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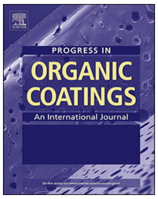

Construction of sustainable polyurethane-based gel-coats containing poly(ε-caprolactone)-grafted lignin and their coating performance

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ABSTRACT

In order to use a lignin as a polyol in polyurethane-based gel-coated films, poly(ε-caprolactone) grafted lignin (PCL-*g*-lignin) was synthesized by a ring-opening polymerization of ε-caprolactone in presence of a pristine lignin. This reaction was confirmed by FT-IR spectroscopy. By usage of the PCL-*g*-lignin, polyurethane-based gel-coated films was prepared through a simple urethane reaction following which the effects of the PCL-*g*-lignin content on the physical properties and surface characteristics of the polyurethane-based gel-coat films was examined. With increased PCL-*g*-lignin content, the decreased cross-linking density resulted in the reduction of physical properties such as the tensile strength and surface hardness of the gel-coated films. Their surface characteristics (e.g., adhesion strength, abrasion, and gloss) were constant, regardless of the PCL-*g*-lignin content increase in the gel-coated films.

1. Introduction

Generally, gel coats, one of the top-coating films, are specially designed in-mold surface coatings to protect a surface or edge of fiber reinforced plastics (FRP) structures [1,2]. Gel coats are used for both functional and aesthetic purposes, such as protective coating against water and UV light as well as the provision of color and gloss to the surface of FRP structures [3]. The most popular ones are based on orthophthalic unsaturated polyester (UPE) with a styrene monomer and can be found on many familiar products, such as boat hulls, ski plates, pools, and automotive body panels [4–7]. Unlike other common coatings, which rely on the evaporation of a solvent to deposit a film of high molecular weight polymers, a UPE-based gel coat is an oligomeric molecular weight polymer resin which passes through a gelation and a cure phase to form a high molecular weight network polymer matrix [8]. However, there are critical health and environmental concerns about UPE-based gel coats that are related to the use of volatile styrene monomers in the gel coat formulation.

Unlike UPE-based gel coats, polyurethane-based ones originate from a near-zero volatile organic compounds (VOCs) formulation because this system does not use any volatile components and solvents. Indeed, polyurethane-based gel coats are typically rapid-curing systems, but their formulation adjustment and the use of catalysts allow modifications of the cure rate to meet the specific needs of end-use applications [9].

Lignin is usually produced as a by-product of the pulping process and it is the second-most common organic material in nature. It has a complex chemical structure that includes a variety of functional groups, namely hydroxyl, methoxyl, carbonyl, and carboxyl moieties. Among them, the hydroxyl groups and free positions in the aromatic ring are the most characteristic functions in lignin, determining its reactivity and constituting the reactive sites to be exploited in polymer chemistry. The utilization of lignin as a macromonomer in polyurethane synthesis often follows two global approaches: (i) direct use of lignin without any preliminary chemical modification, alone or in combination with other polyols [10–13] or (ii) making the hydroxyl functions readily available through chemical modifications, such as esterification and etherification reactions [14–17].

Hence, this study describes a new strategy to fabricate an eco-friendly hybrid gel coat consisting of polyurethane and natural lignin. To build up a homogeneous hybrid polyurethane-based gel coat, chemically modified lignin was designed to obtain a high solubility in the polyurethane precursor and many hydroxyl groups, which can react with isocyanate moieties in the polyurethane precursor. A ring-opening polymerization of ε-caprolactone was conducted on the lignin particles to form hydrophobic poly(ε-caprolactone) grafted lignin particles (PCL-*g*-lignin). The high functionality associated with lignin-based polyols makes them ideal for the construction of polyurethane-based gel coats. PCL-*g*-lignin was used as a polyol in polyurethane-based gel coats and its coating performance was evaluated by the PCL-*g*-lignin content.

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2. Experimental section

2.1. Materials

Organosolv lignin (pH = 6.9–7.1; Ash < 16%) was purchased from BOC Sciences (BIOSCI Inc., Shirley, NY, USA. All reagents used in this study were of analytical grade and used without further purification steps: ε-caprolactone (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan), polyethylene glycol (Ave. Mw = 1900–2100, KPX Chemical Co., Ltd., Seoul, Republic of Korea), isophorone diisocyante (IPDI; Alfa Aesar, Tewksbury, MA, USA), 1,3-butanediol (Samchun Pure Chemical Co., Ltd., Pyongtaek City, Republic of Korea), acrylic polyol (Hydroxy value = 83 ± 5, Aekyung Chemical Co., Ltd., Seoul, Republic of Korea), tin(II) 2-ethylhexanoate (Sigma-Aldrich Corp., St. Louis, MI, USA), and di-*n*-butyltin dilaurate (Alfa Aesar, Tewksbury, MA, USA).

2.2. Preparation of poly(ε-caprolactone)-grafted lignin (PCL-g-lignin)

Lignin was dispersed in xylene using a homogenizer (T10 basic ULTRA-TURRAX, IKA; Sigma-Aldrich). ε-caprolactone and di-*n*-butyltin dilaurate were added as catalysts to the suspension mixture and stirred for 1 h. The reaction mixture was mixed for 24 h at 150 °C and, after cooling by the ambient temperature, quenched into an excess amount of methanol. The heterogeneous solution was filtered through a fritted disk funnel to isolate the chemically modified lignin from the solution. The obtained power was several times washed with cold methanol and then dried overnight in a vacuum oven at 80 °C. The hydroxyl index for the PCL-*g*-lignin was determined according to the ASTM D1638 standard, which involves dissolving a product's weighed amount in pyridine, treating it with a known excess amount of phthalic anhydride under reflux for 1 h, and back-titrating the unreacted mixture of acid and anhydride [18].

2.3. Preparation of NCO-terminated urethane prepolymer

Polyethylene glycol (40 wt-%), 1,3-butanediol (4 wt-%), IPDI (56 wt-%), and di-*n*-butyltin dilaurate (catalyst amount) were charged into a two-neck round flask and mixed for 30 min at room temperature. The mixture was then kept at 80 °C and stirred at 80 rpm for 6 h. The isocyanate content was determined by a titration technique with *N*,*N*'-dibutylamine (ASTM D-2572). The hard/soft segment ratio was defined as the ratio of the combined IPDI and 1,3-butanediol weight to that of the polyethylene glycol in the starting formulation.

2.4. Preparation of the gel-coat syrup and gel-coated film

The gel-coated syrup was prepared according to the prepolymer method. A weighted quantity of dried polyol (acrylic polyol or a mixture of acrylic polyol and PCL-*g*-lignin) was charged into a flask equipped with a mechanical stirrer and a prepared NCO-terminated urethane prepolymer then added to the flask, mixed at room temperature to obtain the NCO/OH index of 1.05 (Table 1). The syrups were coated onto a Teflon-covered soda-lime glass using a bar-coater (1.5 μm thickness) and then cured in a convection oven for 24 h at 60 °C.

Table 1
Formulations of the gel-coat syrups with PCL-g-lignin content.

Sample code	Urethane prepolymer (g)	Acrylic polyol (g)	PCL-g-lignin (g)
PCL-*g*-lignin_00	50	131	0
PCL-*g*-lignin_05	50	124	10
PCL-*g*-lingin_15	50	109	30
PCL-*g*-lignin_25	50	94	50
PCL-*g*-lignin_35	50	80	70

2.5. Equipment and experiments

A Nocolet 380 FT-IR Thermo Scientific Co.) was used to confirm the chemical modification for pristine lignin. DSC measurements were performed using a DSC Q20 (TA Instruments). The measurements were taken between 25–200 °C at a heating rate of 5 °C/min under a nitrogen atmosphere. Thermogravimetry (TG) was carried out in a nitrogen atmosphere using a TGA Q50 (TA Instruments) at heating rate of 20 °C/min in the temperature range from 30 to 600 °C. Tensile tests were conducted by using a LSK30 K Plus Universal Testing Machine (Lloyd Instruments) with a strain speed of 100 mm/min. Dynamic-mechanical analyses were performed with a Q800 DMA (TA Instruments). The measurements were conducted at 5 °C/min between 25 and 100 °C in the tensile mode. The hardness of the gel-coated films was measured by a GS-702N Shore D-type durometer (Teclock Co.) (ASTM D2240) and their pull-off strength by an Elcometer 106 pull-off adhesion tester (Elcometer Instruments) (ASTM D-4541). The pull-off test is a near-to-surface method in which a circular steel disc (dolly) is attached to the surface of the concrete with an epoxy. An abrasion test of the gel coats was performed using the Taber Rotary Abraser 5135 (Taber Industries) (ASTM D 4060-07). The abrasion resistance was measured by weighing the material sample before and after subjecting it to a known abrasive stress throughout a known time period. The load was 1 kg on each side and the number of cycles 1000 rounds using a CS-17 wheel. The gloss of the gel coats on the polycarbonate plate was measured by an Elcometer 408 Glossmeter (Elcometer Instrument) (ASTM D523). Gloss is measured by directing a light beam with a constant intensity at a fixed angle (60°) to the coating surface and assessing the amount of reflected light. The fractural morphologies of the gel coats were examined by JSM–7100 F FE-SEM Field-Emission Scanning Electron Microscopy (Jeol) at 10 kV. The XPS spectra were acquired with a K-Alpha instrument (Thermo Scientific Co.) using a monochromatic Al Kα source operating at 72 W.

3. Results and discussion

Although natural pristine lignin has a complex chemical structure including many functional groups, there are enough for the hydroxyl groups to react on the outer layer of the lignin particle with other functional groups such as silane, isocyante, and carboxylic acid. [19–22] Owing to the reactivity of ε-caprolactone with the hydroxyl groups on the lignin to form OH-terminated lignin-based star-like copolymers consisting of a lignin core and a PCL arm segment, [23] this architecture shows a high potential for use as a polyol part in polyurethane synthesis.

In this study, we designed and constructed a PCL-*g*-lignin with an OH-terminated PCL arm anchored on the lignin particle. The hydroxyl groups on the pristine lignin can play an initiating role for ring-opening polymerization (ROP) with ε-caprolactone. Thus, the polymerization of pristine lignin and ε-caprolactone should form PCL-grafted lignin. Evidence of ROP catalyzed by a Tin(II) catalyst was routinely analyzed through FT-IR. The FT-IR spectra were normalized against a specific ATR crystal adsorption. This technique has already been used previously to enable comparisons between the pristine lignin and the modified one with PCL polymer chain arms [24,25]. Fig. 1 displays the FT-IR spectra of the pristine lignin, neat PCL, and PCL-g-lignin. In case of the pristine lignin, the hydroxyl-stretching region (3000–3700 cm^{-1}) and the carbonyl-stretching region (1680–1760 cm^{-1}) are present, due to the acetyl groups of the pristine lignin. [26] However, in case of the neat PCL, the hydroxyl-stretching mode is not as strong as that of lignin which should be attributed to the low concentration of PCL hydroxyl chain-end groups. As shown in Fig. 1, several aspects indicate the occurrence of PCL grafting on the lignin: (*i*) an increase in the band at 2840–2980 cm^{-1} due to the stretching mode of aliphatic groups (CH_3, CH_2, and CH), (*ii*) a reduction in the intensity of the carbonyl band at 1730 cm^{-1}, (*iii*) an elevation in the absorption band of the C–O

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