Polymer Testing 70 (2018) 73–80

Contents lists available at ScienceDirect

Polymer Testing

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

Serviceability analysis of wood–plastic composites impregnated with paraffin-based Pickering emulsions in simulated sea water–acid rain conditions

Liangpeng Jiang[a], Chunxia He[a,*], Jingjing Fu[b], Lei Wang[a]

[a] College of Engineering, Nanjing Agricultural University, Nanjing, 210031, China
[b] Nanjing Research Institute for Agricultural Mechanization, Ministry of Agriculture, Nanjing 210014, China

ARTICLE INFO

Keywords:
Wood–plastic composites
Paraffin-based Pickering emulsions
Corrosion
Serviceability

ABSTRACT

In order to enhance the serviceability of sorghum straw/polyvinyl chloride composites in simulated sea water–acid rain conditions, paraffin-based Pickering emulsions stabilized by attapulgite particles were prepared as an anti-corrosion coating of the composites, and a worst-case simulated sea water and acid rain corrosion scenario was employed. The results showed that Pickering coating can have superior leaching resistance in the sea water-acid rain conditions. The coated composites had higher water-resistance and hardness than non-coated composites. The presence of Pickering coating resists the degradation effects of simulated corrosion through better water-resistance and hardness, as well as better mechanical and wear properties of the composites. Prior to the corrosion, the thermal stability of the composites was slightly reduced due to the presence of paraffin, while after 12 d corrosion, Pickering emulsions endowed the coated composites with higher thermal stability than non-coated composites.

1. Introduction

Wood–plastic composites (WPCs) are green bio-materials using plant fibers as reinforcement and thermoplastic plastics as matrix, which have been widely used as exterior construction materials such as decking and fencing [1,2]. However, the hydrophilic character of plant fibers has limited the practical application of WPC materials under outdoor conditions, especially under the high humidity conditions [3]. The service properties of WPC materials are reduced after water absorption, due to diffusion of water into the composites, which induces undesirable variation in the quality of bonding between the two phases (i.e., fiber and matrix phases) [4].

The paraffin emulsions treated wood-based materials could greatly improve its water resistance [5]. Wang et al. [6] have investigated the effect of paraffin emulsions on the water resistance of wood, the results showed that the wood treated with paraffin emulsions would exhibit an obvious enhancement in water repellency. However, using paraffin emulsions stabilized by surfactant alone would be lack of long-term stability [7,8]. Solid particles-stabilized emulsions, namely Pickering emulsions, usually exhibited better long-term stability when compared with surfactant-stabilized emulsions. Its stability mechanism depends on the irreversible adsorption of solid particles between the oil-water interface, which could prevent the droplets from the coalescing and Ostwald ripening [9,10]. Therefore, the basic properties of Pickering emulsions can be controlled by altering the type of solid particles used. Inorganic particles such as clays (montmorillonite, kaolinite and laponite), silica, barium sulfate, or calcium carbonate proved efficient stabilizers of biphasic dispersions [11,12]. However, there have been very few studies of Pickering emulsions stabilized by attapulgite particles [13,14]. Attapulgite has the potential to be used as a Pickering emulsifier owing to its unique layered chain structure with a high specific surface area, and a good capacity for dispersion as well as adsorption [15–17]. In our previous work, we found that corrosion by simulated sea water (salinity 3.5%, temperature 55 °C) and acid rain (pH 2.5, temperature 55 °C) can significantly reduce the wear resistance of sorghum straw/polyvinyl chloride composites [18]. And the follow-up works has studied on the modification of wood-plastic composites to improve its wear and corrosion resistance under the simulated sea water and acid rain conditions [19,20]. In the present study, the aforementioned corrosion conditions were used to create a worst-case corrosion scenario such as a heavy acid rain region near the sea in midsummer. Based on this scenario, composites impregnated with paraffin-based Pickering emulsions stabilized by attapulgite particles were analyzed for a wide range of physical properties (contact angle,

* Corresponding author.
E-mail address: chunxiahe@hotmail.com (C. He).

https://doi.org/10.1016/j.polymertesting.2018.06.031
Received 25 March 2018; Received in revised form 5 June 2018; Accepted 23 June 2018
Available online 26 June 2018

dimensional variation, water absorption, and hardness) and mechanical properties (impact, tensile, and flexural strength), as well as their wear behavior. In addition, the thermal properties and micro-morphology were studied by thermogravimetry and micro-imaging techniques (optical and electron microscope), respectively. This study will broaden the potential applications of attapulgite particles, and also provide a technical parameters foundation in the preparation of WPC material with high water and corrosion resistance.

2. Experimental

2.1. Materials

Sorghum straw (Nanjing, China) was ground and screened to a particle size of 149 μm. The sieved fiber was dipped in 4.5% NaOH at 100 °C for 1 h followed by rinsing with deionized water until pH 7 was achieved. The alkali-treated fiber was oven-dried at 90 °C for 24 h. Polyvinyl chloride (PVC, SG-5) was purchased from Tianye (Group) Co., Ltd., Xinjiang, China. Silane coupling agent (KH-550) was purchased from Chuangshi Chemical Additives Co., Ltd., Nanjing, China. Ca/Zn composite stabilizer (603) and PE wax (H-108) were purchased from Wenhua Chemical Pigment Co., Ltd., Shanghai, China. Fully-refined paraffin (58#) was purchased from PetroChina Co., Ltd., Beijing, China. Attapulgite (nanoscale particles), polyoxyethylene (20) sorbitan monostearate (T-60), and sorbitan monostearate (S-60) were purchased from Usolf Chemical Technology Co., Ltd., Shandong, China.

2.2. Methods

2.2.1. Sample preparation

Nine g of KH-550 were dissolved in 45 mL ethanol. This was sprayed onto 300 g of fiber, and then the fiber was air-dried for 12 h and oven-dried at 90 °C for 12 h (moisture content < 3%). Finally, the homogeneous mixture of silane-treated fiber, PVC, stabilizer and PE wax (300, 300, 24 and 15 g, respectively) was melt-blended by a conical twin-screw extruder (RM200C, Hapro Electric Technology Co., Ltd., Harbin, China) with a screw temperature of 150–165 °C and a screw speed of 20 rpm. The obtained composite samples had a width of 10 mm and a thickness of 7 mm, as well as a density of 1.32 ± 0.02 g cm^{-3}.

2.2.2. Emulsion preparation

Pickering emulsions were prepared in two steps. In the first step, 90 wt% T-60 and 10 wt% S-60 were mixed using a magnetic stirrer (ZNCL-BS 180*180, Longshun Instrument Co., Ltd., Nanjing, China) at 1000 rpm for 5 min. The obtained hybrid surfactant exhibited better emulsify in comparison to other ratios in our preliminary experiment. Meanwhile, attapulgite particles were ultrasonically dispersed in 10% KH-550 (diluted with ethanol) using an ultrasonic cleaner (JP-040 S, Skymen Cleaning Apparatus Co., Ltd., Shenzhen, China) at 40 KHz for 30 min, followed by extraction by a high-speed centrifuge (H1650, Cence Laboratory Instrument Development Co., Ltd., Hunan, China) at 3000 rpm for 5 min. The silane-treated attapulgite exhibited higher dispersibility compared with untreated attapulgite. In the second step, 4 wt% silane-treated attapulgite, 16 wt% molten paraffin, 10 wt% hybrid surfactant, and 70 wt% deionized water were magnetically stirred at 2000 rpm for 5 min at 85 ± 1 °C, and then the compounds were homogenized in a high-pressure homogenizer (APV-2000, Pudi Biotech Co., Ltd., Shanghai, China) at 40 MPa for 2 passes, to obtain the Pickering emulsions.

To verify whether the stability of paraffin emulsions would be enhanced by the attapulgite particles, the Pickering emulsions were left for 30 d at ambient temperature (25 ± 1 °C), paraffin emulsions (the same preparing process without attapulgite particles) was used as the control group (Fig. 1). As shown in Fig. 1, the paraffin emulsions were slightly stratified while the Pickering emulsions without stratifying after 30 d storage. Additionally, there was no significant variation in the particle sizes of the Pickering emulsions, ranging from 562.4 ± 7.0 nm (before storage) to 567.9 ± 8.2 nm (after 30 d storage), which were measured using a laser particle sizer (DP-02, OMEC Instrument Co., Ltd., Zhuhai, China). Above results indicates that the existence of attapulgite particles in paraffin emulsions would strengthen the delamination resistance of surfactant-stabilized emulsions.

2.2.3. Ultrasonic impregnation and corrosion design

The impregnation parameters (ultrasonic power and time) were determined by the pre-experiment of evaluating the impregnation efficiency of wood-plastic composites under different ultrasonic power and time, according to the weight gain rate after 7 d storage under ambient temperature conditions. The samples were oven-dried at 90 °C for 12 h at first to get the composites with lower moisture content (< 3%) for improving the impregnation quality. Then the composites were ultrasonically impregnated with Pickering emulsions at 40 KHz for 30 min. The weight gain rate after 7 d storage was 8.7 ± 0.3%, which was extremely close to the weight gain rate (8.5 ± 0.3%) in our preliminary experiment.

In order to simulate a worst-case corrosion scenario of an acid rain region near the sea in mid-summer, simulated sea water with a salinity of 3.5% was prepared by diluting NaCl (CP, wt% ≥ 99.5) with deionized water. Simulated acid rain with a pH of 2.5 was prepared by diluting a mixture of H_2SO_4 and HNO_3 (with a SO_4^{2-}: NO_3^- ratio of 5:1) with deionized water [21]. The corrosion design was comprised of three consecutive cycles: the composites were immersed in sea water at 55 ± 1 °C for 2 d followed by immersion in acid rain at 55 ± 1 °C for 2 d. On each of the four days (i.e., one cycle), some of the composite samples were removed and used for testing.

After impregnation or corrosion, the composite samples were left for 7 d at ambient temperature before further testing. The physical, mechanical and wear tests were carried out at ambient temperature.

2.2.4. Characterization

Contact angle measurements: Contact angles were measured using a contact angle analyzer (JC2000D1, Zhongchen Digital Technology Apparatus Co., Ltd., Shanghai, China). A 3 μL droplet of deionized water was placed on the surface of the composite, and the contact angle was determined after 5 s based on a five-point fitting method.

Dimensional variation and water absorption measurements: A dimensional variation model was established based on the thickness swell of the composites with a measurement precision of 0.01 mm. A water absorption model was established based on the weight gain of the composites in deionized water at 23 ± 1 °C for 24 h, according to the Chinese standard (GB/T) 17657-2013. The thickness swell and weight gain were calculated using equations (1) and (2), respectively:

$$TS = (T_1 - T_0)/T_0 \times 100 \quad (1)$$

where TS (%) is the thickness swell, T_0 (mm) is the initial thickness of the composites before corrosion, and T_1 (mm) is the swelling thickness after corrosion.

$$WG = (W_1 - W_0)/W_0 \times 100 \quad (2)$$

where WG (%) is the weight gain, W_0 (mg) is the dry-weight of the composites (oven drying, 50 °C, 48 h) before immersion, and W_1 (mg) is the wet-weight (after removing surface water) following immersion.

Hardness and mechanical tests: The hardness was evaluated using a plastic Rockwell hardness tester (XHR-150, Lianer Testing Equipment Co., Ltd., Shanghai, China) at a load of 60 kg, according to GB/T 3398.1–2008. The impact strength was evaluated using a beam impact testing machine (XJJ-5, Jinjian Testing Instrument Co., Ltd., Chengde, China) at an impact energy of 2 J, according to GB/T 1043.1–2008. The tensile and flexural strength were evaluated using an electronic universal testing machine (CMT6104, MTS Industrial Systems Co., Ltd., Shanghai, China) at a loading speed of 2 mm min^{-1}, according to ASTM D 638-14 and ASTM D 790-10, respectively.