UV-Curable, Seed Oil-Based Coatings by Free-Radical Photopolymerization: Part 1

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This is the first of a two-part series.

A number of seed oil-based, UV-curable coatings have been synthesized and reacted via UV-initiated, free-radical polymerization. These UV-curable, seed oil-based coatings include acrylated tung oil (UVTO), tung oil alkyd (UVTA) and norbornene linseed oil (NLO). Both the chemical structure and coating properties were investigated. Not only UV-curable clear coatings, but also pigmented and inorganic/organic UV-curable hybrid coatings were developed. A schematic model for UV-curing hybrid coatings was proposed.

Introduction

Environmentally benign coatings have been the focus of attention for many years.[1,2] With increasing environmental regulations, there has been a growing interest in radiation-curable monomers and many natural products have been modified to be UV-curable materials. The natural reactivity, inherent low viscosity[3] and ease of modification of seed oils make this type of binder a superior candidate for environmentally benign coatings.[4,5] Naturally occurring seed oils are mainly triglycerides consisting of a mixture of saturated oleic, linoleic and linolenic fatty acid. They represent a biomass alternative technology that is in need of modification to be competitive with modern polymeric binders. Seed oils such as tung oil and linseed oil have traditionally been used as drying oils and raw materials for alkyd resins.[6] Tung oil has been used as a protective coating for hundreds of years. The primary usage of tung oil is as a wood varnish. Advantages of using tung oil as a coating include faster drying time, higher water resistance and higher hardness compared to unconjugated drying oil (such as soybean oil).[6,7] In addition, since tung oil is conjugated, it can more easily be chemically modified to achieve desirable properties.

Free-radical polymerization of acrylic monomers initiated by UV radiation has been drawing much attention in coating applications—and it has been increasingly important in recent years. This is mainly due to the extensive use of this process in photoactive polymer-based systems.[8] This process has a large source of available raw materials. It also has extremely fast curing rates, well-known chemical reactions, and high or 100% solids content. In a free-radical, photopolymerizable formulation, the photoinitiator decomposes into free radicals when it is irradiated by UV light and then the crosslinking reaction leads to the formation of a three-dimensional network. The drawback of free-radical photomerization is the oxygen inhibition. However, the surface curing can be obtained by high rates of radical polymerization not only to consume oxygen located at the

FIGURE 1

Chemical structures of tung oil and UV-curable tung oil (UVTO)

150 °C, 1.5 hr
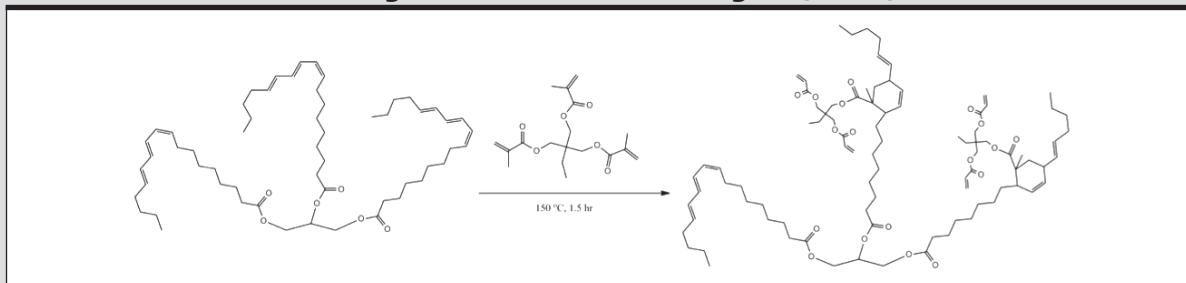
surface, but also to overcome the rate of oxygen diffusion in resins.[9]

In the past few years, our group of researchers has developed and studied a series of UV-curable, seed oil-based coating materials, especially tung oil and linseed oil-based, UV-curable coatings. In this paper, UV-curable coatings crosslinked by free-radical photopolymerization are discussed. UVTO and UVTA are crosslinkable through an acrylate group. Thiol-ene photopolymerization of NLO and a new thiol siloxane colloid was also developed and studied for the UV-curable organic/inorganic hybrid coatings.

Tung Oil-Based, UV-Curable Clear Coatings

Free-radical-based photocuring—in particular, acrylate or methacrylate monomers—has advantages of fast cure along with industrial acceptance.[10] Since tung oil contains ~80% α-eleosterate, and, thus, has conjugated double bonds, tung oil functions as a moderately active diene. A number of modified drying oils have been prepared with various dienophiles.[11,12] Our group developed UV-curable, tung oil-based coatings by free-radical photopolymerization. A synthetic scheme for UVTO and UVTA are shown in Figures 1 and 2.

UVTO and UVTA were prepared by reacting trimethylolpropane trimethacrylate (TMPTMA) onto the α-eleosterate of a tung oil and tung oil alkyd molecule via a Diels-Alder reaction. The reactions were conducted at elevated temperature and atmospheric pressure. An inhibitor (phenothiazine) was added to avoid homopolymerziaton of TMPTMA. The UVTO and UVTA were formulated with a free-radical reactive diluent, tripropylene glycol diacrylate (TPGDA), and photoinitiator Irgacure 2100. Photocuring kinetics of the UVTO and the UVTA were investigated by Photo-DSC. The change of heat flow as a function of time from DSC thermogram proved the capability and, thus, demonstration of the concept of UV-curing for both UVTO and UVTA. The UVTO and UVTA were characterized by ^{1}H NMR, ^{13}C NMR, MALDI-TOF mass and Gel Permeation Chromatography (GPC). Details about the synthetic chemistry and characterization can be found in the previously published papers.[13,14]

It is important to note that drying oils and alkyds are complex mixtures that are exceedingly difficult to characterize with the degree of certainty that a single reactant can be characterized. The fact that the triacrylate group can react with one or more of the eleosterates was observed in the propensity to gel. However, when the reaction conditions were controlled, the Diels-Alder reaction

could be used to functionalize both tung oil and tung oil-based alkyd. The high content of α-eleosterate (~80 wt%) of tung oil triglyceride is considered a major source of conjugated diene, while the acrylate molecule is a decent dienophile. The carbonyl group on acrylate serves as an electron-withdrawing group, which plays an important role by lowering the activated energy of the reaction. The study by Trumbo and Mote[12] also reported the Diels-Alder cycloaddition between tung oil and diacrylate monomers, 1,6-hexanediol and 1,4-butanediol diacrylate, at elevated temperature without catalyst. However, the resultant products in their study were copolymers of tung oil and diacrylate.

Our group used a trifunctional acrylate instead of a diacrylate monomer. The flexibility and lack of steric hindrance of the previously reported diacrylate system were the primary factors in telechelic-acrylic end groups reacting with the diene. In contrast, after the first Diels-Alder reaction of the triacrylate with the α-eleosterate, the subsequent Diels-Alder reactions were sterically hindered. This left the remaining two acrylic groups available for UV-polymerization. Maleic anhydride was introduced onto the tung oil molecule via a Diels-Alder reaction

FIGURE 2

Chemical structures of tung oil alkyd and UV-curable tung oil alkyd (UVTA)
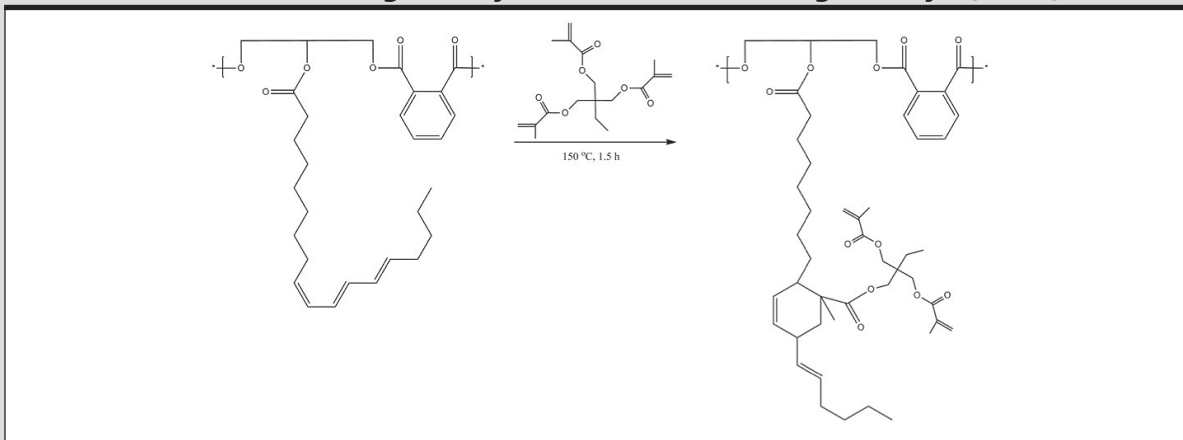
and then esterified with ethylene glycol to form tung oil-modified polyol. This polyol was formulated with a cycloaliphatic epoxide and cured. In contrast, the modification of tung oil for UV curing reported by our group was based on free-radical polymerization of the acrylate group. Although there have been UV-curable derivatives of drying oils, this study was the first UV-curable tung oil alkyd in the literature. It is hoped that the concept of UV-curable alkyd will have great potential for widespread use in the field of coatings. Both the UV-curable drying oil and alkyd represent a considerable step forward in the replacement of solvents for the compliance of both North America and European environmental regulations.

Tung Oil-Based, UV-Curable Pigmented Coatings

Besides the UVTO and UVTA clear coating, our group also developed and investigated the UVTA-based pigmented coatings.[14] Alkyd resins today are still one of the most important classes of coating resins. They are used in both clear and pigmented coating. UV-curing technology would result in low energy consumption and no volatile organic compounds. Formulation of pigmented UV-curing coatings has been a major challenge since the earliest stage of their development, mainly due to the reflection and absorption characteristics of pigment particles. Pigments prevent sufficient penetration of UV energy to efficiently activate the photoinitiated crosslinking reaction, resulting in the amplification of the cure gradient in the film, which is responsible for the creation of wrinkles on the film surface.

A complete pigmented formulation was developed based on UVTA in our previously published paper.[14] A variety of reactive diluents were selected to be formulated with the UVTA, such as TMPTMA, TPGDA, propoxylated trimethylolpropane triacrylate (POTMPTA), propoxylated neopentyl glycol diacrylate (PONPGDA), neopentyl glycol diacrylate (NPGDA), 1,6 hexanediol dimethacrylate (HDMA), dicyclopentadienyl methacrylate (DCPDMA), lauryl acrylate (LA), isodecyl methacrylate (IDMA) and isobornyl acrylate (IBOA). The color of yellow was chosen. The light source, photoinitiator and reactive diluent were evaluated and optimized for both through-cure and surface cure. After curing, pencil hardness, conical mandrel, impact resistance, cross-cut adhesion and gloss were measured. In addition, the viscoelastic properties of the optimized formulations were investigated.

An important aspect of pigmented coating—and especially UV-curable coating—is the degree of pigment dispersion. The dispersion was checked for each coating formulation via personal observation and a rub test. There are also numerous methods that have been employed to quantify degree of dispersion,[15] but most of them are comparative rather than absolute and some of them depend on factors other than dispersion (e.g., gloss).[16] To validate the observation, the degree of dispersion was determined by optical microscope and scanning electron microscope (SEM) as shown in Figure 3. It is observed in both micrographs that the pigment is well dispersed.

According to Burrel,[17] Basu,[18] Payne,[19] Wicks and Chen,[20] wrinkles usually originate from the curing gradient of the film, high cure rate at the surface and low cure rate at the bottom. Therefore, an ideal solution to eliminate wrinkles is to decrease the

cure rate at the surface and increase the cure rate at the deeper level. However, it is difficult to separately control the cure rate of the two parts. A fundamental approach is to adjust the cure speed of the whole system by reducing or increasing the cure functionality. According to our results,[14] lowering the cure speed of the systems is a better way to minimize the curing gradient since all the formulations with multifunctional monomers produce wrinkling films at pigment levels around 8.2 wt%, while those formulated with the monofunctional monomers do not. Consequently, it was decided to exclude the multifunctional monomer from the later work.

The UVTA was formulated with a mixture of pigments, reactive diluents, photoinitiators, dispersing additive and silicone additive to create a UV-curable, alkyd-based pigmented coating. Through-cure limited the maximum pigment level in formulations to 14 wt%. High quality pigment dispersions were obtained. A monofunctional monomer, isodecyl methacrylate (IDMA), was found to impart excellent flexibility, impact resistance and adhesion to the metal substrate. Using a combination of initiators—IRGACURE 819 at ~2 wt% and DAROCUR 1173 at ~2-4 wt%— with UVTA and IDMA, a pigmented coating with a good balance of film properties could be prepared.

Linseed Oil-Based, UV-Curable Hybrid Coatings

NLO can be photopolymerized and used in UV-curable coatings and inks. However, without reactive dilution, the NLO suffers from a sluggish reaction rate. Therefore, it would be very beneficial to develop a novel functional oligomer that can enhance the polymerization rate of seed oil derivatives. A new thiol siloxane colloid was developed for UV-curable inorganic/ organic hybrid films by our group.[21]

Multifunctional thiol siloxane oligomer was prepared by the sol-gel method from mercaptopropyltrime-thoxysilane (MPTS). The formation of MPTS/NLO hybrid film involves the simultaneous polymerization either by thiyl radical with norbornylized linseed oil or directly by reaction between the reactive –SH groups in thiol siloxane oligomer with cyclic-olefin bonds in norbornylized linseed oil. There is a large fraction of –SH reactive groups in the MPTS oligomer that could increase the rate of UV-curing polymerization and the crosslink density. These –SH reactive groups are distributed throughout the inorganic particles and could bond inorganic particles to the organic phase. Therefore, it is anticipated that the MPTS colloids will function as a hyperbranched crosslinker. A model for UV curing of MPTS/NLO hybrid films is shown in Figure 4. In this model, silica cluster is embedded in the norbornene linseed oil matrix through the chemical bonds connected to organic matrix. A partially inter-locked network was formed by the crosslinked norbornene linseed oil. It would be reasonable to assume that the highest crosslink density would be located around the periphery of the MPTS colloid.

The kinetic data indicated that as the content of MPTS colloid was increased, the value for the integrated exotherm increased and reached a maximum at 15 wt% and 10 wt% MPTS colloid loading with a light intensity of $60mV/cm^2$ and $200mV/cm^2$, respectively. These results showed that norbornenes were quite sensitive to the amount of thiol and the thiyl radical, and the MPTS thiol colloid could greatly increase the

FIGURE 3

Representative optical image of pigment dispersion and SEM image of pigment dispersion via cross-sectional view
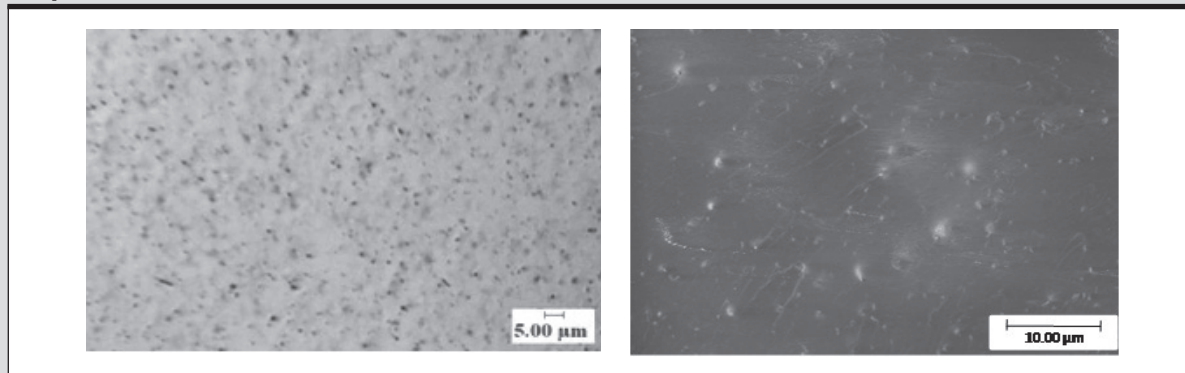
UV-curing polymerization activity of NLO. This was probably due to the low steric hindrance of the norborynl alkene which induces a complicated stereoelectronic effect. In addition, the reaction of the thiol or thiyl radical to the cyclic olefin is less reversible. The conversion rate of cyclic olefin with MPTS colloid loading was much faster than the one without MPTS colloid; and the polymerization rate of MPTS/NLO systems was significantly

FIGURE 4

Schematic models for UV curing MPTS/NLO hybrid film
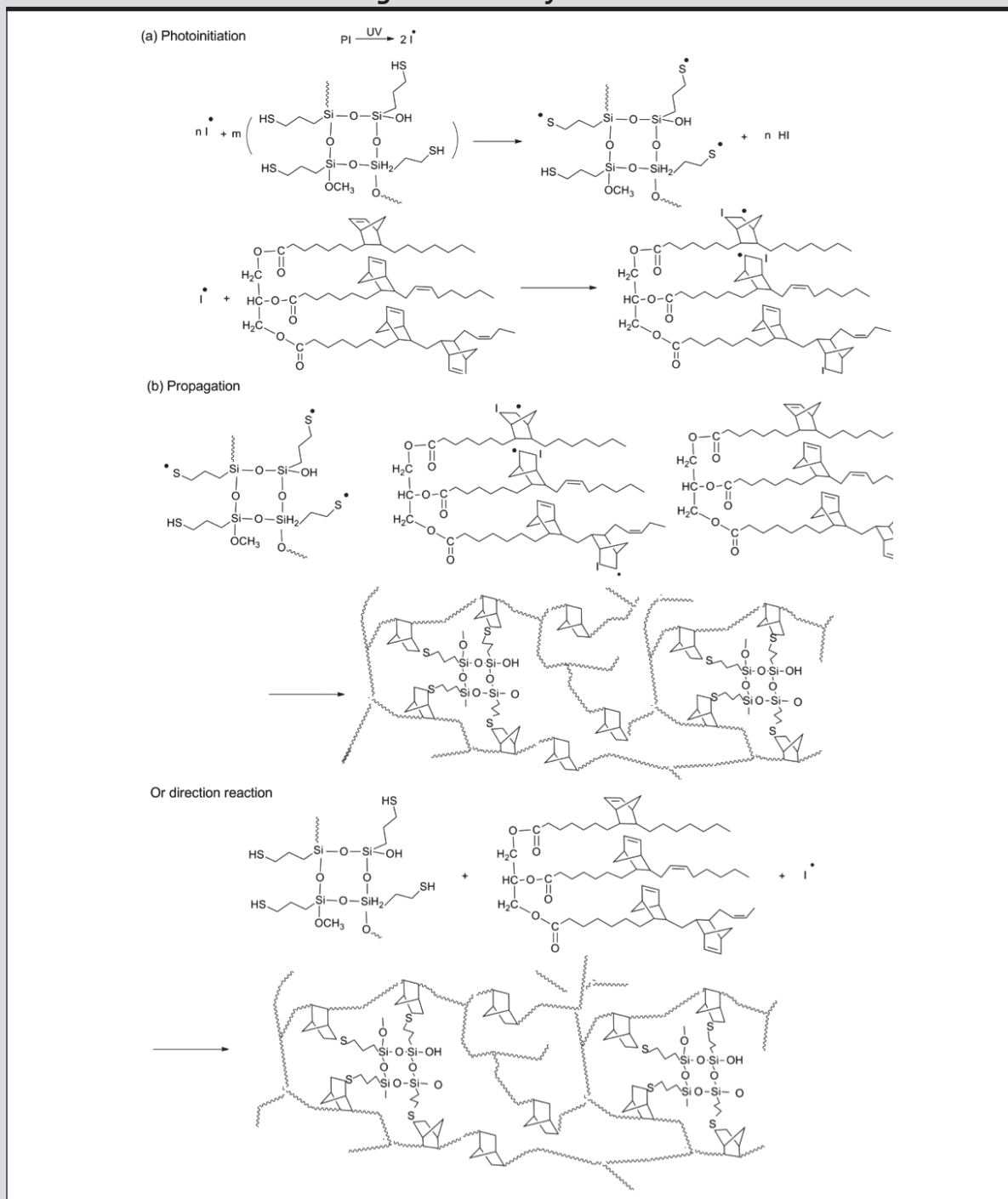
affected by MPTS colloid since MPTS colloid acted as a photoinitiator and a hyperbranched crosslinker. These results were consistent with results from photo-DSC. The final conversion of thiol was lower than that of cyclic olefin, which could be explained by the fact that NLO could homopolymerize under free-radical condition. With thiol siloxane MPTS colloid loading, high photocuring rate, high cure content and high crosslink density was achieved compared with the pure NLO systems. MPTS thiol siloxane oligomer could be used in an extensive range of UV-curable, organic-inorganic hybrid systems.

Summary

With the efforts of materials scientists, renewable and environmental friendly seed oil-based materials have already showed promising application in the coating industry. In the past few years, our group has focused on tung oil- and linseed oil-based, UV-curable coating materials' development and properties studies. A series of UVTO and UVTA were synthesized and studied. The UV-curable clear coatings as well as the UV-curable pigmented coatings and inorganic/organic hybrid coatings were developed and investigated. Much work was done to optimize coating properties. With this knowledge, it is just the beginning of modifying natural source materials and applying them to coating industries. There is still a long way for coating chemists and formulators to go to exploit the new materials in nature and make them "green" coatings. ◗

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