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Preparation and properties of waterborne bio-based polyurethane/siloxane cross-linked films by an in situ sol–gel process

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ABSTRACT

Waterborne castor oil-based polyurethane-silica hybrid materials with chemically bonded polymer matrix and silica nanoparticles were designed and prepared. The formation of cross-linking structures in the waterborne polyurethane system was confirmed by Fourier transform infrared spectroscopy. Transmission electron microscopy images indicated that nano-silica was encapsulated by polyurethane and exhibited an apparent core–shell structure. The nano-silica in the polyurethane matrix was vital in improving both the hydrophobicity and thermal stability of the resulting hybrid polyurethane films. With increased silicone content, the roughness, hydrophobicity, and thermal stability of the films were enhanced, but the transparency of the films in the 300–800 nm region was decreased. These results can aid in the design of bio-based hydrophobic waterborne polyurethane films with favorable thermal stability and optical transmittance.

1. Introduction

Nowadays, the field of bio-based renewable polymers continues to grow, and the pursuit for novel bio-based polymers with efficient performance and high renewable carbon content is still one of the main goals in the research and development of inherent bio-based polymers [1]. Plant oils are an important bio-renewable resource of bio-based polymers because of availability and competitively low price [2]. Among the large number of bio-based polymers, plant oil-based polymers have attracted great interest [3]. Through a versatile chemistry method [4–7], plant oils can be modified into various polymerizable bio-based monomers, such as plant oil-based polyols [5,6] and diisocyanates [7], which are the most important components for plant oil-based polyurethanes. Plant oil-based polyurethanes have some advantages, such as the favorable processability, versatile structure–property relationships, and excellent elasticity of the polyurethane films. Previously, fully bio-based waterborne polyurethane dispersions have been prepared successfully by our group through the utilization of carboxylated castor oil as the hydrophilic chain extender and an undecylenic acid-based diisocyanate [7]. Compared with conventional solvent-based polyurethanes, waterborne polyurethanes have been widely used in environment-friendly coatings and adhesives, given that waterborne polyurethanes are nontoxic, non-flammable, and non-air polluting [8–10]. However, because of the introduction of hydrophilic groups, some characteristics such as the water resistance and hardness of the waterborne polyurethane films are inferior to those of solvent-based PUs.

To improve the properties of waterborne polyurethanes, several methods have been explored, such as the introduction of nano-particles [11–24], chemical cross-linking [4], and UV curing [25]. Among these methods, the introduction of nano-particles into the WPUs to obtain organic–inorganic hybrid materials have attracted great interest in the past years, given that this method has significantly improved the mechanical, thermal, and barrier properties. Over the years, many nano-particles such as graphene oxide [11], silica [12–19], attapulgite [20,21], and organoclay [22–24] have been introduced into the waterborne polyurethane system to generate organic–inorganic hybrid materials. Among these nano-particles, nano-silica has provided excellent properties in WPU reinforcement. Recently, many researchers have also attempted to introduce nano-silica into plant oil-based solvent-based polyurethanes through the sol–gel method. The major advantage of the sol–gel method is the mild reaction conditions, such as the low temperature used for preparing silica nanoparticles. However, one drawback of the sol–gel method

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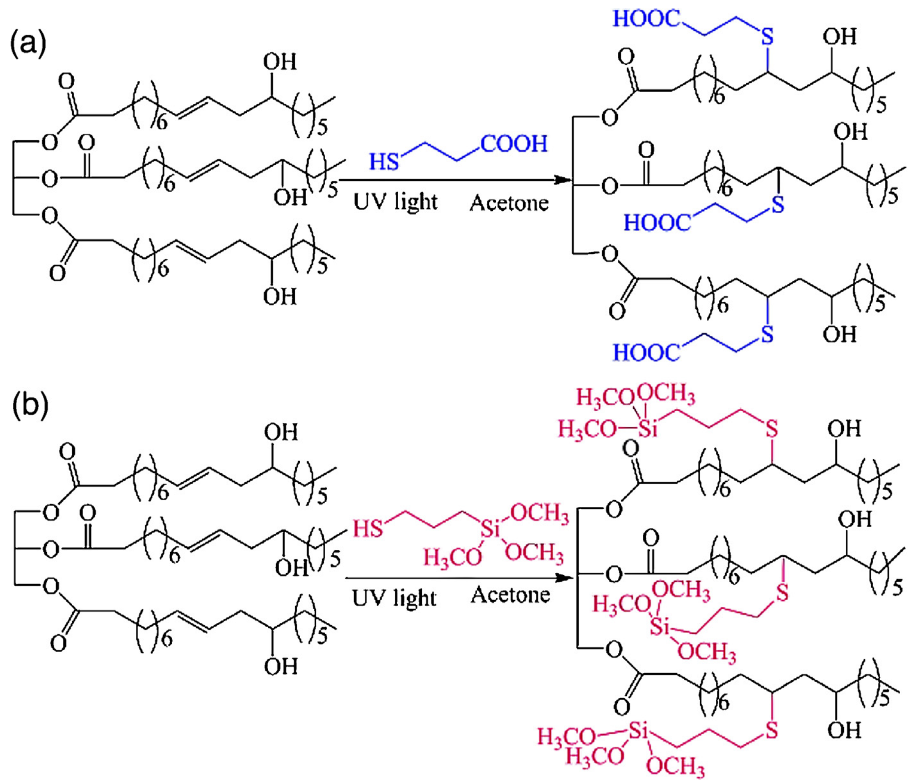

Scheme 1. Synthesis route of (a) MACO and (b) MSCO.

is that the silica is not perfectly compatible with the polymer matrix. To overcome this drawback, some cross-linking agents, such as 3-aminopropyl trimethoxysilane [17–19], are used in situ in the sol–gel method. Allauddin et al. have obtained a polyurethane/urea-silica hybrid coating with favorable properties using 3-aminopropyl trimethoxysilane-modified castor oil and isophorone diisocyanate (IPDI) as raw materials [15]. Mohamed et al. have reported castor oil-based polyurethane/siloxane cross-linked films using 3-aminopropyl trimethoxysilane as the end-capping reagent of the isocyanate terminal castor oil-based polyurethane prepolymer, which exhibited positive thermal stability and optical transmittance [19]. In an earlier study, we have also demonstrated the feasibility of obtaining homogeneous silica hybrid castor oil-based films using alkoxysilane castor oil [26]. Xia et al. prepared waterborne castor oil-based polyurethanes by incorporating silica moieties, using 3-aminopropyl trimethoxysilane as the precursor and crosslinking agent [16]. However, the research on plant oil-based polyurethane/silica hybrid water dispersions remains relatively limited.

In this study, castor oil-based functional monomers, carboxyl castor oil (MACO), and alkoxysilane castor oil (MSCO), are synthesized using castor oil with 3-mercaptopropionic acid (MPA) and 3-mercaptopropyl trimethoxysilane (MPTS), respectively, through the thiol-ene coupling reaction (TEC). The chemically bonded waterborne castor oil-based polyurethane-silica hybrid materials with polymer matrix and nano-silica are then prepared using MACO, IPDI, and MSCO through an in situ sol–gel process. MACO is used as the hydrophilic chain extender agent. MSCO is an organofunctional alkoxysilane monomer that can undergo both sol–gel polymerization of the alkoxy groups and reaction with the NCO functionality in the prepolymer to form a hybrid network with covalent bonds between the organic and inorganic phases. This step is used as an inorganic precursor for the preparation of waterborne polyurethane–silica hybrid coatings. The structure and properties of the obtained dispersion and hybrid films are thoroughly investigated.

2. Experimental

2.1. Materials

Castor oil (CO) was obtained from Sigma Aldrich China; and IPDI, MPA, and MPTS were purchased from Aladdin China. 2-Hydroxy-2-methylpropiophenone was purchased from Jiuri Chemical Co., Ltd. of China. Dibutyltin dilaurate (DBTDL), triethylamine (TEA), $CHCl_3$ and acetone were obtained from Beijing Chemical Works. All the materials were used without any further purification. The water used in this study was deionized and doubly distilled.

2.2. MSCO and MACO synthesis

MSCO and MACO were used as functional polyols for the preparation of the bio-based waterborne polyurethane dispersion. The MSCO and MACO were prepared according to our previous work [7,26]. Scheme 1 shows the synthesis route.

2.3. Preparation of castor oil-based polyurethane/silica (SiWPU) nanocomposites

Scheme 2 shows the method used for the preparation of the waterborne SiWPU. The SiWPU nanocomposites were synthesized in a double-necked, round-bottom flask equipped with a magnetic stirrer and a N_2 inlet. Calculated amounts of MSCO, IPDI, DBTDL, and acetone were then added to the flask. Subsequently, the mixture was heated to 75 °C for 3 h, and MACO was then added to react with the mixture for 3 h. The completion of the reaction was monitored through the absence of the NCO-group IR absorption at 2270 cm^{-1}. After confirming the completion of the reaction,