Progress in Organic Coatings 95 (2016) 100–106

Contents lists available at ScienceDirect

Progress in Organic Coatings

journal homepage: www.elsevier.com/locate/porgcoat

Preparation and performances of novel waterborne intumescent fire retardant coatings

Zhitian Liu*, Mengqin Dai, Yunfei Zhang, Xiang Gao, Qi Zhang*

School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430073, Hubei, PR China

ARTICLE INFO

Article history:
Received 8 November 2015
Received in revised form 20 January 2016
Accepted 29 February 2016
Available online 16 March 2016

Keywords:
Intumescent fire retardant coating
Fire resistance performance
Core–shell emulsion
Organic-modified montmorillonite

ABSTRACT

The core–shell organic-modified montmorillonite (OMMT)/epoxy resin/styrene-acrylic emulsion was prepared using semi-continuous seeded emulsion polymerization and used as the binder of the waterborne intumescent fire retardant coating to improve the fire resistance performance and other basic performance such as water resistance performance, anti-yellowing and adhesion to substrates. Observation with transmission electron microscopy showed that core–shell emulsion had been synthesized successfully. The small angle X-ray diffraction results showed that OMMT was exfoliated and dispersed well in the emulsion within the appropriate content. Fire resistance test, thermal analysis, scanning electron microscopy (SEM), water resistance and yellowing resistance test respectively demonstrated that OMMT greatly improve fire resistance, thermal stability, water resistance and yellowing resistance performance with the addition of in the range of 1.5–2.5 wt.%. Moreover, the core–shell styrene-acrylic emulsion with 5 wt.% epoxy resin (E-44) improve the adhesion of the film to plywood (from 2 grade to 0 grade).

1. Introduction

Intumescent fire retardant coating, used as passive fire protection, is one of the easiest, most economical and efficient way to block the rapid spread of fire to protect materials [1–7]. However, intumescent fire retardant coating must be used as a decorative coating long before the fire broke out. Hence, it must not only have excellent fire resistance performance but also meet the basic demands for everyday use, such as environmentally friendly characteristics, water resistance, anti-yellowing, good adhesion to substrates and so on. Intumescent fire retardant coating consists of four parts: polymer binders, fire retardant additives (acid source, carbon source, blowing agent), fillers and other additives [6–11]. During the process of combustion, fire retardant additives can interact to expand and form a honeycomb-like carbon layer, thus preventing the spread of fire [7–9,12–14]. In everyday use, the polymer binder as a film-forming component plays a key role in basic performances mentioned above and preventing or remarkably reducing the migration of fire retardant additives. However, conventional intumescent coatings have some drawbacks, for example, the char structure formed from the intumescent coating is easily damaged at high temperature, and the intumescent coating is vulnerable to aging [15]. Moreover, the adhesion to substrates of a lot of waterborne intumescent fire retardant coating are poor, resulting in sagging and loss at high temperature, thereby its fire protection is greatly reduced. Consequently, it is necessary to improve the fire retardancy and basic performance for everyday use of the intumescent coating.

Although the styrene-acrylic emulsion has become one of the most common emulsion species in the field of conventional coatings and adhesives due to low price, stain resistance and corrosion resistance, etc, it is rarely used in the field of intumescent fire retardant coating because of high minimum film-forming temperature, poor adhesion to substrates, poor yellowing resistance and water resistance. In order to overcome these problems and enhance overall performance of the intumescent fire retardant coating, many efforts must be done. Recent advances [16,17] demonstrated that epoxy resin could exhibit good adhesion to wood, metal, ceramics, glass and other materials because of some polar groups such as epoxy, hydroxyl, ether bond, ester bond etc. Hence, epoxy resin was used to modify styrene-acrylic emulsion, which can effectively improve the adhesion of the film of emulsion to various substrates. In addition, several studies [6,15] have shown that the incorporation of MMT into different resins can effectively enhance the water protection performance and fire resistance performance of

---

* Corresponding authors.
E-mail addresses: able.ztliu@wit.edu.cn (Z. Liu), 463784980@qq.com (M. Dai), zyf3006@126.com (Y. Zhang), gaoxiang@hust.edu.cn (X. Gao), whzq_2014@163.com (Q. Zhang).

http://dx.doi.org/10.1016/j.porgcoat.2016.02.024
0300-9440/

intumescent fire retardant coating. To obtain favorable dispersion in polymers or coatings, MMT is modified by intercalating organic modifier such as quaternary ammonium salt into the interlayers to prepare organic-modified montmorillonite (OMMT) [6]. However, OMMT and epoxy resin are seldom used simultaneously to modify the styrene-acrylic emulsion. Furthermore, it is not applied in the intumescent fire retardant coatings.

In order to prepare a fire retardant coating with excellent comprehensive performance, the inexpensive core–shell styrene-acrylic emulsion modified by OMMT and epoxy resin were used as binder to prepare a waterborne intumescent fire retardant coating in this work. OMMT was used to improve the fire protection, water and yellowing resistance of fire retardant coating and epoxy resin was used to improve adhesion to substrates. The influences of different contents of OMMT and epoxy resin on the properties were studied respectively, and the mechanism of how OMMT and epoxy resin affect on the coating was analyzed and discussed.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA), butyl acrylate (BA), styrene (St), acrylic acid (AA), sodium bicarbonate ($NaHCO_3$), ammonium persulfate (APS) and triethylamine were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium dodecyl sulfate (SDS) and octylphenol polyoxyethylene ether (OP-10) as the emulsifier mixture system (OP-10:SDS = 2:1) were supplied by Sinopharm Chemical Reagent Co., Ltd and Tianjin Kemiou Chemical Reagent Co., Ltd, respectively. Raw materials mentioned above were used as received. The Na-montmorillonites (a cation exchange capacity of 90 mmol/100 g) were obtained from Zhejiang Feng Hong Clay Chemical Co., Ltd. Epoxy resin E-44 (bisphenol A epoxy resin, the average epoxy value of 44/100) were supplied by Yuehua Organic Chemical Plant of Yueyang Petrochemical General Factory, and acetone obtained from Sinopharm Chemical Reagent Co., Ltd. Nitrogen as shielding gas were purchased from Wuhan Tonghe Gas Manufacturing Co., Ltd. Ammonium polyphosphate (APP, $n > 1000$), pentaerythritol (PER), melamine (MEL), ammonium dihydrogen phosphate (MAP) and titanium dioxide (TiO_2, rutile) were purchased from Sinopharm Chemical Reagent Co., Ltd. The thickener, defoamer, dispersant and mildew preventive as promoters were obtained from Nantong Chemical Co., Ltd. Deionized water was prepared in our laboratory.

2.2. Preparation of samples

2.2.1. Modification of Na-montmorillonites

10 g of Na-montmorillonites were added into 200 mL of deionized water and fully stirred to get Na-montmorillonite suspensions, and 6.56 g of Cetyltrimethyl Ammonium Bromide (CTAB) were added into 100 mL of deionized water, then the CTAB aqueous solution was slowly dripped into the Na-montmorillonite suspension. When the CTAB aqueous solution was completely fed, the mixture was put in the ultrasonic instrument at 75 °C for 3 h, then kept still at room temperature for another 3 h. Then the mixture was filtered, and the precipitate was rinsed with water repeatedly until no Br^- existed. The powder was dried by infrared lamp and passed through a 70 mesh sieve.

2.2.2. Preparation of the core–shell OMMT/styrene-acrylic/epoxy resin hybrid emulsion

The core–shell OMMT/styrene-acrylic/epoxy resin hybrid emulsions were prepared by semi-continuous seeded emulsion polymerization. The reaction was carried out under nitrogen atmosphere in a 250 mL four-neck flask which was equipped with an inlet for nitrogen gas, a dropping funnel, a mechanical stirrer and a reflux condenser. The descriptive information of the content of each component is presented in Table 1 and the detailed synthesis is described as below.

Synthesis of seed latex. Deionized water, $NaHCO_3$, 1/2 of OMMT and 1/3 of the emulsifier aqueous solution were added into a four-neck flask with a high-speed mechanical stirrer. Then the mixture was heated to 80 ± 1 °C in a thermostated water bath followed by the further addition of the seed monomers. After the seed monomers were added completely the mixture went through 15 min of high-speed mixing in nitrogen atmosphere. Then 1/3 of initiator solution was dropped into the four-neck flask with a stirring rate of 200–220 r min^{-1}. Polymerization was kept at 80 °C for 30 min.

Shell phase pre-emulsification. The rest of emulsifier aqueous solution, 1/2 OMMT and monomers of shell phase were introduced into a 250 mL four neck flask with a high-speed mechanical stirrer and pre-emulsified for about 1 h until the mixture in the flask became white.

Synthesis of core–shell emulsion. Following the synthesis of seed latex, the shell pre-emulsion was added using a dropping funnel and the rest of initiator solution in the dropping funnel was also fed into the flask with an appropriate dropping rate simultaneously. Polymerization was kept at 80 °C for 2 h. Then epoxy resin dissolved in acetone was dropped into the flask under mechanical stirrer within 30 min. The curing process was carried out at 85 °C for 1 h after epoxy resin was dropped completely. Finally, when the emulsion was cooled down to 45 °C, triethylamine was dropped into it to adjust the pH value of emulsion into the range of 7–8.

2.2.3. Preparation of emulsion films

OMMT/styrene-acrylic/epoxy resin hybrid emulsion films were produced by casting the resulting latex on a clean glass plate and allowing the water to evaporate at room temperature. Then the continuous films were used for subsequent measurements of X-ray diffraction (XRD), adhesion to plywood, yellowing resistance test, water resistance test and thermal properties.

2.2.4. Preparation of coatings

Formulations of the intumescent coatings are listed in Table 2. Polymer binders, fire retardant additives (APP, PER, MEL, MAP), fillers (TiO_2), other additives (promoters) and water were mixed for about 1 h in an agate mortar to further grind and disperse after all solid fillers were grinded by a ball grinder. Then the samples were coated on the surface of one side of a plywood plate with a size of 100 × 100 × 5 mm and were dried for at least 72 h before use at room temperature. The thickness of coated dry coating was 0.4 ± 0.01 mm.

2.3. Transmission electron microscopy (TEM)

Morphology of the synthesized core–shell OMMT/styrene-acrylic/epoxy resin hybrid latex particles was observed via transmission electron microscope (TEM, JEM/100CXII). The samples were diluted by distilled water and stained by 2% phosphotungstic acid solution.

2.4. X-ray diffraction (XRD)

XRD was used to study the dispersion of OMMT in core–shell hybrid emulsion. X-ray diffraction (XRD) analysis of the emulsion film, MMT and OMMT were recorded using the CuKα radiation source and the diffraction patterns were collected within the 2θ range of 1–10° using a scanning rate of 0.6 °/min.