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Hybrid film properties of the linseed oil based alkyd resin modified with glycidyl polyhedral oligomeric silsesquioxane

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ABSTRACT

A simple strategy was developed for the modification of linseed oil-based alkyd resin with glycidyl polyhedral oligomeric silsesquioxanes (GPOSS) to obtain a hybrid material. The incorporation of GPOSS into alkyd resin was done by simultaneous reactions between hydroxyl groups coming from ring-opened epoxides of GPOSS and partial glycerides and carboxylic acid groups of phthalic anhydride. The obtained hybrid material has significantly improved film properties and thermal stabilities compared to unmodified neat alkyd resin. Notably, the samples containing 5% GPOSS showed better film properties such as flexibility, adhesion, drying time, resistances to alkali, acid and water. Thus, this product can be used as an oil-based binder.

1. Introduction

Hybrid materials based on incorporation of nano-sized inorganic particles into polymer matrices have gained considerable attention due to consisting of advantages of organic and inorganic fractions, such as lightweight, flexibility, high thermal stability and good impact resistance, processability and chemical resistance [1–5]. Principally, two different approaches can be used for the formation of hybrid materials: i) well-defined preformed building blocks are reacted with each other to form the final hybrid material in which the precursors still at least partially keep their original integrity and ii) one or both structural units are formed from the precursors that are transformed into a novel network structure [6].

Alkyd resins are the polyesters which are obtained by esterification of polyols with polycarboxylic acids. The resins prepared in this way are brittle and can not be employed as a coating material. Due to this fact, oils were used to modify the alkyd resins [7–12]. Because of the long chains of the fatty acids incorporated into the resin matrix, the brittleness is prevented and the film becomes flexible. Actually, the vegetable oils are very versatile materials for oil-based binder production. Besides giving flexibility, they provide additional crosslinking through the oxidative polymerization. In the coating industry, the most commonly used oil-modified alkyd resins include drying (linseed) or semi-drying (sunflower, soybean etc.) oils for enhancement of the drying characteristics of films [11–14]. In the oil modified alkyd resins production, fatty acid chains are inserted to the structure by two different processes namely the fatty acid process and the monoglyceride process [11]. In the present study in order to improve the film properties, oil-based alkyd resin was further modified with polyhedral oligomeric silsesquioxane (POSS).

The POSS nanoparticles are three-dimensional oligomeric, organosilicon compounds with cage frameworks surrounded by functional groups on the periphery [15–17]. POSS monomers have been recently drawn much attention in the preparation of nanohybrid composites due to their excellent contributions such as integrability to polymer matrix, high oxidation resistance and providing high glass transition temperature [17–26]. There are a few reports for the synthesis of hybrid materials from vegetable oil-based resin and multi-functional POSS structures [27–29]. In these studies, photocrosslinking reactions of thiol-functionalized POSS with acrylate-modified castor oil [27], methacrylate-functionalized POSS with methacrylate-modified camelina oil [28] and glycidyl-functionalized POSS with epoxidized linseed oil [29] were carried out. However, there has been no report on the synthesis of thermally cured hybrid materials based on alkyd resin modified with POSS monomer in view of coating purposes. Consequently, in the present study, it was found to be worth working to use POSS in the modification of alkyd resin.

In the present study, a series of hybrid materials were synthesized through typical linseed oil alkyd resin (LA) by modification with different glycidyl polyhedral oligomeric silsesquioxanes (GPOSS). The

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Table 1
A typical alkyd resin formulation modified by linseed oil.

Step	Ingredient	Part by Weight (g)
First Step	Oil	2000
Partial Glycerides	Glycerol	580
Preparation	Lime	2
Second Step	Phthalic anhydride	1400
Polyesterification		

formulation of LA which was used in modification process was taken from literature [30]. In the process, the GPOSS molecules were chemically linked to LA by means of esterification reaction between the hydroxyls formed by ring-opening of epoxides and partial glycerides with phthalic anhydride. The obtained GPOSS modified linseed oil-based alkyd resin was found to be applicable as an oil based binder.

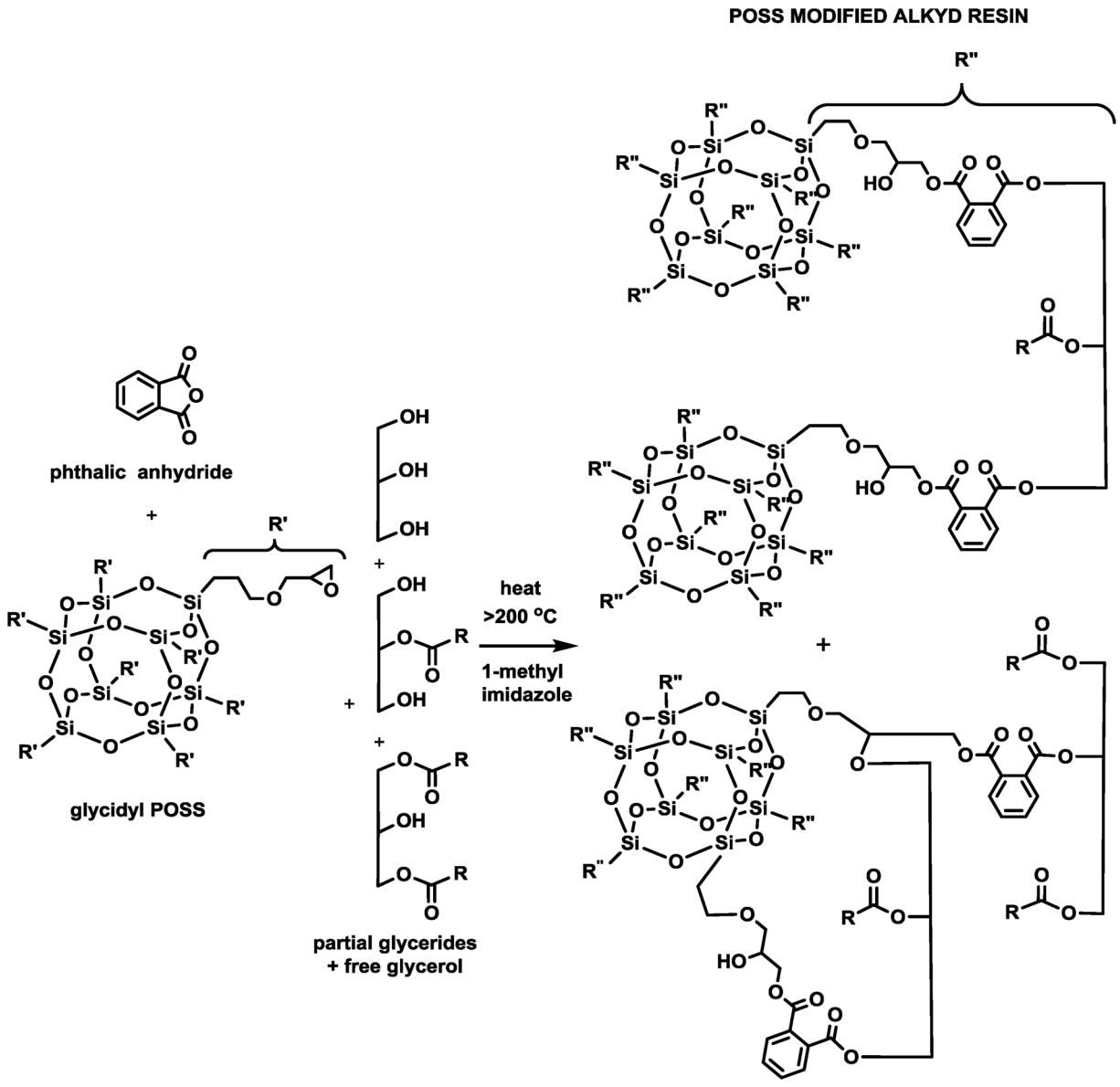
2. Material and methods

2.1. Materials

Commercially purchased linseed oil was used as the oil component. 1-Methylimidazole (1MI, 99%, Aldrich), glycidyl POSS (GPOSS, cage content ≥65%, Hybrid Plastics) phthalic anhydride (PA, 99%, Merck), toluene (Reagent European Pharmacopoeia, Merck), acetone (Reagent European Pharmacopoeia, Merck), glycerol (> 99.5%, Merck) and calcium hydroxide (99%, Merck) were used as received.

2.2. Methods

FT-IR spectra were recorded on a Perkin Elmer FT-IR Spectrum One B spectrometer. ^{1}H-NMR spectra were recorded on an Agilent NMR System VNMRS 500 spectrometer at room temperature in $CDCl_3$ with Si $(CH_3)_4$ as an internal standard. Differential scanning calorimetry (DSC) was performed on an ExStar SII DSC 7020 at a heating and cooling rate of 10 °C min^{-1} under a nitrogen atmosphere in the temperature range 25–250 °C. The values were reported from the second heating cycle. Thermal gravimetric analysis (TGA) was performed on ExStar SII TG/



Scheme 1. The route of modification of LA with GPOSS.