

UV-Curable, Seed Oil-Based Coatings by Cationic Photopolymerization: Part 2

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A number of seed oil-based, UV-curable coatings have been synthesized. These UV-curable, seed oil-based coatings are mainly crosslinked by cationic photopolymerization, including epoxynorbornene linseed oil (ENLO) and epoxidized linseed oil (ELO). Both the chemical structure and coating properties were investigated. Organic clear coatings and inorganic/organic, UV-curable hybrid coatings were studied. Mechanisms for the photoinitiated cationic polymerization of ENLO were proposed.

Introduction

In order to reduce the dependence on petroleum as a chemical feedstock for coatings, there has been a push to develop new classes of coating resins and reactive diluents from renewable resources. Biological resources may be a way to reduce cradle-to-grave pollution. The inherent low viscosity,¹ natural reactivity and ease of modification of seed oil make this type of binder a superior candidate for environmentally benign coatings.^{2,3} In fact, vegetable oil derivatives such as alkyds and epoxy esters are widely used as low-cost coatings.⁴ Seed oils (such as tung oil and linseed oil) have traditionally been used as drying oils and raw materials for alkyd resins.⁵ Linseed oil has one of the highest drying indexes of the most common drying oils conventionally used in the paint and varnish industry.

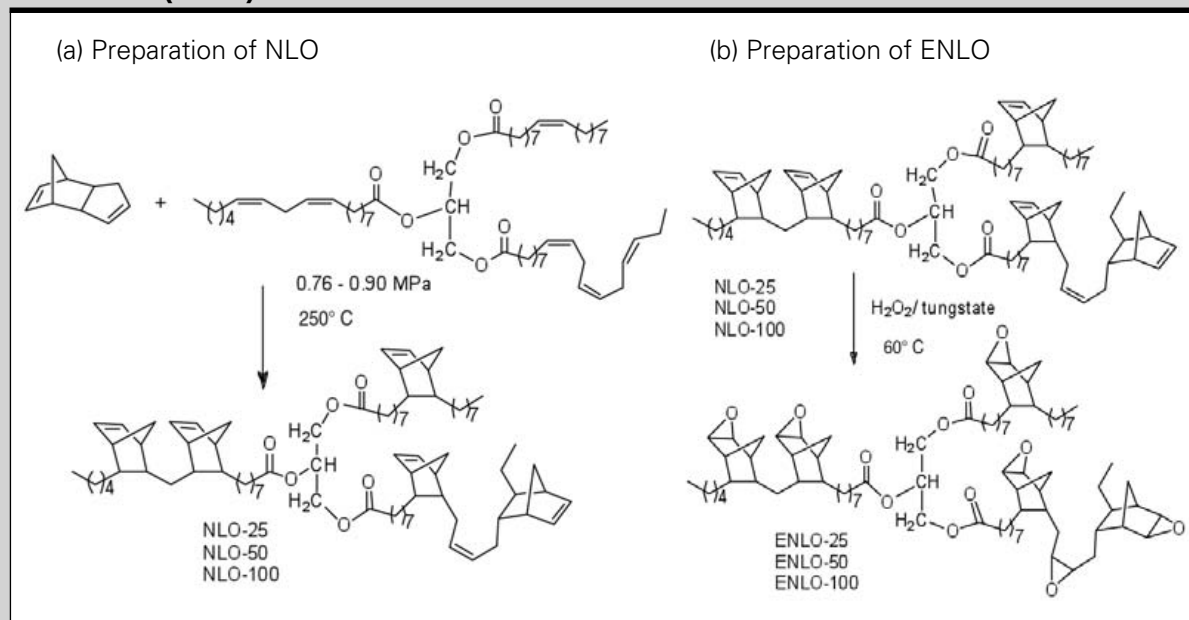
The carbon-carbon double bond on oleic, linoleic and linolenic fatty acid can be epoxidized by reaction with peroxyacids, dioxirane or hydrogen peroxide. Epoxidized oils are also used as inks. However, epoxidized seed oils have found only modest application in specialty coating systems.⁶

Cationic photopolymerization has been used in ring-opening polymerization of epoxy systems and other strained ring systems.² Cationic systems have the advantage of absence of oxygen inhibition compared to free-radical photopolymerization and improved metal adhesion.⁷ Cationic chemistry is relatively more expensive and cure systems can be sensitive to humidity. However, the cationic photopolymerization once initiated may continue to proceed after the light source has been removed, called “dark reaction.” This is due to the ability of the relatively long-lived acid species to continue the polymerization without radiation.⁸

In the past few years, our group has developed and studied a series of UV-curable, seed oil-based coating materials, especially linseed oil-based, UV-curable coatings. These coating materials were basically crosslinked by UV-initiated cationic polymerization. In this paper, coating materials based on linseed oil were synthesized and characterized, including epoxynorbornene linseed oils and epoxidized linseed oils.

FIGURE 1

Preparation of (a) norbornene linseed oil (NLO) and (b) epoxynorbornene linseed oil (ENLO)



Synthesis of Linseed Oil-Based, UV-Curable Coatings

As we know, an epoxy group can undergo cationic photopolymerization with a photoinitiator. Epoxidized seed oils are used as reactive diluents⁹ and toughening materials for commercial epoxy resins.¹⁰ However, epoxidized seed oils were associated with a slow cure rate. The Diels-Alder reaction is the most widely employed synthetic method for producing cyclic ring systems. A major limitation of the Diels-Alder reaction is the intrinsic slowness and inefficiency of reactions for electronically neutral addends. This has resulted in considerable interest in developing methods for both activated and inactivated Diels-Alder reactions. Lewis acids catalyzed reactions of dienophiles activated by carbonyl or nitrile groups or electron-transfer catalyzed reactions occurring via cation-radicals have been previously reported.^{11, 12}

Photopolymerization of epoxides is strongly dependent on the structure of the monomer. Glycidyl esters are less reactive than glycidyl ethers, which are less reactive than epoxidized seed oil. The most reactive monomers are cycloaliphatic epoxides due to their larger ring strain as compared to the other epoxides.¹³ Based on the previously reported reactivity, it is proposed that epoxy norbornyl group would show higher photopolymerization rate than epoxidized seed oils. Partially norbornylized linseed oil (Dilulin) was commercially available. However, it only has 0-3 norbornyl groups per triglyceride.

Our group has developed a series of norbornyl epoxidized linseed oils that have a higher number of norbornyl epoxide functional groups on each molecule. These norbornyl epoxidized linseed oils were synthesized via a high-pressure and high-temperature

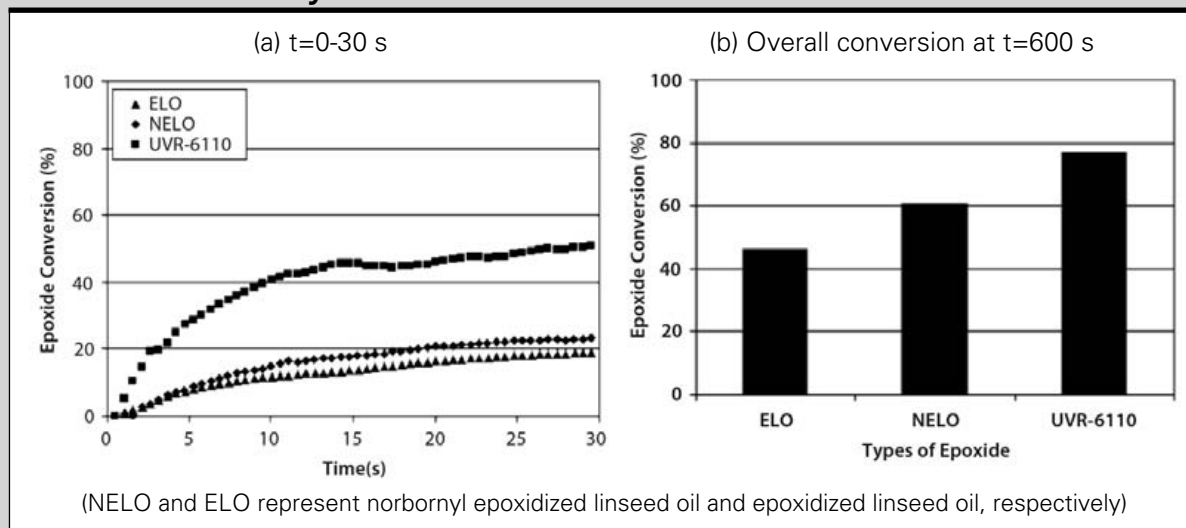
Diels-Alder reaction, followed by the epoxidation with hydrogen peroxide. The reaction scheme is shown in Figure 1. Details about the chemistry and structure characterization can be found in our previously published paper.¹⁴

Mechanisms for the Cationic Photopolymerization of Linseed Oil-Based, UV-Curable Coatings

A comparison of the UV-curing kinetics of the epoxidized linseed oil, norbornyl epoxidized linseed oil and cycloaliphatic epoxide (UVR-6110) is shown in Figure 2. Norbornyl epoxidized linseed oil showed a higher UV-curing rate and overall epoxide conversion than epoxidized linseed oil due to the higher ring strain. However, norbornyl epoxidized linseed oil has a lower curing speed and overall conversion than UVR-6110. For example, at 600 seconds after UV irradiation, the overall epoxide consumption for

FIGURE 2

Effect of types of epoxide on curing reaction, with a 3.5 s exposure and a 20% relative humidity



UVR-6110 was 76.6%, but for the norbornyl epoxidized linseed oil it was only 60.5%. The higher curing speed of UVR-6110 was attributed to the less steric hindrance of the cycloaliphatic oxirane ring¹³ and the lower viscosity in comparison with norbornyl epoxidized linseed oil. The lower viscosity increased the mobility of both the monomer and the growing polymer chain, which led to the higher curing speed and overall epoxide conversion.

We also synthesized norbornyl epoxidized linseed oil with a varied degree of norbornylation and studied the effects of the reactive diluents (vinyl ether) and nonreactive diluents on the photopolymerization kinetics. A series of epoxy norbornene linseed oils (ENLO) were prepared as a function of norbornene content via Diels-Alder reaction.^{14, 15} The cationic photopolymerization of the ENLOs was extensively investigated using real-time infrared spectroscopy and photo-DSC. The chemical structures of a cationic photoinitiator used in the formulation are shown in Figure 3. The effects

of reactive diluents and nonreactive diluents on the polymerization rate were also studied. The reactive diluents were found to decrease the viscosity of formulation and accelerate the rate of polymerization of ENLO and increase their final conversion. The effected reactive diluents were

compared for ENLO and ELO. It was observed that the relative reactivity of oxiranes was not as important as the viscosity of the reacting system and the cationic photopolymerization of ENLO was controlled by diffusion.

There are three pathways for the homopolymerization of ELO-type

FIGURE 3

Chemical structure of cationic photoinitiator used in the formulation

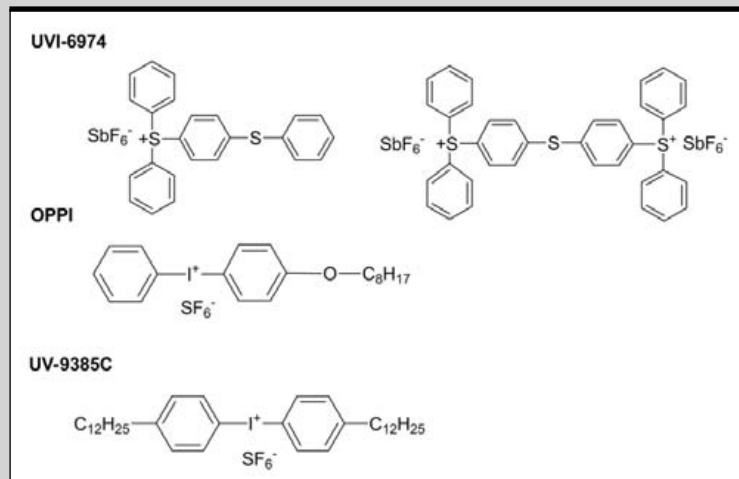
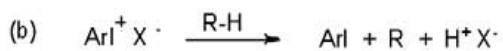
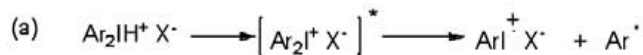


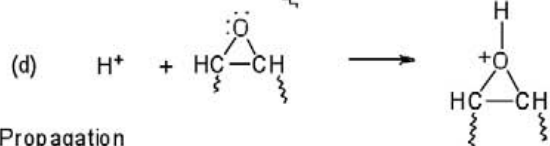
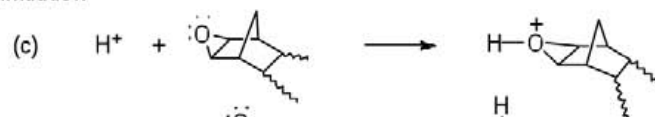
FIGURE 4

Proposed mechanisms for the photoinitiated cationic polymerization of ENLO

Photolysis of Photoinitiator



Initiation



Propagation

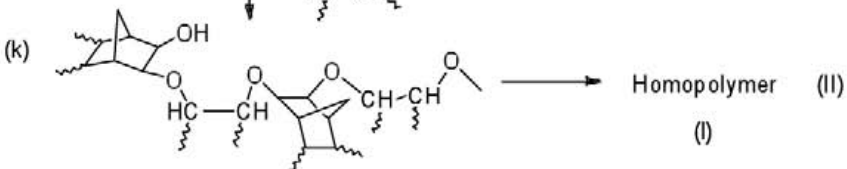
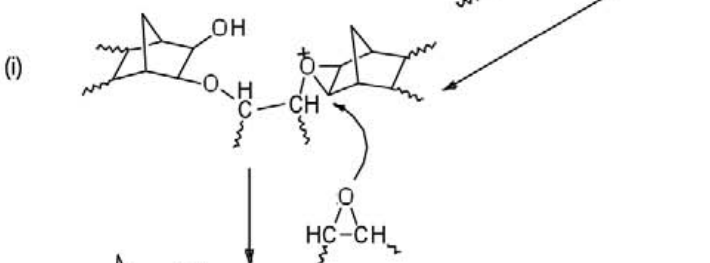
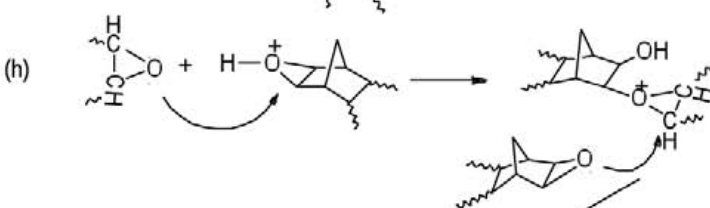
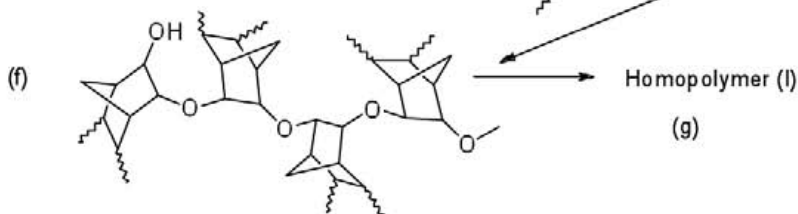
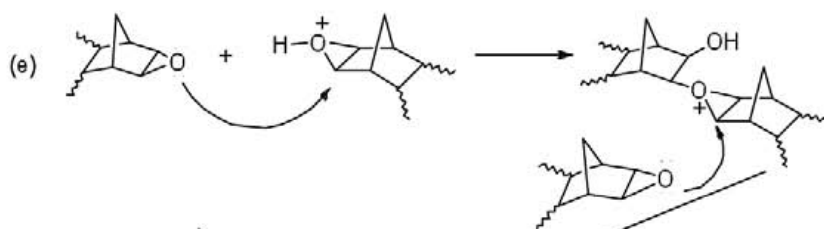


TABLE 1

Physical properties and tack-free cure speed of ENLO and ELO

	EEW ^a	Weight of epoxy (%)	M _n	M _w /M _n	Viscosity (Pa·s)	Tack-free cure speed (m/min)		
						UVI-6974	OPPI	DDI-9385C
ELO	175.3	24.54	924	1.06	0.62	6.10	12.28	10.20
ENLO-25	262.2	16.40	1,127	1.05	2.92	4.88	7.62	6.10
ENLO-50	279.4	15.40	1,189	1.06	4.92	4.26	7.62	6.10
ENLO-100	327.8	13.12	1,326	1.05	22.30	3.04	5.08	5.08

a: Epoxy equivalent weight

oxiranes—homopolymerization of ENLO oxiranes and copolymerization of ELO and ENLO oxiranes. It was found that the greater the ratio of acyclic oxirane groups (ELO type), the less steric hindrance during propagation. In previous published data, Crivello and coworkers found that epoxyoxirane functional monomers were slightly less reactive than monomers with analogous structures containing the epoxyhexane functional group.¹³ The lower reactivity was attributed to the greater steric hindrance present in the epoxyoxirane monomers. In contrast, we found that ENLO photopolymerization is faster than ELO photopolymerization in the presence of a reactive diluent.¹⁵

The proposed mechanism for the cationic ring-opening polymerization of ENLO is shown in Figure 4 (page 33). The protonation of the epoxy group by the superacid (HSbF₆) to generate oxiranium ions (c, d) should be very fast. Subsequently, the initiation of cationic polymerization should occur through nucleophilic attack of an epoxide monomer on the oxiranium ions to form trialkyl oxonium ions (e, h). During homopolymerization, the trialkyl oxonium ions were attacked by other oxirane molecules and chain propagation occurs (f, i, k) to form polyether chains.

Formulations containing different ENLO or ELO samples and 4.0 wt% photoinitiator were prepared to measure the reactivity of these epoxy resins. The ENLO was poorly compatible with UVI-6974. It was presumed that the polar onium salt had poor interaction with the nonpolar structure of alkyl chain.¹⁶ In contrast, OPPI and DDI-9385C have good solubility in ENLO. The tack-free cure speed data is also listed in Table 1. The ELO displayed higher tack-free cure speed than that of ENLO.

The kinetics studies of epoxy conversion versus irradiation time were obtained by real-time Fourier transformed infrared (RT-FTIR). The conversion of epoxy groups at a given time and rate of photopolymerization can be calculated.¹⁵ The slope ($R_p/[M]_0$) of the curve gives a measure of the relative rates of photopolymerization of ENLO and ELO. The R_p of ELO was 8.16 mol L⁻¹s⁻¹, while the R_p of ENLO-100 was 2.06 mol L⁻¹s⁻¹ within 20 seconds of exposure. The RT-FTIR indicated the rate of cationic photopolymerization of ELO is faster than that of ENLO. The reactivity order without reactive diluents was ELO > ENLO-25 > ENLO-50 > ENLO-100. These results were corroborated by “tack-free” cure speed from the conveyor of the UV processor

and Photo-DSC studies that indicate the very short irradiation time did not initiate ring-opening polymerization. Longer irradiation time was required to form enough of the reactive species to initiate the ring opening of epoxide. The ring-opening polymerization was then able to proceed in the dark to afford high degrees of conversion. This dark polymerization clearly demonstrated the presence of long-lived propagating species in the cationic-photoinitiated polymerization of epoxides.

The addition of reactive or nonreactive diluents reduced the viscosity of formulations and was found to have a significant effect on the epoxy conversion and the rate of polymerization of ENLO. Results from RT-FTIR indicate that both the rate of polymerization and the epoxide conversion increased with increasing content of reactive diluents, which is consistent with the previous reports.^{17,18} The nonreactive diluents also exhibited an acceleration of the ring-opening polymerization of the epoxide groups in the presence of di-(ethylene glycol) diethyl ether (DEGDDE) which does not contain the reactive vinyl functionality.

When a formulation contains 20 wt% DEGDDE, the initial rate of polymerization is slower than the rate of the neat ENLO-100. However, the

final epoxide conversion was higher than the neat ENLO-100. The slowing of the initial photopolymerization rate may be attributed to the ether bond of DEGDEE which competes with oxiranium ion formation. The higher epoxide conversion may attribute to the mobility of reactive species in propagation or termination step as the nonreactive diluents increased. In order to eliminate the effect of functional groups in the diluents on the rate of polymerization and the epoxy conversion, and to further clarify the viscosity effect, a nonreactive diluent (decane) was introduced into the formulation of ENLO. The rate and the conversion of the epoxide ring-opening polymerization of ENLO increased as the amount of decane was increased. The reduced viscosity of the formulation facilitates diffusion of the reactive species.

As the viscosity increases, diffusion of oxiranium ions and epoxide monomers is significantly suppressed. Although the epoxynorbornane groups have higher strain energy than that of alicyclic epoxy groups, this can be offset by the diffusion process. The viscosity of ENLO-100 increased 36 times higher than ELO. It was proposed that the high initial viscosity of ENLO affects the diffusion of reactive species and reduces the mobility of monomers. The diffusion control was supported by the RT-FTIR experiments performed with or without reactive diluents.

The cure rate of ENLO-25 or ENLO-50 was faster than that of ENLO-100 for the UV-curable system. Without reactive diluents, ENLO reacted slower than ELO. The ENLO reactivity was proportional to norbornyl content (without reactive diluents) and the relative reactivity

was also found to be proportional to viscosity. As viscosity of the ENLO systems was decreased with diluents, the rate of photopolymerization increased. The mechanism of photopolymerization suggested that the different reactivity between ENLO and ELO was attributed to a diffusion of active species with the acceleration effect of diluents on the rate of photopolymerization of ENLO being dependent on the viscosity of formulation.

Photo-DSC was also used to characterize the reaction kinetics and determine the rate constants and propagation lifetime for cationic photopolymerization.¹⁵ The rate of polymerization of the formulations can be determined directly from the heat released from the photopolymerization under isothermal conditions. The short peak time to the maximum exotherm

FIGURE 5

Tensile properties of hybrid films as a function of TEOS oligomers—(a) tensile modulus, (b) elongation-at-break and (c) tensile strength

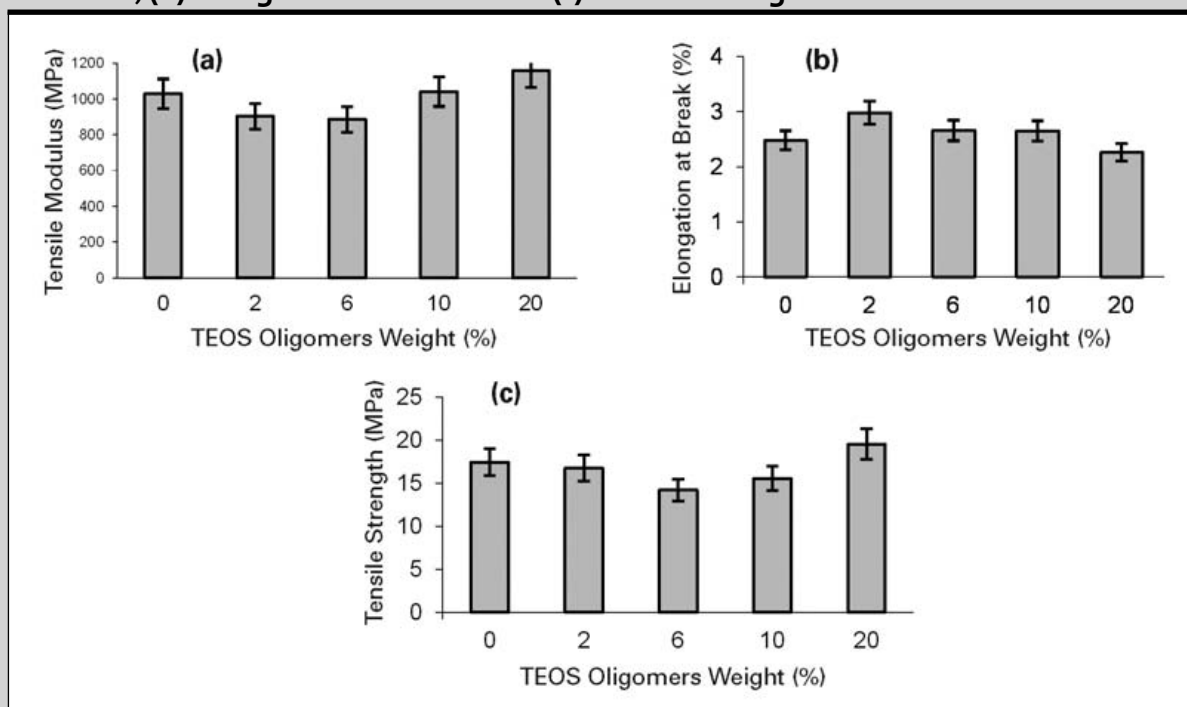
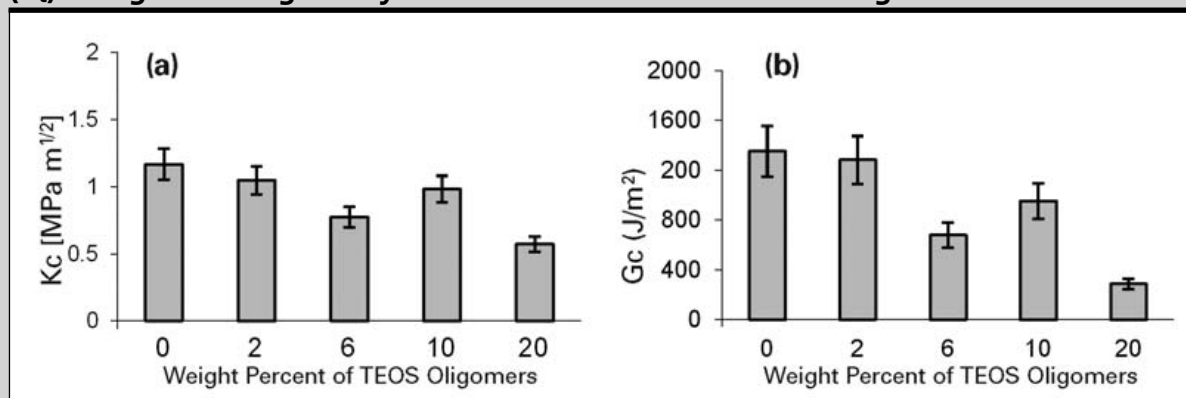


FIGURE 6

(a) Fracture toughness (K_c) and (b) energy release rate per unit crack area at fracture (G_c) of organic/inorganic hybrid films as a function of TEOS oligomers content



indicated fast initiation and fast propagation. The value t_{\max} was able to qualitatively evaluate the relative reactivity of monomers. The time to reach the maximum exothermic peak for ELO, ENLO-25, ENLO-50 and ENLO-100 was 63.8, 73.7, 74.3 and 74.9 seconds, respectively. The results indicated that ELO has higher reactivity than that of ENLO without diluents.

Linseed Oil-Based, UV-Curable Hybrid Coatings

Organic/inorganic hybrid coatings provide improved abrasion resistance, chemical resistance, adhesion and mechanical properties.^{19, 20} We have studied UV-curable organic/inorganic hybrid film based on epoxynorbornene linseed oil (ENLO) that prepared using the *in-situ* method of TEOS oligomers and also a new thiol siloxane colloid.^{21, 22} The sol-gel technique of alkoxy silanes is one of the useful methods to prepare organic/inorganic hybrid materials.^{20, 23-25} The advantage of the sol-gel technique is that the reaction proceeds at ambient temperature to form ceramic materials compared to the traditional methods at high temperature.

Three levels of norbornylation of linseed oil (25, 50 and 100%) were studied by our group.²¹ The effects of TEOS oligomers on ENLO film properties (such as Young modulus, tensile strength and elongation-at-break) and the coated film properties (pencil hardness, impact resistance, adhesion, chemical resistance and contact angles) were investigated. The tensile strength, elongation-at-break and modulus of the hybrid films as a function of TEOS oligomers are shown in Figure 5. The plane-stress fracture toughness (K_c) and energy release rate per unit crack area at the fracture (G_c) of ENLO films and hybrid films as a function of content of TEOS oligomers are shown in Figure 6. A fracture toughness instrument was designed in our laboratory. It consisted of a micrometer stage of the microscope, stationary clamp and movable clamp. The plane-stress fracture toughness (K_c , stress intensity factor at fracture) was calculated using the following equation²⁶

$$K_c = \sqrt{3.94 \left(\frac{2w}{\pi a} \right) \tan \left(\frac{\pi a}{2w} \right)} \sqrt{a \left(\frac{F}{[w-a]b} \right)}$$

where w is the specimen width, b is specimen thickness, a is notch depth

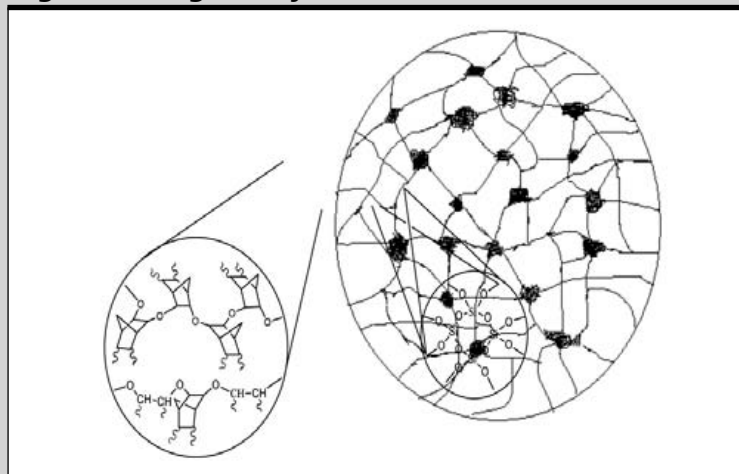
and F is the load at which crack propagation begins. The energy release rate per unit crack area at fracture (G_c) can be calculated by the following equation^{26, 27} $G_c = K_c^2 / E$ where E is the tensile modulus. The energy release rate was calculated using the average values of fracture toughness and tensile modulus. The tensile modulus decreased from 1,029 MPa to 885 MPa with addition of 6 wt% TEOS oligomers. After which, the tensile modulus increased from 885 MPa to 1,157 MPa as TEOS oligomers were loaded to 20 wt%. The tensile strength displayed a similar trend as the tensile modulus. The elongation-at-break decreased as the level of TEOS oligomers was increased to 20 wt%. Fracture toughness and the energy release rate are a measure of resistance to crack extension. The results indicated that cured ENLO film had higher fracture toughness than that of hybrid films. The fracture toughness of hybrid films decreased from 1.17 to 0.57 MPa m^{1/2}, when the content of TEOS oligomers increased from 0 to 20 wt%. This result suggested that the cured ENLO film changed from a ductile to a brittle material after loading with TEOS oligomers.

The organic/inorganic hybrids involve either inorganic phase formation within organic phase or a simultaneous polymerization of both organic and inorganic reactive groups. The simplified model of the hybrid films can be envisioned as a crosslinked silica gel of various sizes embedded in the organic matrix. Since these are acid-catalyzed, sol-gel reactions, a large fraction of $\equiv\text{Si}-\text{OEt}$ and $\equiv\text{Si}-\text{OH}$ groups distributed throughout these inorganic particles. The ring-opening polymerization of epoxylinseed oil proceeds efficiently in the presence of a photogenerated protonic acid to form a polyether. It is proposed that the hydroxyl groups generated from the ring-opening polymerization of epoxy groups would react with the ethoxyl or silanol groups on the silica network to form a “tethered” structure between the organic and inorganic phase.

The interactions between organic phase and inorganic phase, especially the “tethered” structure, improve the compatibility of the silica gel and ENLO phase and would result in the production of a higher crosslink density as compared to the cured ENLO film. Higher crosslink density should translate to higher hardness and modulus, and lower elongation. The higher modulus of the hybrid films can be explained by poor flexibility and low fracture toughness. The results from tensile properties, fracture toughness and dynamic mechanical analysis indicated that hybrid films that had smaller amounts of the TEOS oligomers (<6 wt%) results in lower modulus. While at higher content of TEOS oligomers (>20 %), the hybrid materials had a higher modulus. However, the hybrid films also became brittle and the resistance to crack extension of hybrid films decreased. At this point, the ceramic character of the inorganic phase begins to dominate

FIGURE 7

A model structure of the UV-curable organic/inorganic hybrid film



the mechanical behavior of the coatings. The formulations including ~10 wt% TEOS oligomers provided optimum balance for the properties of hybrid films such as Young's modulus, tensile strength, thermomechanical properties, fracture toughness and general coating properties.

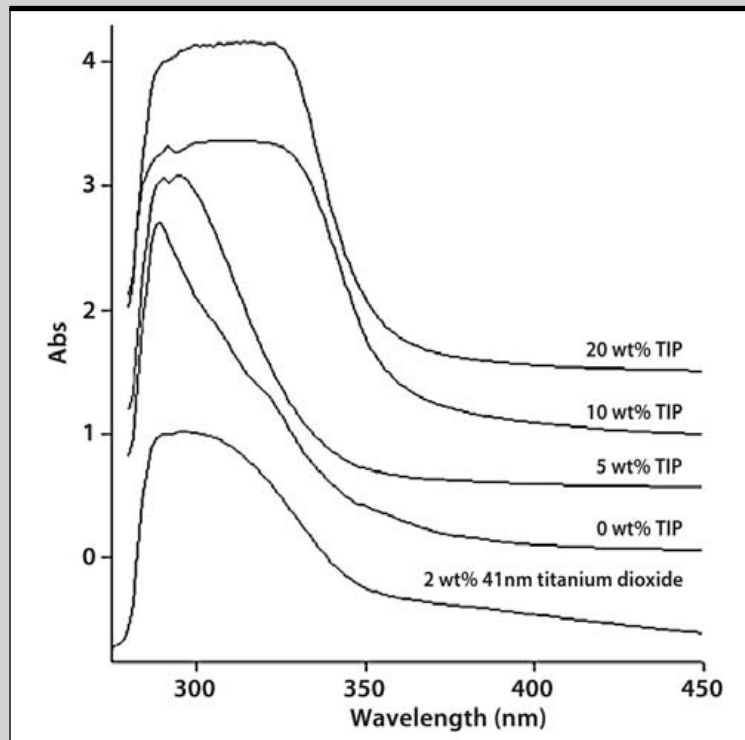
The morphology of UV-curable organic/inorganic hybrid materials prepared with a cycloaliphatic epoxide adduct of linseed oil with tetraethylorthosilicate (TEOS) oligomers via a cationic UV-curing process was also studied in our previously published papers.²⁸ A schematic model for the UV-curable hybrid films is proposed and shown in Figure 7. The scattered small dark regions represent the silicate-rich domain and the connecting lines represent the organic crosslinked polymers formed by the photopolymerization of ENLO. A similar model of such hybrid materials has been proposed by Wilkes.²⁹ Their model structure described the highly condensed silica “cluster” connecting with organic-rich matrix (tether structure), which may not

truly illustrate the hybrid materials structures. Since the UV-curing process is a very fast ring-opening polymerization, not all of the reactive groups such as ethoxyl and silanol would react with hydroxyl groups. Therefore, except the “tethered” structure, the silica gel formed by highly self-condensed TEOS oligomers embedded into the polymer matrix (ENLO).

Titanium dioxide and epoxidized linseed oil-based organic/inorganic coating was also developed and studied by our group.³⁰ The hybrid coating was prepared by titanium sol-gel precursor and UV-curable epoxidized linseed oil. The premise of this approach is that the photolytically generated super-acid would concomitantly initiate crosslinking in the organic phase (epoxidized linseed oil) and catalyze the sol-gel process forming the inorganic phase. This research provides a method to form nano-sized titanium-oxo-cluster with cluster sizes < 2 nm without measurable agglomeration. To our knowledge, this is the first time that a titanium sol-gel precursor has been photocured to

FIGURE 8

UV-Vis Spectra of UV-cured epoxidized linseed oil containing 0 to 20 wt% titanium (IV) isopropoxide (TIP) and 2 wt% 41 nm TiO₂ particles.



form a UV-blocking/absorbing ceramer film. The co-continuous organic/inorganic network maintains physical permanence, improved toughness and optical clarity (visible light). Amorphous ceramer composites that are transparent to visible light and can block UV light can be used as a UV filter for optics. Also, control of titanium-oxo-cluster size can lead to exploration of the edge of TiO₂ photonic properties.

The UV-Vis absorbance spectrum of the cured ceramer films as a function of sol-gel precursor concentration is shown in Figure 8. The films appear to be dependent on the concentration of TIP and are comparable in absorbance to the films cured with titanium dioxide nanoparticles. The ELO film has a strong absorbance at 285 nm

that can be attributed to carbonyl chromophores in the respective medium. Upon addition of 5 wt% TIP, a second narrow peak appears near 300 nm. When the percentage of TIP is increased from 5 to 10 wt%, the absorbance increased from 280 to 360 nm. The broadening peak can be attributed to the sum of individual auxochromic shifts associated with various structures formed during the organic titanium oxide oligomerization. At higher concentrations, the same broad peak is observed with a proportional increase of intensity. Between 5 and 10 wt%, the transition from a narrow absorbing peak to a broad absorbing peak is associated with the hydroxyl concentration of the ELO. At 5 wt%, there is insufficient TIP to overcome the

hydroxyl concentration resulting in the transesterification of TIP to form ELO-TIP bonds. At greater than 5 wt% TIP concentration, Ti-O-Ti bonds can form resulting in auxochromic shifts.

Summary

UV-curable, seed oil-based materials combine the advantages of being renewable and environmentally benign to make them a great choice for coating materials. In the past few years, our group has focused on various linseed oil-based, UV-curable coating materials development and properties studies. A series of UV-curable ENLO and ELO were synthesized and studied. UV-curable organic coatings and inorganic/organic hybrid coatings were investigated. A lot of research was done on optimum properties of coatings, such as Young's modulus, tensile strength, thermomechanical properties, fracture toughness and general coating properties. The UV-curable hybrid films exhibited higher coating properties compared to the organic coatings. This work proved the possibility of modifying natural source materials and applying them to coating industries. ▀

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