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Synthesis, properties, and applications of hybrid polyurethane–urea obtained from air-oxidized soybean oil

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ABSTRACT

This study explores the synthesis of hybrid polyurethane (PU)–urea obtained from air-oxidized soybean oil. The effect of the oxidation time of the soybean oil on the production of soy poliol and hybrid PU–urea films employing (3-aminopropyl) trimethoxysilane was investigated. Soybean polyols and hybrid PU–urea materials were characterized by various techniques such as ^{1}H and ^{29}Si nuclear magnetic resonance, Fourier transform infrared spectroscopy (FTIR), gel-permeation chromatography (GPC), gel content, scanning electron microscopy (SEM), wide-angle X-ray diffraction (WAXD), synchrotron small-angle X-ray scattering (SAXS), contact angle, and glow-discharge optical emission spectroscopy. Furthermore, the physicomechanical properties of the materials were characterized and their corrosion resistance was determined. The produced ecofriendly materials exhibited a dependency of the hybrid network on the degree of gel content. The phase morphology developed during the polymerization reaction influences the size of hard domains and their organization. This study provides a direct relation between the corrosion resistance and material hydrophobicity and the nature of the heterogeneity of the phase morphology formed during one-step polymerization procedure.

1. Introduction

In recent years, the use of renewable feedstock to replace petroleum-based materials for the development of polymers has attracted much attention. Natural oils are emerging as an alternative renewable chemical because of their availability and ease of chemical modification to suit many purposes [1]. Their importance is also because of their simple preparation yet highly promising applications in several fields such as coatings [2,3], foams [4], and polymer addtives [5,6]. Polyurethanes (PUs) are among the most important polymeric materials, exhibiting functional properties that make them suitable for use in many fields such as footwear, machinery, coatings and paints, rigid insulations, elastic fibers, and medical devices [7].

In the last decade, PU materials have been the subject of numerous studies aimed at determining a solution for the replacement of petro-based polyols and isocyanates with bio-based molecules in response to concerns about the depletion of petrochemical resources [8]. A current trend is the use of chemical feedstock based on vegetable oils, which involves the valorization of natural oil polyols [9]. Soybean oil, for example, is utilized in the preparation of a renewable polyol [10–12]. However, soybean oil molecules require chemical modification to generate hydroxyl groups. The most commonly used reactions are epoxidation [13,14] with subsequent ring opening [15], oxidation [5], and others [16,17]. The literature has shown that it is possible to obtain polyols with hydroxyl indexes in the range of 60–110 mgKOH/g and low acid index values through air oxidation at 100 °C–120 °C [5,18]. According to the mechanism proposed by Fornof and coworkers, the formation of hydroxyl groups occurs through the consumption of double bonds present in fatty acids in soybean oil molecules [18]. These polyols can also be used in the production of coatings [18] or as secondary plasticizers for PVC [5].

The PU polymerization reaction is, in general, the reaction of isocyanate (NCO) and hydroxyl (OH) groups, and in the reaction with amines, the final product is the urea group. The final material resulting from a combination of these three components is PU–urea [7,19]. This approach can also be used to obtain hybrid materials, in which partial replacement of OH groups by alkoxide silanes such as amino silanes is employed, giving rise to organic–inorganic hybrid materials [20–23].

Such hybrid structures provide unexpected properties derived from unique combinations of the organic and ceramic components [24–26].

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Table 1
Characteristics of the polyols obtained by air oxidation.

Oxidation time (h)	[a]OH index (mgKOH/g)	Acid number (mgKOH/g)	[b]Viscosity (Pa.s)	[c]Density (g/cm^3)	[d]Mn (g/mol)	M_w/M_n	[e]Mol of double bonds per mol of triacylglyceride
0	0.26 ± 0.12	0.63 ± 0.11	0.05	0.92 ± 0.01	1030	1.1	3.90
24	46.35 ± 3.50	3.18 ± 0.21	0.42	0.96 ± 0.01	1591	2.1	1.77
48	58.80 ± 1.70	4.07 ± 0.03	4.20	0.98 ± 0.01	2050	6.9	1.61

[a] Determined using ASTM D4274.
[b] Determined at 25 °C according to literature procedure [5].
[c] Determined using ASTM D1217.
[d] Determined by GPC measurements.
[e] Determined by ^{1}H NMR and literature procedure [38].

The organo-functional silane provides opportunities for the development of hybrids containing inorganic fillers and organic polymers with improved adhesion, mechanical, and tribological properties, such as tensile strength, impact strength, and abrasion resistance [27,28]. The literature shows several routes for the preparation of hybrid materials, but one of the most widely used methods is the sol – gel technique [29]. The attractive features of the sol – gel technique are the generation of an inorganic phase within the organic polymer matrix after moisture-cured hydrolyzed silanol groups undergo condensation, thus leading to crosslinking [30,31]. Through condensation reactions, the alkoxy groups produce crosslink bonds and form a three-dimensional (3D) hybrid network. The 3D network formed is able to increase the chemical stability and resistance to swelling of the organic component [19,30]. The γ-aminopropyltriethoxysilane (APTES) acts as network former in organic–inorganic materials, water is usually needed for the hydrolysis of the alkoxy groups [32]. However, after hydrolysis, condensation reactions take place where hydrolysed APTES molecules react with other APTES molecules through a self-condensation process, or with different molecules containing hydroxyl groups through a condensation reaction [33,34]. Similar behavior occurs with others aminosilane such (3-aminopropyl) trimethoxysilane (APTMS) [35].

The preparation of hybrid materials based on renewable sources has been successfully applied for applications in calcified tissue repair [36] and coatings with excellent thermal stability [37–39]. Allauddin and coworkers [40] have developed hybrid PU–urea films for coating applications using modified castor oil with succinic anhydride. The hybrid phase used was 3-glycidoxypropyltrimethoxysilane, and the 3D network was formed by hydrolysis and condensation of the alkoxysilane molecules. The use of alkoxysilanes in the preparation of hybrid PUs allows the development of materials with good adhesion on aluminum surfaces. Hardness and tensile strength are also improved with increasing amounts of an inorganic precursor [40]. Recently, the same research group obtained PU based on polyol from epoxidized soybeans and subsequently hydrolyzed it for coating applications [41].

The majority of the hybrid materials reported in the references were prepared using castor oil or epoxidized soybean oil [30,31,38,39,41]. In contrast, we propose another production route to polyols, namely, air oxidation, which is a straightforward and inexpensive technique for the production of green materials. Here, we focus on describing the effect of the oxidation time of the soybean oil in the production of hybrid films of PU–urea employing (3-aminopropyl) trimethoxysilane (APTMS) at different concentrations. The relation between the NCO/OH/NH_2 ratios in the hybrid films and their morphological, physicomechanical, and surface properties were investigated. Subsequently, we apply these films on metal surfaces for evaluation of their integrity as coatings. Our research focuses on the development of a novel route to green hybrid composites and their application as coatings, which could be potential candidates for partially or completely replacing petroleum-based PU materials.

2. Materials

Commercially refined soybean oil (Primor, Bunge Alimentos S.A, Brazil) with an acid number of 0.63 ± 0.11 mgKOH/g and 3.90 mol of double bonds per mol of triacylglyceride molecules, a density of 0.92 ± 0.01 g/cm^3, and an average molecular weight of 1030 g/mol (according to the ^{1}H NMR and GPC measurements) was used. Polymeric 4,4′-methylene diphenyl diisocyanate (MDI; CAS number 9016-87-9) with a free isocyanate index of 31.00 ± 1.07% and a mean functionality of 2.7 was supplied by BASF. Also, 3-(aminopropyl)trimethoxysilane (APTMS; CAS number 13822-56-5) was provided by Wanda, China.

3. Methods

3.1. Polyol preparation

The soybean-based polyols were prepared by air oxidation in a round-bottomed flask (1 L), which was mechanically stirred at 250 rpm and maintained at 120 °C ± 1 °C for 24 or 48 h. The induced air oxidation of the soybean oil was carried out using ambient air at a constant flow rate of 25 L/min. This procedure was also used by Ourique and coworkers [5]. Table 1 shows the main characteristics of the soy oil and polyols.

3.2. Polyurethane–urea hybrid material synthesis

3.2.1. Preparation of films

The hybrid materials were prepared in two steps. Initially, the polyol and the APTMS were added to a flask and mechanically stirred at 250 rpm for 5 min at 25 °C. To reduce the viscosity of the medium, distilled acetone was added, maintaining the ratio of monomer to solvent of 30 wt.%. Subsequently, MDI was added to the reaction medium and stirred for 5 min at 250 rpm. Films were prepared by casting the mixture onto a glass plate coated with Teflon. The ratios of the functional groups NCO/OH/NH_2 were maintained at 1.2/1/0, 1.2/0.4/0.6, 1.2/0.5/0.5, and 1.2/0.3/0.7 for the polyols obtained by induced air oxidation for 24 and 48 h. The final polymerization was performed in two steps: one at 60 °C for 12 h and the other for thermal hydrolysis and condensation silanol groups at 160 °C for 1 h. The consumption of the NCO groups during the polymerization was followed by monitoring the FTIR band at 2241 cm^{-1}.

3.2.2. Application to steel plates

The surfaces of carbon steel SAE 1006 (70 mm × 120 mm × 1 mm) were cleaned using aqueous a NaOH 5 wt.% solution, rinsed with Milli-Q water, and dried. The deposition of the PU–urea films on the steel surfaces was performed by dip coating. Subsequently, the final polymerization procedure was performed as previously described. Physicomechanical test, corrosion resistance and in-depth chemical profiles were made of polyurethane-urea coatings deposited on the surface of the steel.