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Novel biobased dual-cure coating system

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ABSTRACT

Sucrose esters consisting of acetoacetates and fatty acids were invented as novel biobased amine-cured and autoxidation dual-cure coating systems, in the presence of diamine crosslinker and metal salt driers. Acetoacetylated sucrose soyate (ASS) was an intramolecular system containing both acetoacetates and fatty acids in the same molecule. Miscible bicomponent blends, made of ASS and partially enamine alkyl substituted acetoacetylated sucrose (p-EAS), was an intermolecular curing system. Compatibility between the two components was achieved by reacting acetoacetylated sucrose (AS) with alkyl amines, in which the compatibility could be adjusted by either the alkyl chain length or the degree of enamine alkyl substitution, DES. Sucrose esters were characterized by gel permeation chromatography (GPC), Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and differential scanning calorimetry (DSC). The properties and drying times of coatings cured through autoxidation, amine-acetoacetate reactions, and by dual-curing were studied. It was found that acetoacetate chemistry improved the attributes of sucrose ester of fatty acids in ambient curing conditions, as well as providing dual-cure coatings having a good balance of properties.

1. Introduction

The contribution of the chemical industry to 'Sustainable Development' has been demonstrated by the utilization of renewable raw materials, such as polysaccharides, natural oils and fats [1–4]. In coatings science, drying oils, which are naturally occurring triglycerides of unsaturated fatty acids, have been used in the formulation of coating resins for centuries. In the 1920s drying oils were combined with diacids and polyols to generate high molecular weight polyester resins, most commonly known as alkyd resins. Alkyd resins quickly became the dominating resin technology for coatings. With the advent of higher performance petrochemical-based resin technologies—such as acrylics, polyurethanes, and epoxies—the demise of alkyd resins was said to be imminent, but alkyd resins continue to be produced in large quantities today. One limitation today in the use of alkyds has been in the preparation of extremely high solids solventborne coatings. Due to the stochastic nature of the polyesterification process, a broad distribution of polymer chains are formed during alkyd synthesis, which is magnified as the molecular weight is reduced to achieve higher solids, resulting in poor quality coating films. To overcome this limitation, some innovative design strategies in this area are currently being employed, such as reacting fatty acids with hyperbranched polyols [5–8] (i.e. dipentaerythritol and its derivatives) to obtain high-solids alkyd resins.

Sucrose is a naturally occurring polyol having eight hydroxyl groups, which potentially can be esterified by eight fatty acids to yield a well-defined compact macromolecular structure. Sucrose esters of unsaturated fatty acids (SEUFA) were first explored as coating vehicles in the 1960s [9,10]. These early studies indicated that the highly substituted SEUFA had a uniform fatty acid distribution, low viscosity, rapid air-drying time and good coating properties. However, it appears that these resins were never commercialized at that time. More recently, Procter & Gamble Chemicals has developed an efficient process for industrially producing SEUFA resins having a high degree of substitution with the brand name SEFOSE [11–13]. These commercially available products are mixtures of sucrose hexa-, hepta-, and mainly octa-esters (a minimum of 70 wt% of total ester mixture). Due to the compact molecular structure of these resins, the viscosities of these materials are very low (300–400 cPs). This is approximately the application viscosity for high solids coatings, thus requiring only minimal amounts of solvent. Thus, these materials have been explored as binders and diluents for air drying high solids coatings.

Acetoacetylated sucrose (AS) is another attractive sucrose ester compound with acetoacetates as the functional groups. The synthesis was first reported in the 1960s by reacting diketene with sucrose in dimethylformamide in the presence of triethylamine catalyst [14]. About twenty years later, Elam et al. improved the preparation of saccharide acetoacetates by reacting saccharides

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with 2,2,6-trimethyl-4H-1,3-dioxin-4-one, requiring neither a catalyst nor a solvent [15]. In the 1990s, new products and synthesis techniques started to be available to facilitate the preparation of AS by reacting sucrose with alkyl (i.e. methyl, ethyl, and t-butyl) acetoacetates via transesterification [16].

The broad variety of promising applications of acetoacetate chemistry in the preparation of thermoset coatings were explored by chemists at Eastman Chemical Company, who showed that acetoacetylated polymers can be derivatized or crosslinked using a variety of chemicals, such as melamines, isocyanates, aldehydes, amines (enamine formation), and acrylates (Michael Reaction) [17,18]. In the early 2000s, the two most common and efficient methods for covalently bonding acetoacetates to make high-solids coatings resins were [19]: (a) free-radical polymerization of acetoacetoxyethyl methacrylate (AAEM) with other vinyl monomers; (b) transesterification of *t*-butyl acetoacetate (*t*-BAA) with polymers containing pendant hydroxyl groups. In the latter method, the attractive attributes of substituting hydroxyls with acetoacetates on polyester resins include reduced solution viscosity and glass transition temperature. Therefore, acetoacetate chemistry provides coating resins with wide latitude for the formulation of high-solids systems with crosslinking versatility for both high temperature and ambient curing.

Acetoacetate chemistry has been introduced into alkyd resins, which contain unsaturated fatty acids as functional groups for autoxidation. Bors et al. disclosed air-drying curable alkyd latex (emulsion polymerization) formulated by pendant acetoacetate functionalized polymer, unsaturated fatty acids and metal salt driers (i.e. cobalt drier) [20]. Kuo et al. disclosed high-solids solventborne and waterborne air-drying curable acetoacetate functionalized alkyds via transesterification [21,22]. Interestingly, the observations in both studies indicated that acetoacetate promoted the autoxidation process. Powell et al. made the statement that acetoacetate is able to work as a reactive copromoter in alkyd resins [23]. “Copromoter” means that acetoacetate has the capability of facilitating hydroperoxide decomposition (either oxidation or reduction) by interacting with cobalt, which accelerates autoxidation. “Reactive” means that acetoacetate can cure into the polymer matrix. However, the details of the exact reactions occurring have not been demonstrated, nor has an extensive study on the influence of acetoacetate groups on autoxidation been reported.

Sucrose fatty esters are 100% biobased resins only containing fatty acids as functional groups, but they possess more promising autoxidation curing than normal triglycerides due to their higher functionalities and unique macromolecular structure. Based on the above literature studies, the work reported herein was initiated by the idea of chemically introducing acetoacetates into sucrose fatty ester resins or blending acetoacetylated sucrose with sucrose fatty esters. The novel coating system would consist of sucrose esters having both acetoacetates and fatty acids as the functional groups. This coating system could be dual-cured by enamine formation and autoxidation. The applications of acetoacetate chemistry on sucrose fatty ester resins are promising, and enamine derivatizing and crosslinking using amines was explored in this study.

2. Experimental

2.1. Raw materials

Sucrose (assay ≥99.5%, HPLC), β-D-fructofuranosyl-α-D-glucopyranoside, was purchased from Sigma–Aldrich, Inc. (St. Louis, MO). Tertiary-butyl acetoacetate (*t*-BAA, >98%) was kindly supplied by Eastman Chemical Company (Kingsport, TN). Butylamine, hexylamine, octylamine, decylamine, dodecylamine and octadecylamine were purchased from Sigma–Aldrich, Inc. (St. Louis, MO). Fully esterified sucrose soyate (SS, SEFOSE 1618U) and partially esterified sucrose soyate (p-SS, SEFOSE 1618U B6) were kindly supplied by Procter & Gamble Chemicals (Cincinnati, OH). COBALT HEX-CEM (12%) and ZIRCONIUM HEX-CEM (18%) were provided by OMG (Westlake, OH). Nuxtra Zinc (8%) was provided by DURA Chemicals, Inc. (Alameda, CA). These metal salts were used as driers in autoxidation. AMICURE PACM curing agent (AHEW = 52.5 g/mole), 4,4′-methylenebiscycloheexanamine, was a gift from Air Products and Chemicals, Inc. (Allentown, PA). All materials were used as received without further purification.

2.2. Synthesis of acetoacetylated sucrose soyate (ASS)

In a 500 mL four-neck flask equipped with a mechanical stirrer, nitrogen inlet, thermocouple, reflux condenser and Dean-Stark trap, 100 g (0.054 moles) of p-SS (SEFOSE 1618U B6) and 17.2 g of *t*-BAA (0.108 moles) were added. After 30 min nitrogen prepurge, the reactants were heated to 130 °C. During the reaction, the nitrogen inner pressure was kept positive, and 9.1 g of *t*-butanol (0.108 moles) was collected in the Dean-Stark trap as a byproduct. The reaction was stopped when no more *t*-butanol evolved. A light yellow liquid was produced, called acetoacetylated sucrose soyate (ASS).

2.3. Synthesis of acetoacetylated sucrose (AS)

In a 500 mL four-neck flask equipped with a mechanical stirrer, nitrogen inlet, thermocouple, reflux condenser and Dean-Stark trap, 50.0 g (0.146 moles) of sucrose and 184.9 g of *t*-BAA (1.169 moles) were added. The reactants were stirred and heated to 130 °C. During the reaction, the nitrogen inner pressure was kept positive, and 84.8 g of *t*-butanol (1.145 moles) was collected in the Dean-Stark trap as a byproduct. The reaction was stopped when no more *t*-butanol evolved. A yellow viscous product was obtained, known as acetoacetylated sucrose (AS).

2.4. Synthesis of enamine alkyl substituted acetoacetylated sucrose (EAS)

A series of enamine alkyl substituted acetoacetylated sucrose compounds (EASs) were prepared with different enamine alkyl chain lengths and different degrees of enamine substitution (DES) by reacting AS with primary monoamines. Here, a specific reaction using dodecylamine to synthesize EAS with full enamine substitution is used as an example. In the same reaction setup for AS preparation, 50.0 g (0.050 moles) of AS and 73.0 g (0.400 moles) of dodecylamine were added. The reactants were stirred and heated to 110 °C. During the reaction, the nitrogen inner pressure was kept positive, and 7.1 g of water (0.400 moles) was collected in the Dean-Stark trap as a byproduct. The reaction was stopped when no more water evolved. Finally, a red-yellow viscous product was obtained. Other compounds were synthesized using a similar procedure.

2.5. Gel permeation chromatography

Molecular weight was determined using a Waters 2410 gel permeation chromatograph equipped with refractive index detector. Polystyrene standards were used for calibration. A 1.5% sample solution in THF using a flow rate of 1 ml/min was used.

2.6. Fourier transform infrared (FTIR) spectroscopy

FTIR measurements were done with a Thermo Scientific Nicolet 8700 FTIR spectrometer. Samples were prepared in THF solution, and the concentration was exactly controlled as 4 mg/ml. For each sample solution, a 200 μL drop was deposited by micropipette and