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Research paper

Synthesis and characterization of soy polyol-based polyurethane nanocomposites reinforced with silylated palygorskite

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ABSTRACT

Soy polyol-based polyurethane (PU) nanocomposites were synthesized with 3-glycidoxypropyltrimethoxysilane modified palygorskite (GPTMSPal). The GPTMSPal PU nanocomposites were characterized using XRD, DMA, TGA, SEM, and universal test machine. GPTMSPal increased the glass transition temperature as well as significantly improved tensile strength and Young's modulus of the GPTMSPal PU nanocomposites. Compared to neat PU, GPTMSPal PU nanocomposite with 12 mass% GPTMSPal exhibited a 13.1 °C increase in the glass transition temperature, a 303% improvement in tensile strength, and a 518% increment in Young's modulus, respectively. TGA results showed that the thermal stability of GPTMSPal PU nanocomposites improved with increased GPTMSPal loading. Furthermore, SEM revealed a uniform dispersion of GPTMSPal in the PU matrix.

1. Introduction

In recent years, the use of vegetable oils as platform chemicals for polyurethane (PU) synthesis has attracted great academic and commercial research interests because of their attractive properties related to the specific structures of the oils, as well as concerns about the environment and sustainability (Desroches et al., 2012; Lligadas et al., 2010; Petrovic, 2008). Vegetable oils are predominantly made up of triglyceride molecules containing reactive sites like ester groups and double bonds, and in some oils other groups such as hydroxyl may be available. Vegetable oils can be converted into polyols by various methods, such as epoxidation followed by ring-opening (Findley et al., 1945; Guo et al., 2000), hydroformylation (Guo et al., 2002), ozonolysis (Petrovic et al., 2005) and transesterification (Schuchardt et al., 1998). The resulting polyols can partially replace petroleum-based polyols crosslinked with different isocyanates to prepare PU materials. PU derived from vegetable-oil-based polyols can potentially combine the excellent properties of PU with the biocompatibility and biodegradability of vegetable-oil-based polyols (Petrovic et al., 2010).

Since the pioneering use of nylon–clay nanocomposites in Toyota cars (Kojima et al., 1993; Usuki et al., 1993), a great deal of effort has been devoted to the development of clay polymer nanocomposites (CPN) (Alexandre and Dubois, 2000; Bergaya et al., 2013; Chen et al., 2008; Galimberti et al., 2013; Gilman, 1999; LeBaron et al., 1999; Liu, 2007; Ray and Okamoto, 2003). The incorporation of clay into the PU matrix can significantly improve the comprehensive performance of CPN (Barick and Tripathy, 2011; Shi et al., 2009). As a hydrated magnesium aluminum silicate, the palygorskite (Pal) is an ideal reinforcing agent for CPN due to its fibrous morphology with large surface areas and reactive –OH groups on the surface (Bradley, 1940). The key to obtain superior CPN is to disperse the individual Pal into polymer matrix (Salahuddin et al., 2010). The surface modification of Pal is beneficial to improve Pal dispersion and load transfer efficiency. Silanes are usually recognized as efficient coupling agents extensively used in CPN, which can create a chemical bridge between the reinforcement and matrix (Xie et al., 2010). So far, there are limited reports focused on the synthesis of polymer nanocomposites from silylated Pal (Sun et al., 2009; Wang and Sheng, 2005; Wang et al., 2013; Xue et al., 2006; Zuo et al., 2013).

In previous study, the effects of acid activated and silane coupling agent (γ-methacryloxypropyltrimethoxysilane) modified Pal loading on the properties of soy polyol-based PU matrix were studied (Wang et al., 2012; Wang et al., 2014). The aim of this work was to determine the effect of the 3-glycidoxypropyltrimethoxysilane modified palygorskite (GPTMSPal) on the properties of GPTMSPal

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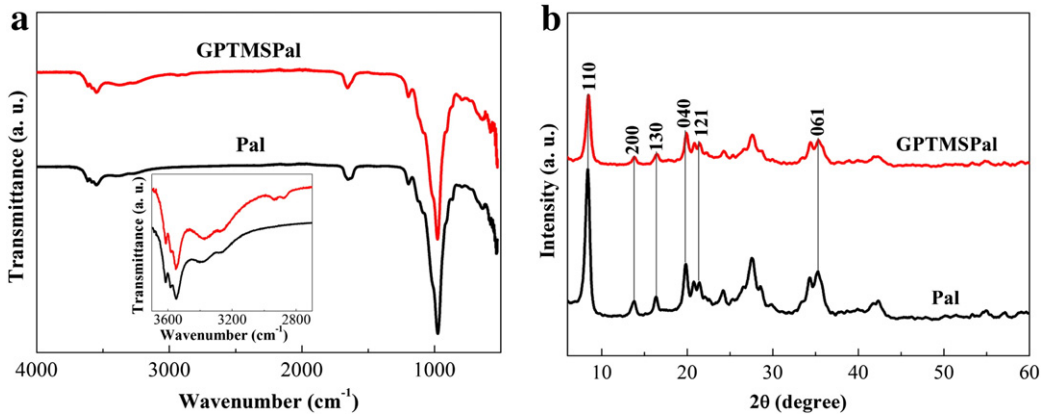

Fig. 1. FT-IR spectrum (a) and XRD pattern (b) of Pal and GPTMSPal.

PU nanocomposites derived from soy polyol. The morphology, thermal and mechanical properties of GPTMSPal PU nanocomposites have been thoroughly investigated by various characterization techniques.

2. Experimental

2.1. Materials

Epoxidized soybean oil (ESO) containing 5.9% oxygen was provided by the Xiamen Vive Material Co., Ltd. (Xiamen, China). Analytical-grade methanol, isopropyl alcohol, ammonia (30%), acetone, toluene, and tetrafluoroboric acid (48%) were all purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Silane coupling agent (3-glycidoxypropyltrimethoxysilane, GPTMS) was supplied by the Trustchem Silanes Co., Ltd. (Nanjing, China). The raw Pal with an average diameter of 11.4 μm (1250 mesh) was obtained from the Jiangsu Golden Stone Palygorskite R&D Co., Ltd. The chemical composition (mass%) of the raw Pal determined by X-ray fluorescence spectrometer (ARL-9800) is as follows: SiO_2 67.6; MgO 13.1; Al_2O_3 10.1; Fe_2O_3 5.8; K_2O 1.2; TiO_2 1.1; CaO 0.6; P_2O_5 0.3; and MnO 0.1. Isophorone diisocyanate (IPDI) was supplied by Crendva Speziaichemie, Germany.

2.2. Preparation of GPTMS modified Pal (GPTMSPal)

The raw Pal was dispersed in toluene to form 5 mass% dispersion by an ultrasonic treatment for 30 min. Isopropyl alcohol/GPTMS/water mixture solution (72/20/8, v/v/v) was adjusted with acetic acid to set pH value to 3–4. This solution was then blended with the Pal dispersion for 4 h refluxing under electromagnetic stirring at 110 °C. Finally, the product was filtered and washed thoroughly with toluene and acetone. The obtained GPTMSPal was dried at 120 °C in vacuum for 12 h.

2.3. Preparation of GPTMSPal PU nanocomposites

The details of the synthesis of soy polyol were described in previous reports (Dai et al., 2009). The polyol-based ESO with 5.9% oxygen was prepared by oxirane ring opening with methanol and the hydroxyl number of polyol was 168 mg KOH/g. The neat PU was prepared from the polyol with IPDI using previously reported methods (Wang et al., 2009a,b). The prepared PU was shortened as PU168. The GPTMSPal PU nanocomposites were prepared as follows: the GPTMSPal was dispersed in dry acetone by sonication (60 min, 100 W). The soy polyol was added to the GPTMSPal dispersion and stirred vigorously for 24 h at 30 °C. Then the solvent acetone was evaporated at 80 °C. After cooling to room temperature, the IPDI was added to the solution and the mixture was stirred for another 30 min. The mixtures with different GPTMSPal loadings were poured into a polytetrafluoroethylene mold, which was left under vacuum to evacuate bubbles and then were thermally treated respectively at 90 °C for 2 h and 110 °C for 24 h to complete the reaction. The samples were then naturally cooled down to room temperature and remolded. The resulting CPN were denoted as GPTMSPalx-PU (x is the GPTMSPal mass percentage in the CPN).

2.4. Characterization and measurement

The Fourier-transform infrared (FT-IR) measurements were performed with a Thermo Nicolet iS10 FT-IR spectrometer using the attenuated total reflectance (ATR) technique. X-ray diffraction (XRD) study was carried out on a Shimadzu XRD-6000 using crystal monochromated Cu K_α radiation over the range of $6° < 2\theta < 60°$ at a scanning rate of 6°/min.

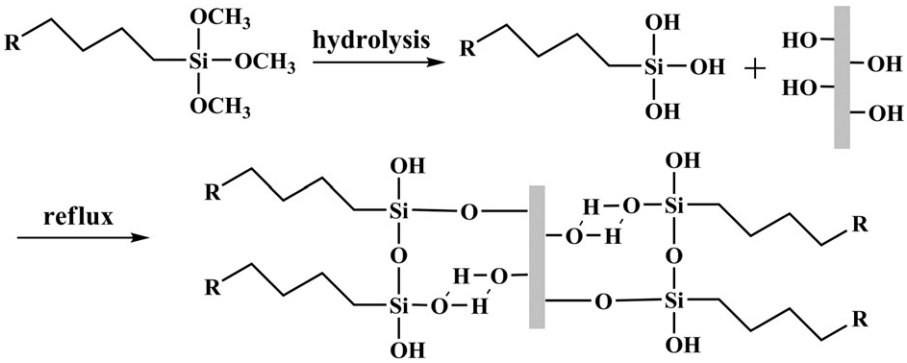

Fig. 2. Schematic representation of reaction between GPTMS and Pal surface.