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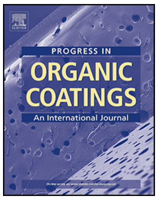

Modification of polycaprolactone-styrene-vinyl trimethoxysilane terpolymer with sunflower oil for coating purposes

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ABSTRACT

Polycaprolactone-styrene-vinyl trimethoxysilane terpolymer was prepared and then modified with sunflower oil partial glyceride (SFOPG) via a sol–gel method for use as a binder in coating applications. Therefore, a vinyl-functionalized polyester-based macromonomer (HPCL) was prepared via ring-opening polymerization of ε-caprolactone (CL) using 2-hydroxyethyl methacrylate (HEMA) followed by copolymerization with styrene (St) and vinyl trimethoxysilane (VTMS) to yield a terpolymer (HPCL-St-VTMS). The terpolymer was characterized by FTIR, GPC and ^{1}H NMR. To overcome the fact that the cured film of HPCL-St-VTMS was slightly soft, SFOPG was used as a modifier and was inserted to the structure via a sol–gel reaction between the hydroxyl groups and methoxy silane moieties of the terpolymer. After this modification, the softness disappeared. Nanosize inorganic domains were observed in the SEM image. Thermal analyses of the resulting cross-linked film of SFOM-HPCL-St-VTMS were performed with DSC and TGA. SFOM-HPCL-St-VTMS, which does not melt, resulted in a higher char yield and decomposition temperature at 5% weight loss compared to the unmodified HPCL-St-VTMS film. An evaluation of the film properties indicated that SFOM-HPCL-St-VTMS can be used as a coating material.

1. Introduction

Polymeric binders are one of the most vital components of organic coatings because they serve as a material that integrates with the other components in the formulation. In this context, the molecular structure of polymeric binders should be designed to benefit the specific purposes of the coatings (i.e., protection against corrosion, abrasion and microbial fouling) [1–4].

A broad range of polymers, including polyesters, epoxides, polyurethanes, polyureas, acrylics, vinyl acetates, silicones, silicates, polyvinyl chlorides, phenolics and vinylidiene fluorides, are used as binders for organic coating materials [5]. These polymers are primarily produced from petrochemical raw materials. Due to the detrimental influence of fossil fuel resources on environmental and economic issues, renewable resources have recently gained considerable importance by virtue of their benefits, such as being inexpensive, abundant and biodegradable with a low toxicity and high purity [2,6–11]. In addition to being a food source, triglyceride oils, which are a renewable resource, have been widely used for technical applications, such as in the manufacture of soap, surface-active materials and oleoresinous binders. In their direct use as a binder, they form a film with insufficient properties based on its drying speed, hardness, adhesion and durability. Due to this fact and to improve their performance, triglyceride oils are used in coating formulations along with alkyds, epoxy esters, uralkyd resins and other synthetic polymers [2,6,10,11].

Further progress for converting triglycerides into a more useful product with an improved coating performance involves the preparation of their copolymers. Therefore, a number of studies were previously performed in our laboratory to enhance film properties [12–17]. Macromer and macroinitiator methods have been developed. In the macromer method, a vinyl functionality was inserted into the oil structure, and the resulting oil-based vinyl macromers were copolymerized with vinyl monomers, such as styrene (St) [15–20]. For the styrenated oil preparation, the formation of homopolystyrene, which causes opacity in the films, was minimized. In the macroinitiator method, thermally labile azo groups were inserted into the oil molecule via reaction with 4,4′-azobis(4-cyanopentanoyl chloride). For the preparation of styrenated oil, this macro azo initiator was heated in the presence of the St monomer, and a styrenated oil was formed without the homopolymer [12–14].

In addition to free radical polymerization, controlled free radical living polymerizations, such as nitroxide mediated radical polymerization (NMRP) in the presence of 2,2′,6,6′-tetramethylpiperidinyl-1-oxy (TEMPO) and reversible

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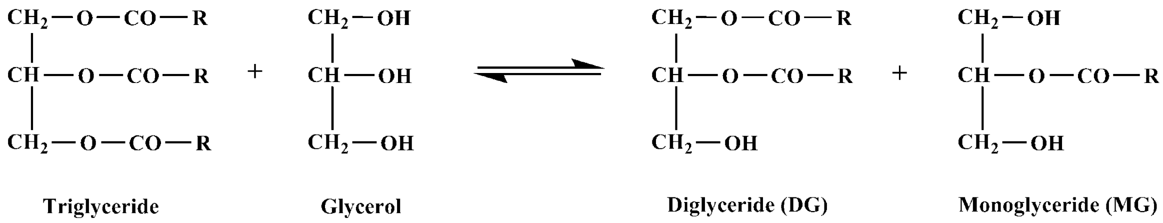

Scheme 1. Synthesis of SFOPGs.

addition-fragmentation chain transfer polymerization (RAFT), have also been reported in our previous publications [21–24]. The obtained copolymers, which possess low polydispersity, resulted in good film properties. In addition to these studies, non-vinyl monomers of 3-aminopropyltriethoxysilane [25], benzoxazine [26,27], diisocyanates [28] and methylolated abietic acid [29] were also used for the triglyceride oil modification. 3-Aminopropyltriethoxysilane causes cross-linking via the sol–gel reaction producing a film with a nano hybrid composite structure [25]. In our recent study, benzoxazine, which is a non-vinyl monomer, was also used in the formulation [26,27]. It is well known that the benzoxazine monomer has attracted great interest in polymer synthesis due to its unique properties including its high thermal stability, high glass transition temperature, good mechanical performance, rich molecular design flexibility, volumetric stability upon curing, good flame retardance, no strong acid catalysts or additives for curing, low moisture absorption, high char yield and the absence of by-products during curing [26,27]. To incorporate these features into the film, an oil-based polyester was prepared via ring opening polymerization (ROP) of ε-caprolactone (CL) using SFOPG. Then, this intermediate was further modified with benzoxazine. The resulting product resulted in a sample with improved film properties [26].

As a continuation of these studies, in the current study, sunflower oil partial glyceride (SFOPG) was used as a modifier for the synthetic resin prepared in the laboratory by copolymerization of vinyl functional polyester (HPCL) with styrene (St) and vinyl trimethoxysilane (VTMS) to yield a terpolymer (HPCL-St-VTMS). HPCL was prepared by ROP of CL using 2-hydroxyethyl methacrylate (HEMA) as the initiator. Because the cured film of HPCL-St-VTMS was slightly soft, SFOPG was incorporated into HPCL-St-VTMS via a sol–gel method. Sunflower oil-modified HPCL-St-VTMS (SFOM-HPCL-St-VTMS) exhibited good film properties due to the cross-linking and flexibility conferred by the inserted oil moiety.

2. Experimental

2.1. Materials

Sunflower oil (SFO) was purchased from the market and used as received. ε-Caprolactone (CL, 99%, Alfa Aesar) monomer was dried over calcium hydride (95%, Aldrich) for 48 h at room temperature and distilled under vacuum. Styrene (St, 99%, Aldrich) was passed through a basic alumina column to purify it from the inhibitor. Stannous octoate (Tin (II) 2-ethylhexanoate) (SO, 95%, Aldrich), vinyl trimethoxysilane (VTMS, 98%, Aldrich), benzoyl peroxide (BPO, Aldrich), 2-hydroxyethyl methacrylate (HEMA, 99%, Fluka) and hydroquinone (98%, Fluka) were used as received. All of the other chemicals were of analytical grade and used as received.

2.2. Synthesis of partial glycerides of sunflower oil (SFOPG)

SFOPG was synthesized using the glycerolysis reaction (Scheme 1) between SFO and glycerol [30]. 120 g of SFO and 10.4 g of glycerol were placed into a three-necked round-bottomed flask equipped with a reflux condenser. The mixture was heated slowly to 218 °C with nitrogen bubbling, and then, $Ca(OH)_2$ was added to the flask as a catalyst, which constituted 0.1% by weight of the oil portion. The temperature was increased to 230 °C, and the reaction was conducted for 1 h under a nitrogen atmosphere. At predetermined time intervals, samples were taken from the reaction mixture and poured into a three-fold amount of ethanol. When the alcohol solution became clear, the transesterification was terminated. The reaction mixture was cooled and dissolved in diethyl ether, washed with dilute sulfuric acid and distilled water to remove the catalyst and free glycerol, respectively. The ethereal solution was dried over anhydrous Na_2SO_4, and the solvent was removed. The hydroxyl and acid values of dry SFOPG were determined [31].

Table 1
Preparation of the terpolymer ($HPCL_w$-St_x-$VTMS_y$-BPO-z[a]) by varying the initiator and monomer ratios.

Sample	Mole ratio [VTMS/St]	BPO wt%
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-5.0[a]	0.5	5.0
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-3.0	0.5	3.0
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.5	0.5	1.5
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-1.0	0.5	1.0
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.5	0.5	0.5
$HPCL_1$-St_{50}-$VTMS_{25}$-BPO-0.27	0.5	0.27
$HPCL_1$-St_{50}-$VTMS_{50}$-BPO-1.5	1.0	1.5
$HPCL_1$-St_{50}-$VTMS_{75}$-BPO-1.5	1.5	1.5

[a] The w, x and y subscripts denote the moles of the relevant monomer. The z abbreviation indicates the wt% of BPO used in the reaction. For example, $HPCL_1$-St_{50}-$VTMS_{25}$-BPO-5.0 was synthesized with 1 mole of HPCL, 50 moles of St and 25 moles of VTMS in the presence of 5.0 wt% of BPO. BPO percentages were based on the total amount of St and VTMS.

2.3. Synthesis of vinyl functional macromonomer (HPCL)

The vinyl functional macromonomer (HPCL) was prepared by ROP of CL initiated by HEMA using the SO catalyst similar to the previously reported procedure [26]. HEMA (8.8 mmol, 1.15 g), CL (108.3 mmol, 12.36 g), SO (0.271 mmol, 0.11 g) and dried toluene (5 mL) were added to a 50 mL four-necked flask. The reaction flask, which was equipped with a dry nitrogen inlet tube, a reflux condenser, a thermometer, and a magnetic stirrer, was placed in a temperature-controlled oil bath at 120 °C. 0.35 g of hydroquinone was added to the reaction medium to inhibit the polymerization of the vinyl functionality during the ROP of CL. After 3 h, the polymerization was immediately terminated by cooling the flask in an ice bath. Then, the mixture in the flask was precipitated into refrigerated methanol and repeatedly washed with methanol to remove the unreacted monomers. The product was filtered off and dried in a vacuum oven at 40 °C for 24 h.

2.4. Synthesis of $HPCL_w$-St_x-$VTMS_y$-BPO-z terpolymer

The terpolymer samples were prepared by free radical polymerization using BPO as the initiator. Table 1 describes the terpolymer

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