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Properties of alkoxysilane castor oil synthesized via thiol-ene and its polyurethane/siloxane hybrid coating films

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ABSTRACT

We developed a new silanized castor oil (MSCO) composed of castor oil and 3-mercaptopropyl trimethoxy silane via thiol-ene coupling (TEC). This MSCO was used as a functional polyol in the preparation of a series of bio-based polyurethane/siloxane (SiPU) hybrid coatings through reactions with different castor-oil-and-isophorone-diisocyanate (IPDI) ratios. The SiPU films exhibited better mechanical and thermal properties than castor oil-based coatings without MSCO. The cross-linked structure of the obtained hybrid materials was confirmed by Fourier transform infrared (FTIR) spectroscopy, whereas the morphologies and surface roughness of the hybrid-coating films were observed by scanning electron microscopy (SEM). A slight phase separation was observed in the obtained hybrid materials. The introduction of a silica network can reduce the surface energy of the obtained hybrid materials. The thermal stability of the obtained hybrid materials increases with increasing Si content. The obtained hybrid materials can be applied in coatings as a result of these characteristics, and this study provides an alternative method of preparing hybrid materials from renewable sources.

1. Introduction

The replacement of petroleum-based raw materials, which are obtained from finite fossil resources, with renewable resources is a major contemporary challenge in terms of both economic and environmental aspects [1,2]. Vegetable oils are considered to be one of the most important classes of renewable sources that can be used as reliable starting materials to access new products with strong chemical transformation potential [3–7]. The contribution of plant oils to sustainable development not only involves the use of renewable raw materials but also chemical-process transformation [8–10]. The application of environment friendly and highly efficient processes has drawn considerable interest recently [3,8–10]. Thiol-ene coupling (TEC) has emerged as a green methodology, providing new opportunities in the synthesis and modification of polymeric materials with targeted properties [9]. TEC has been used in previous studies to modify plant oils to obtain functional monomers and polymers [3,11–15]. The double bond of plant oils can be functionalized in situ through consecutive TEC with various commercially available, functional thiols such as 2-mercaptoethanol [11] and 3-mercaptopropionic acid [13,14].

Castor oil (CO) is an important renewable resource because of its unique structure. Both its double bond and hydroxyl can be modified. Double-bond modification has not been fully explored until the present time despite the abundance of literature available regarding hydroxyl utilization [16–19]. The double bond in CO reacts with 3-mercaptopropyl trimethoxysilane (MPTS) via TEC in our study. Silanized castor oil (MSCO) contains three important functional groups, namely, long hydrophobic carbon chains, reactive hydroxyl groups, and hydrolyzable methoxysilane groups. The hydroxyl groups are very reactive and easily react with diisocyanate; the methoxysilane groups are easily hydrolyzed to yield hydroxysilane groups; the hydroxysilane groups are capable of self-condensing or reacting with other inorganic substrates containing hydroxyl functional groups; and the long, hydrophobic, carbon chains of fatty acid generate a thick and hydrophobic interface [20].

Vegetable oil-based polymeric materials alone generally do not possess the adequate rigidity and strength required in structural applications [18]. Combining inorganic materials such as silica with bio-based organic polymer matrices can improve overall polymer performance. The sol–gel method is an important technique in organic–inorganic hybrid-material preparation [21,22], and the major advantage of using the sol–gel method is its mild reaction conditions [19,20], such as low temperature. However, silicon is not compatible with polymer matrices. Organic–inorganic hybrid materials are prepared by in situ hydrolysis and alkoxysilane polycondensation reaction

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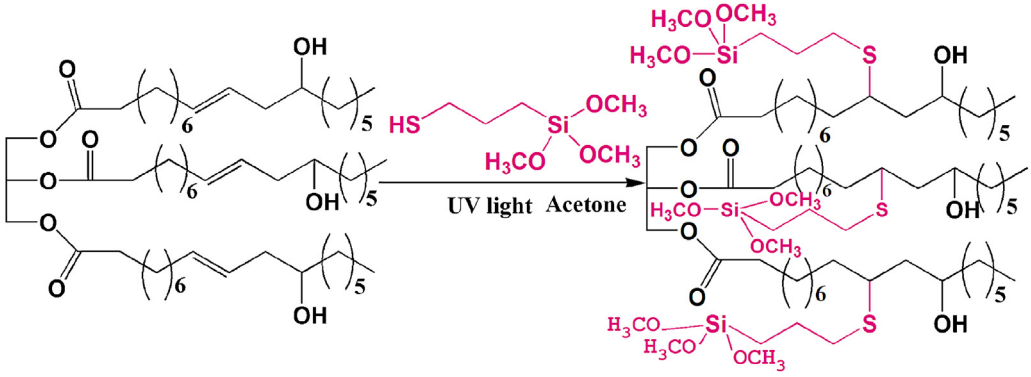

Scheme 1. MSCO preparation.

in organic polymer matrices using the sol–gel process to overcome this drawback [16,17,19,20]. Two main methods are used to introduce the alkoxysilane into the bio-based polymer main chain: one uses 3-aminopropyltrialkoxysilane as an end-capping reagent of CO-based polyurethane (PU) [17,19,21], and the other involves the preparation of vegetable-oil-based monomers containing alkoxysilane through complicated methods, such as through the reaction of maleic-anhydride-carboxylated CO with 3-expoxypropylteriethoxysilane [15] or the reaction of acrylated-epoxidized soybean oil with 3-aminopropylteriethoxysilane [19]. The process of preparing vegetable-oil-based monomers containing alkoxysilane involves a minimum of two reactions. However, CO-based monomer containing alkoxysilane can be efficiently and conveniently prepared via TEC reaction.

CO reacts with MPTS to prepare siloxane-functionalized polyols (MSCO) under UV-light irradiation in this study. MSCO then reacts with CO and IPDI as an alkoxysilane-functionalized-bio-based polyol to generate a series of CO-based polyurethane/siloxane hybrid composites through an in situ sol–gel process. We investigate the influence of siloxane content on the structure and thermal and mechanical properties of SiPU films. The covalent linkages between the organic and inorganic components improve the homogeneity of the silica network within the organic matrix. The SiPU film possesses several advantages, including good thermal stability and excellent hydrophobic property. This work provides an effective and promising green method for preparing bio-renewable, highly efficient PU composites.

2. Experimental

2.1. Materials

CO was obtained from Sigma Aldrich, China; IPDI and MPTS were obtained from Aladdin, China. Dibutyltin dilaurate (DBTDL) and 2-hydroxy-2-methylpropiophenone (UV1173) were obtained from Jiuri Chemical, China. Acetone and chloroform ($CHCl_3$) were obtained from the Beijing Chemical Reagent Factory, China. All materials were used as received, without further purification.

2.2. MSCO synthesis

Scheme 1 shows the method used to prepare MSCO. A reaction mixture of CO (9.33 g, 0.01 mol), MPTS (5.89 g, 0.03 mol), UV1173 (0.08 g), and acetone (30 ml) was stirred at room temperature under UV-light irradiation (1700 μW, 365 nm) for 6–8 h. The reaction was monitored using proton nuclear magnetic resonance (^{1}H NMR) spectroscopy based on the absence of double-bond proton peaks. Excess acetone was removed via rotary evaporation after the reaction, and a pale yellow liquid was obtained. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 5.15 (—C<u>H</u>OCO—), 4.09–4.28 (—C<u>H</u>$_2$CHOCO—), 3.62 (—C<u>H</u>OH), 3.45 (—Si(OC<u>H</u>$_3$)$_3$), 2.44–2.54 (—C<u>H</u>SC<u>H</u>$_2$—), 2.25 (—C<u>H</u>$_2$CO—), 1.87 (—C<u>H</u>$_2$CH$_2$Si(OCH$_3$)$_3$), 0.83 (—CH$_3$), 0.68 (—C<u>H</u>$_2$Si(OCH$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 173.30 (—O<u>C</u>OCH$_2$—), 71.44 (—<u>C</u>HOCO—), 68.83 (—CH$_2$<u>C</u>HOH), 62.07 (—<u>C</u>H$_2$OCO—), 50.83 (—CH$_2$Si(O<u>C</u>H$_3$)$_3$), 45.69 (—CH$_2$SCHCH$_2$CHOH), 42.33 (—<u>C</u>H$_2$CHSCH$_2$—), 41.61 (—<u>C</u>HSCH$_2$—), 40.68 (—CHS<u>C</u>H$_2$—), 14.04 (—<u>C</u>H$_3$), 8.61 (—<u>C</u>H$_2$Si(OCH$_3$)$_3$).

2.3. Castor oil polyurethane (COPU) and SiPU film preparation

The COPU and SiPU hybrid composites were prepared using the formulations summarized in Table 1. The SiPU composites were synthesized in a two-necked, round-bottom flask equipped with a magnetic stirrer and a nitrogen (N_2) inlet. Calculated amounts of CO, IPDI, DBTDL, and $CHCl_3$ were then added to the flask. Subsequently, the mixture was heated to 75 °C for 3 h, and MSCO was then added to react with the mixture for 3 h. Reaction completion was monitored by the absence of free-NCO-group IR absorption at 2270 cm^{-1}. The SiPU film was prepared by placing the mixture on polytetrafluoroethylene (PTFE) plates. The films were cured in a moist atmosphere and humid laboratory conditions for 30 days to conduct SiPu-alkoxysilane-group hydrolysis reactions. For comparison, the sample without MSCO was also prepared. This comparison sample is designated as COPU. The COPU film was obtained by drying at 50 °C for 24 h. The synthetic route of the SiPU hybrid film is shown in Scheme 2.

2.4. Characterization

2.4.1. Attenuated total reflection–Fourier transform infrared (ATR–FTIR) spectroscopy

Infrared spectra were obtained using a Bruker-Vertex70 spectrometer in the attenuated total reflection (ATR) mode. An average of 32 scans of each sample ranging from 4000 cm^{-1} to 650 cm^{-1} was obtained.

Table 1
SiPU-film codes and compositions.

Sample code	Compositions				
	CO (g)	MSCO (g)	IPDI (g)	NCO:OH ratio	Si (wt%)
COPU	1.8668	0.0000	0.6018	1:1	0.00
SiPU1	1.4193	0.8004	0.6018	1:1	1.52
SiPU2	0.9443	1.5225	0.6018	1:1	2.73
SiPU3	0.4667	2.2837	0.6018	1:1	3.76
SiPU4	0.0933	2.8928	0.6018	1:1	4.45
SiPU5	0.0000	3.0450	0.6018	1:1	4.60