analyze electrochemical corrosion behavior of zinc rich coating with different contents of zinc powder in 3% of NaCl solution. The research results showed that the anti-corrosion property of waterborne epoxy polyurethane zinc rich coating was better than traditional epoxy oxygen and zinc rich coating.The dosage of zinc powder could affect anti-corrosion effect of the coating to a certain extent and the addition of a small amount of aluminum powder could improve the anti-corrosion property of the coating. In view of the fact that the anti-corrosion performance and mechanical strength are excellent, there is a brilliant prospect in the iron and steel heavy corrosion protection for waterborne epoxy polyurethane zinc rich coating[9].

Pathak S S[10] modified waterborne polyurethane(WPU) with γ-(2,3-epoxy oxypropyl group)GPTMS and MTMS,and then used sol-gel technology to prepare organic silicon polyurethane waterborne coating for the protection of aluminum and aluminum alloy. The research results showed that the addition of silicone could not only reinforce the corrosion resistance of waterborne polyurethane(WPU) coatings, but also enhance the thermal degradation temperature and thermal stability of the film. This kind of silicone modified waterborne polyurethane(WPU) coatings with high performance on heat resistance and corrosion resistance are suitable for ocean field and space field, etc.

Yeh J M[11]dispersed nano-MMT(Na^+-MMT) in aqueous polyurethane emulsion they prepared with water solution dispersion technique to obtain the nano-MMT modified waterborne polyurethane(WPU) composite emulsion.Gas permeability testing machine obtained the following research results, compared to the waterborne polyurethane(WPU) without adding nano-MMT, those adding nano-MMT could reduce the gas permeability and optical clarity but enhance the thermal resistance of the coating.Moreover, there was an excellent corrosion resistance when the content of nano-MMT was 3% for the nano-MMT modified waterborne polyurethane(WPU) coating.

D.Mildew Proofing and Sterilization Waterborne Polyurethane (WPU) Coatings

Mildew proofing and sterilization of waterborne

polyurethane(WPU) coatings is also one of the focuses of scientific research worker at present because the polymer resin, pigments and fillers, additives and water contained in waterborne polyurethane (WPU)coatings are very easy to breed bacteria and produce mildew.There are two ways to fabricate mildew proofing and sterilization waterborne polyurethane(WPU) coatings.One is adding inorganic antimicrobial agent physically , another is adding organic polymer antibacterial agent chemically.

Wei Yang [12]modified waterborne polyurethane(WPU) coatings with nano Fe^{+3}-SiO_2-TiO_2 composite photocatalyst. The bactericidal effect of the composite photocatalytic waterborne polyurethane(WPU) coating he fabricated was obvious with more than 80% of bacteria killed on average , even up to a maximum of 90%.Huang Xiaodong [13] fabricated anatase nano TiO_2 waterborne polyurethane (WPU)composite coating.On this basis,they had a test on the antibacterial property of the film. Test results showed that the photocatalytic oxidation of anatase nano TiO_2 played a part in killing bacteria. The number of bacterial adhesion was inversely proportional to the content of anatase nano TiO_2. This means that the number of bacterial adhesion declined when the content of anatase nano TiO_2 increased. Zhan Yuanyuan [14] modified waterborne polyurethane(WPU) with quaternary ammonium salt and TNO. The antibacterial effect of two kinds of waterborne polyurethane(WPU) they fabricated was increased dramatically along with the content of TNO and quaternary ammonium salt increased.

E.Anti-graffiti Waterborne Polyurethane (WPU) Coatings

It is very important to fabricate anti-graffiti waterborne polyurethane(WPU) coatings for the maintenance of city appearance.The film should be hydrophobic and oleophobic, meanwhile, have good abrasion resistance as there are both water-based and oil-based graffiti[15] . The resins used to modify waterborne polyurethane(WPU) coatings are mainly organic silicon and organic fluorine for the moment.

Li Wei [16]fabricated organic silicon modified polyurethane-acrylate emulsion by chain-extension modification of unsaturated double bond siloxane and amino-group,the film adhesion and contact angle of which were both better than unmodified one. Zhu Yanan[17] fabricated the organic silicon modified waterborne polyurethane(WPU) coating by means of reacting toluene diisocyanate (TDI), dimethylol propionic acid (DMPA)and siloxane monomer with polyether. The organic silicon modified waterborne polyurethane coating(WPU) they fabricated not only had high film hardness, but also good water resistance and stain resistance.

F.Transparency and Heat Insulation Waterborne Polyurethane(WPU) Coatings

Transparency and heat insulation waterborne polyurethane(WPU) coatings can effectively improve the energy saving of the glass.The effective method for the fabrication of transparency and heat insulation waterborne polyurethane(WPU) coatings is adding functional nano powder in waterborne polyurethane(WPU).

Du ZhengShuai [18]fabricated waterborne UV curing transparent heat insulation nanocomposite coating by way of adding functional nano-powder waterborne paste in synthetic polyurethane-acrylate prepolymer. The research results showed that the visible light transmittance of the coated glass was up to 80% when the dosage of heat insulation powder was 4.2% and coating thickness was 8 μm. Compared to the uncoated glass, the equilibrium temperature of the coated glass was decreased and hardness, abrasion resistance and water resistance of the coating were increased. Li Ning [19] fabricated transparent heat insulation nanocomposite coating with nano ATO heat insulation paste,which could form the film at room temperature. Test analysis results of the glass coating showed that the energy saving effect of the glass treated by transparent heat insulation nanocomposite coating was better than ordinary glass, the shading coefficient of which could reach 0.61 with 66.43% of ultraviolet radiation blocked. Liao Yangfei[20]modified waterborne polyurethane(WPU) with nano indium tin oxide(ITO) paste as pigment and filler to fabricate transparent heat insulation nanocomposite coating. The shading coefficient of the nano indium tin oxide(ITO) transparent heat insulation coating was up to 0.57 and the average temperature reduced could reach 15 ℃and above when pigment binder ratio was1:4.

V. Future Development Trend of Nano Materials Applied to Functional Modification of Waterborne Polyurethane Coatings

From the above, we know that effective methods of

functional modification of waterborne polyurethane (WPU)comprise epoxy resin modification,organosiloxane modification , acrylate modification and nano material modification,etc. Among them, nano material modification occupies advantage of simple preparation process, a wide range of sources of raw materials and lower cost prices.However, functional waterborne polyurethane(WPU) coatings depend on the progress of waterborne polyurethane(WPU) coatings.In order to take the place of solvent-borne polyurethane coatings,waterborne polyurethane(WPU) coatings should go a step further for functional modification. Take nano material modification for example,

(1)To make up for the deficiencies of water resistance, hardness and gloss of waterborne polyurethane(WPU) coatings by studying new modified nano material. Adding nano-powder in waterborne polyurethane(WPU) coatings can improve water resistance to some extent, but it is not always make sense for all nanoparticles.

(2)To prepare waterborne polyurethane(WPU) coatings with different functions by developing new functional nano material additives . In terms of nano material, different nanoparticles provide waterborne polyurethane(WPU) coatings with different functions. The key to serve a useful function of nano-modified waterborne polyurethane(WPU) coatings is making nano-powder evenly disperse and stablely exist in polymers.

Therefore, the research emphasis on nano-modified waterborne polyurethane (WPU)coatings in future is choosing suitable nano-powder and nano-powder dispersing agent to overcome the shortcoming of the water resistance of waterborne polyurethane(WPU) coatings and possess the characters which differ from waterborne polyurethane (WPU)coatings'.

VI. Conclusion

In order to enforce the functionality and enlarge the applying scope of waterborne polyurethane(WPU) coatings, researchers have made functional modification of waterborne polyurethane(WPU) coatings become a research focus in recent years. Modification of waterborne polyurethane(WPU) coatings is designed primarily to improve overall performance of flame retardant, waterproof, corrosion protection, mildewproof and sterilization, anti-graffiti, as well as transparency and heat insulation and so on. It is believed that a growing number of waterborne polyurethane (WPU)coatings with different functions and high performance will be applied in production practices and social life of human with the development of modification technology so that there will be extensive applied fields of functional waterborne polyurethane(WPU) coatings.

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