Progress in Organic Coatings 112 (2017) 9–17

Contents lists available at ScienceDirect

Progress in Organic Coatings

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

Electrically conductive palm oil-based coating with UV curing ability

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ARTICLE INFO

Keywords:
Environmentally friendly
UV-curable coating
Palm oil-based binder
Polyaniline
Conductivity
Anti-corrosion

ABSTRACT

Environmentally friendly products are gaining popularity recently, in line with the increasing global demands for green technology. UV-curable coating is one of them since it involves minimal, if any, emission of volatile organic compounds during the curing process. Besides, UV curing technology enables coatings to be cured within a much shorter time compared to the thermal curing process. The aim of this study is to produce an electrically conductive UV-curable coating which is environmentally friendly. Polyaniline is a polymer with excellent electrical conductivity and known to exhibit anti-corrosion properties through passivation. However, polyaniline itself is not a good coating binder, as it tends to produce a brittle film with poor adhesion properties. Therefore, in this work, palm oil-based polyester binder was synthesized and blended with polyaniline to produce an electrically active coating with improved film adhesion properties. The alkyd resin was formulated with a considerable amount of maleic acid formulation in order to render it UV curable. Both alkyd and polyaniline were characterized using FTIR, ^{1}H NMR, TGA, and UV-Vis. Some of the tests carried out to investigate the film properties of the coatings included the pencil hardness test, adhesion tape test, water and chemical resistant test, conductivity, and thermal stability. In addition, corrosion studies of the coatings on mild steels were determined using open circuit potential (OCP) values, Tafel analysis and electrochemical impedance spectroscopy (EIS).

1. Introduction

The ultraviolet (UV) curing technology has attracted industrial interests and begun its commercialization in the late 20th century, starting with UV inks product, followed by UV coating. This UV curing technology has benefitted various industries. UV curable coatings are said to be environmentally friendly since these systems do not emit volatile organic compounds (VOCs) during the curing process. Besides, the speed of cure is one of the unique advantages of UV-curable coatings over thermally curable coatings. Typically, a UV-curable coating can be cured within seconds, thus more economical compared to the conventional coatings that need hours or even days to dry completely. The quasi-instant hardening of clear or pigmented coatings, adhesives, and composites can be achieved in this UV curing system [1,2]. The UV curing system involves chemical curing with crosslinking reaction. Fig. 1 compares the curing mechanisms between physical drying of thermally cured coatings and chemical curing when coatings are UV-irradiated. In physical drying, there are solvent evaporations and no crosslinking occurs after coatings are heated. On the contrary, chemical curing often involves minimal, if any, solvent evaporation. During UV irradiation, chemical polymerization and crosslinking take place to produce an extensive network of cross-linked polymer chains that lead to improved mechanical and chemical resistance of the coating films [1,3].

Conventional conductive coatings are usually prepared with a certain amount of metal content. However, some of the metals such as silver, Ag that has excellent conductivity and stability in the end products, tend to be expensive. The more economical metals such as copper and nickel used to replace the expensive metals are facing some other problems such as oxidation, sedimentation, and being hazardous and harmful to the environment and end-users [4]. As an alternative, conducting polymers are introduced to replace metals in electrically conductive coatings. Most of the conducting polymers have high thermal and chemical stability, and are suitable to be incorporated into coating [5]. Conductive polymer nanocomposites are extensively studied since they have many potential applications, for example sensors, solar cells, energy storages, and energy savings [6–10]. In this work, Polyaniline (PANI) was chosen as the conducting polymer incorporated into alkyd coating owing to a number of advantages such as ease of synthesis, low cost monomer, good electrochemical properties, and tunable properties, and it is stable at room temperature [11,12]. Besides, integrating PANI into the coating allows the product to have potential applications

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http://dx.doi.org/10.1016/j.porgcoat.2017.06.027
Received 8 February 2017; Received in revised form 24 June 2017; Accepted 25 June 2017

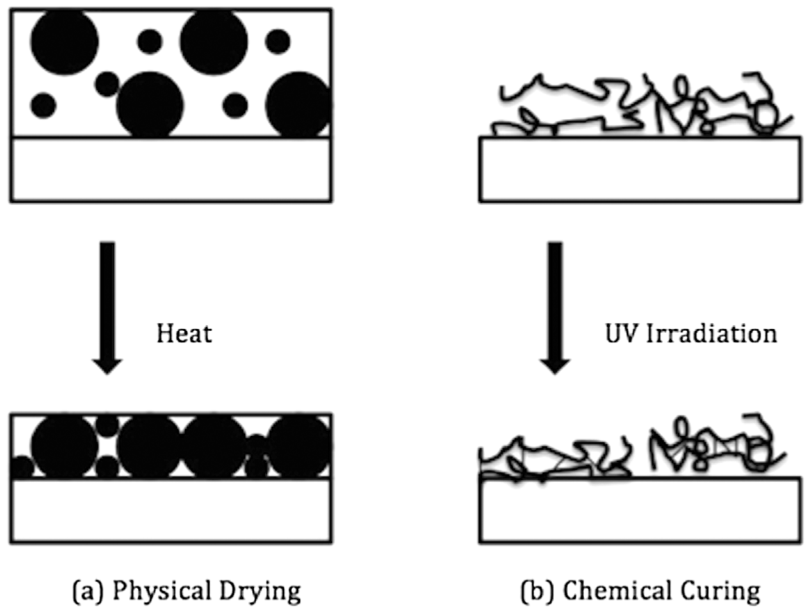

Fig. 1. Curing mechanisms of (a) physically drying coating and (b) chemically curing coating.

in electromagnetic interference (EMI) shielding and giant magnetoresistance (GMR) sensors [13–16]. Furthermore, the product may also be used as metacomposites with negative permittivity [17–20]. PANI has excellent electrical conductivity and is usually reported as anti-corrosive coating films in many studies [11,12,21]. Besides, anti-corrosion properties were reported in other conductive polymer nanocomposite systems, for example polyurethane multiwalled carbon nanotube, Co-doped TiO_2/polypyrrole, and micro/nanocapsules for self-healing coatings [22–24].

Recently, PANI used as fillers to make other conductive polymer nanocomposites has been reported [24–30]. However, it is not common to have neat polyaniline as coatings due to their poor mechanical properties [12]. Therefore, they are usually blended with other polymers or introduced as additive into paints or coatings to render the films electrically active, while maintaining its mechanical strength. There are many works related to blends of PANI with other polymers such as poly(methyl methacrylate), poly(vinly chloride), and cellulose [31,32]. One of the reported systems is alkyd coating containing PANI. There are several works that reported the ability of conducting polymer to improve corrosion resistance of conventional thermal curable coatings [5,33]. In this study, polyaniline was blended with UV-curable palm oil-based alkyd to produce electrically active coating with improved film adhesion properties. Recently, many renewable resources such as palm oil are widely being used in the production of surface coatings binder to replace or serve as an alternative to the existing petroleum-based binders. The unique properties of alkyd resins such as high gloss retention, film flexibility and durability, and good film adhesion reflect its suitability as surface coating binders [34,35]. Several tests inclusive of the pencil hardness test, adhesion tape test, water and chemical resistant test, electrical conductivity, and thermal analysis were conducted to investigate the properties of PANI/alkyd coating blends. The corrosion performance studies of the coating are evaluated by common electrochemical methods: open circuit potential (OCP), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) [36]. The OCP acts as a parameter which denotes the thermodynamic tendency of a material to get oxidized electrochemically in a corrosive medium while EIS verifies the electrical resistance and capacitance measurements of the films [37].

2. Experimental

2.1. Materials

Refined, bleached, and deodorized (RBD) palm olein obtained from Yee Lee Edible Oils Sdn. Bhd. (Perak, Malaysia) was used without further treatment. Glycerol (99.5%), maleic acid (MA) and methyl methacrylate (MMA) were purchased from Friendemann Schmidt (Parkwood, Western Australia) while phthalic anhydride (PA) from R & M Chemicals (United Kingdom). Sodium chloride (NaCl), $Ca(OH)_2$ and hydrochloric acid (HCl) 37% were purchased from Systerm, HmbG Chemicals, and RCl Labscan Limited (Bangkok, Thailand) respectively. Polyaniline (emeraldine salt), trimethylolpropane triacrylate (TMPTA), and benzophenone (99%) were procured from Sigma-Aldrich (Steinheim, Germany). M-cresol and sodium hydroxide (NaOH) were gained from Merck (Darmstadt, Germany) and Macron (Sweden) respectively.

2.2. Methods

2.2.1. Synthesis of alkyd

Alkyd synthesis began with transesterification of 306.6 g of palm olein and 167.9 g of glycerol, using 0.25 g of $Ca(OH)_2$ as catalyst. The reaction mixture was heated at 230 °C for 2 h before cooling down to 150 °C. Then, 179.0 g of phthalic anhydride and 51.0 g of maleic acid were added into the reaction mixture and the polycondensation process was carried out at 220 °C until the acid number dropped below 10% of the initial value.

2.2.2. Characterizations

The IR spectra of palm oil and alkyd were recorded using the Perkin Elmer spectrometer from 400 to 4000 cm^{-1} wavenumber on a KBr cell. The ^1H NMR spectra of palm oil and alkyd were recorded using FT-NMR Lambda 400 MHz spectrometer. The alkyd was dissolved in deuterated chloroform prior to the analysis, and the signal was locked at 0 ppm with tetramethylsilane (TMS). The thermal properties of the alkyd were studied using a thermal gravimetric analyzer (TGA 6, Perkin Elmer), where the sample was heated from 50 °C to 900 °C at 20 °C/min in N_2 atmosphere. The acid number of alkyd was obtained based on the standard test method for acid value of organic coating materials, ASTM D1639 - 90.

For polyaniline (PANI), the characterizations were done using FTIR