Novel "Green" UV-curable Oligomers – Leveraging Chemistry for Delivering Value

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For sustainable development, UV-cure systems must reduce their dependence on petrochemical feedstock. Our research has focused on development of vegetable oil-derived UV-curable oligomers. A novel family of oligomers containing > 70% bio-based content has been developed for both cationic and free-radical UV-cure applications. Specifically, these soybean oil-based oligomers have acrylate or oxirane, and/or silane functionality, with controlled molecular architecture. Using unique dual -cure chemistry, organic-inorganic hybrid nano-composite coatings have been developed with remarkable performance. Effect of functional group type and content, cure conditions and formulation parameters on the characteristics of these UV-cured hybrid films will be discussed. The study demonstrates successful incorporation of bio-based materials in advanced UV-cure coatings – a step toward reducing their environmental foot print.

Introduction

Over the past few decades, coating technology has undergone significant transformation in terms of usage of types of materials and processes, primarily driven by the need to comply with increasingly stringent environmental regulations. Among the compliant technologies that have been successfully commercialized are water-borne coatings, high-solid coatings, powder coatings and radiation cure coatings. Radiation cure technology and more specifically the Ultraviolet (UV)-cure technology has emerged as one of the most promising one due to the number of technical and environmental benefits it offers. The advancement in the areas of UV-curable materials, photo initiators and curing equipments has resulted in significant growth of this technology in the recent years. In the recent years, a number of approaches have been developed that has combined the benefits of UV-cure technology with those of other emergent technologies, such as UV-cure powder technology, dual-cure systems, UV-cure polyurethane dispersions (UV-PUDs). Such development has resulted into substantial broadening of application areas of UV-cure systems.

While above developments have clearly placed UV-cure coating systems as environmentally-friendly advanced coating materials of choice for myriads of end-use applications, their significant dependence on fast depleting petrochemical resources is a major cause of concern for their sustainable development. It is important to develop advanced UV-curable materials from renewable resources for the sustainable development and thereby reduce the carbon foot-print of coatings based on this vital technology. Developments of materials based on renewable resources for replacement of petroleum-based raw materials constitute a major contemporary challenges in terms of economical, environmental and performance aspects.

Natural vegetable oils are one of the most important agro-based renewable resources because of their unique triglyceride structure that allow a number of useful chemical transformations and functionalization combined with their generally low cost and abundant

availability. Direct application of vegetable oils in UV-cure compositions is generally not possible due to their low reactivity towards UV-induced polymerization reactions. Nevertheless, it is possible to functionalization triglycerides and their derivatives through simple chemical transformations to confer reactivity and desirable chemical structure that can add value as components of UV-cure coatings[1-2].

In the present work we report two distinct families of UV-curable coating compositions derived from soybean oil. The first system has unique chemistry that allows formation of organic-inorganic hybrid nanocomposite coatings through a dual-cure mechanism involving cationic curing with concomitant cross-linking through condensation reaction. Organic-inorganic nanocomposite coatings have received great deal of attention in the recent years because of their unusual properties that can be exploited for a number of end-use applications. A number of studies have been reported on vegetable oil based organic-inorganic hybrid coatings[3-8]. It has been shown that with the suitable balance of organic and inorganic components, it is possible to derive coatings with good mechanical, chemical and corrosion resistance properties The second system consists of UV-curable polyurethane dispersion having bio-based content of ~25%. This system cures by classical free-radical mechanism.

Materials and Methods

Materials

Epoxidized soybean oil (ESO), having oxirane oxygen content of 6.9%, was procured from Arkema Inc. (Vikoflex[TM]-7170). 3-glycedoxypropyltrimethoxysilane was procured from Gelest. Irgacure 250 (Iodonium, (4-methylphenyl) [4-(2-methylpropyl) phenyl]-, hexafluorophosphate, 75% active in propylene carbonate) was used as cationic photoinitiator and Darocure 1173 was used as free radical photoinitiator, both were procured from from Ciba Specialty Chemicals. Dimethyloppropionic acid (DMPA) was received from Perstorp chemicals. All other chemicals and reagents were received from Sigma-Aldrich and were of reagent grade. All materials were used as received. Chemical structures of some important compounds used are shown in Fig.1
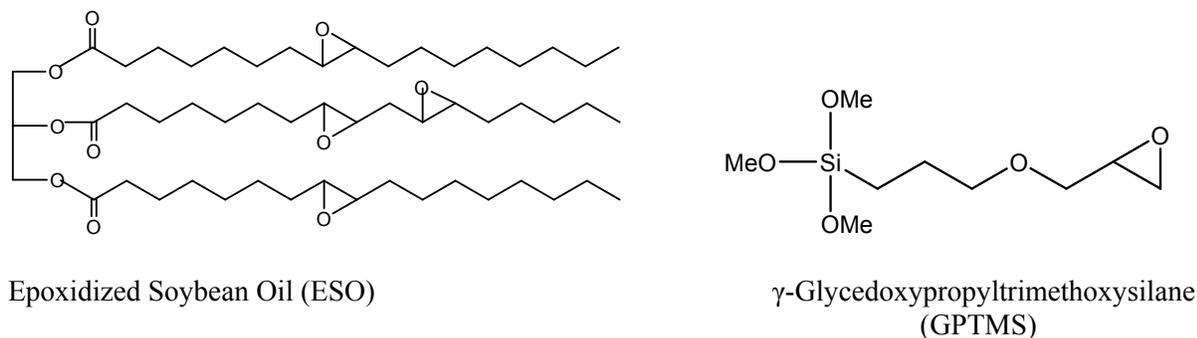

Epoxidized Soybean Oil (ESO)　　　　　γ-Glycedoxypropyltrimethoxysilane
(GPTMS)

Fig. 1 Oxirane functional and silane compounds used in the study

Testing and Evaluation

A Bruker Tensor 27 FTIR was used to characterized intermediates and product oligomers prepared for the study as well as for following cure characterization of UV-cured coatings. Intermediates, products and coatings were characterized using ASTM methods where applicable; % oxirane content (ASTM D-165297), Acid number (ASTM D-1639-96), hydroxyl number (ASTM D - 4274-99)

The physical properties of the cured coatings were determined by several different merthods. Adhesion was tested by a cross-hatch tape pull (ASTM D 3359-02). Scotch 610 tape was used for all tests. Pencil hardness (ASTM D – 3363), impact resistance (ASTM D - 2794-99), Solvent resistance was determined by MEK double rubs (ASTM D - 4752-98). A Sheen 707KP Pendulum Hardness Rocker was used for all König tests. For all samples tested, at least three readings were taken and averaged. Results are reported in seconds. Thermal Gravimetric Analysis was performed with a TGA Q 500 from TA instruments. Aluminum pans were used. The rate of temperature increase was $20°$ C/min and the max temperature was 550°C. The onset of degradation (the temperature at which 95% of the original material remains) was recorded, as was the weight of the residue remaining at the end of the test. Glass Transitions temperatures of the cured films were determined by a Q 2000 Differential Scanning Calorimeter (DSC) from TA instruments. Hermetically sealed T-zero pans were used. The temperature program was as follows: Room temperature to 150° C at a rate of $20°$ C/min; 150° C down to $-80°$ C at a rate of $-5°$ C/min ; $-80°$ C to 150° C at a rate of $20°$ C/min. The water contact angle of the coated film surfaces was determined by a FTA200 Dynamic Contact Angle analyzer from First Ten Angstroms. The coated samples were analyzed by Attenuated Total Reflectance IR (ATR-IR); a Bruker Hyperion ATR system was used. The dynamic mechanical properties of the cured coatings were determined by using Q 800 Dynamic Mechnical Analyzer from TA instruments. Coatings applied on unwashed smooth metal substrate were cured and taken out using blade. Sample film was cut down using standard cutter. Sample dimensions were 5.3 mm breadth, 20mm length and 0.04 mm thickness. Analysis was done using temperature ramp/frequency sweep mode and temperature program was from -40° C to 150° C at heating rate of 3° C/min. This analysis was done at constant frequency of 1.0 Hz.

Experimental

Synthesis of Acrylated Epoxidized soy-monoglyceride (AEMG): Epoxidized monoglyceride (EMG) was synthesized from ESO by glycerolysis process using calcium oxide catalyst. 1 mol of ESO was reacted with 2.0 mol of anhydrous glycerol, in presence of 0.5% by wt. of CaO as catalyst, at 145°C for 1.0 hr. Product was centrifuged to separate any unreacted glycerol, and EMG was decanted the top of the centrifuge tubes. EMG was characterized for hydroxyl number (ASTM D 4274-05) and %oxirane oxygen content ((%OOC) as per ASTM D–1652-04) in addition to the functional group characterization using FT-IR spectrophotometer.

For synthesis of Acrylated EMG (AEMG), EMG (1.0 eq.) along with 0.5% of triethylamine (TEA) catalyst, was put into a 3-neck reaction flask attached with a mechanical stirrer, a water condenser, a thermometer probe and an inlet for nitrogen gas. Flask was placed onto a heating mantle and heated under stirring to 80°C. Acrylic acid ((AA) (216.0g, 3.0 eq.)), along with hydroquinone 1.5% by wt., as free-radical inhibitor, was added drop-wise through an addition-funnel. After addition of AA was complete, temperature of reaction mixture was raised to 110°C, and progress of esterification was monitored by frequent determination of acid number and % oxirane oxygen content. Once the desired acid number and %OOC was obtained, reaction mixture was cooled to room temperature, and washed its etharal solution with distilled water till neutral. Product was dried and stored in refrigerator. A simplified reaction scheme for preparation of AESO is shown in Fig.2.
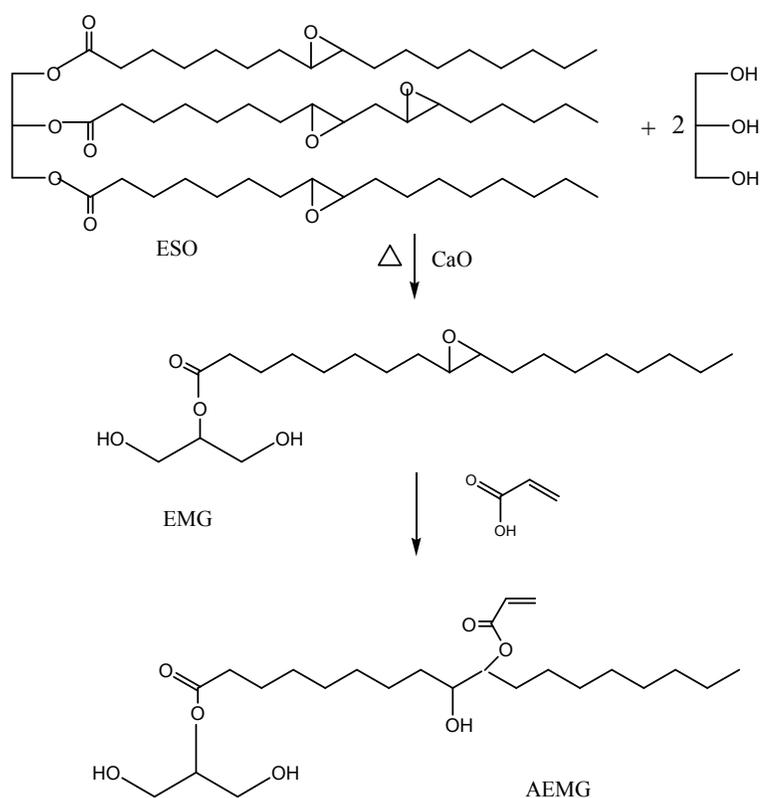

Fig. 2 Reaction scheme for synthesis of Acrylated soy epoxidized monoglyceride (AEMG)

Synthesis of UV-curable PUD (UV-PUD)

A series of UV-PUDs were prepared by isocyanate prepolymer process, using small amount of NMP and acetone as solvent to control viscosity and dispersion particle size. IPDI, DMPA, AEMG were reacted in varying ratio to obtain isocyanate prepolymers of varying molecular weight. Two different isocyanate index (NCO/OH ratio) of 1.4 and 1.5 were used. The

NCO-prepolymers was either chain extended using ethylenediamine or end-capped with 2-hydroxyethyl acrylate to incorporate additional acrylate functionality. Products were then neutralized with triethylamine followed by dispersion in DI water under high-speed disperser. The composition and characteristics of UV-PUD prepared for the study are shown in Table-4.

Fig. 3 shows a simplified general reaction scheme for preparation of UV-PUD based on soy-polyol.
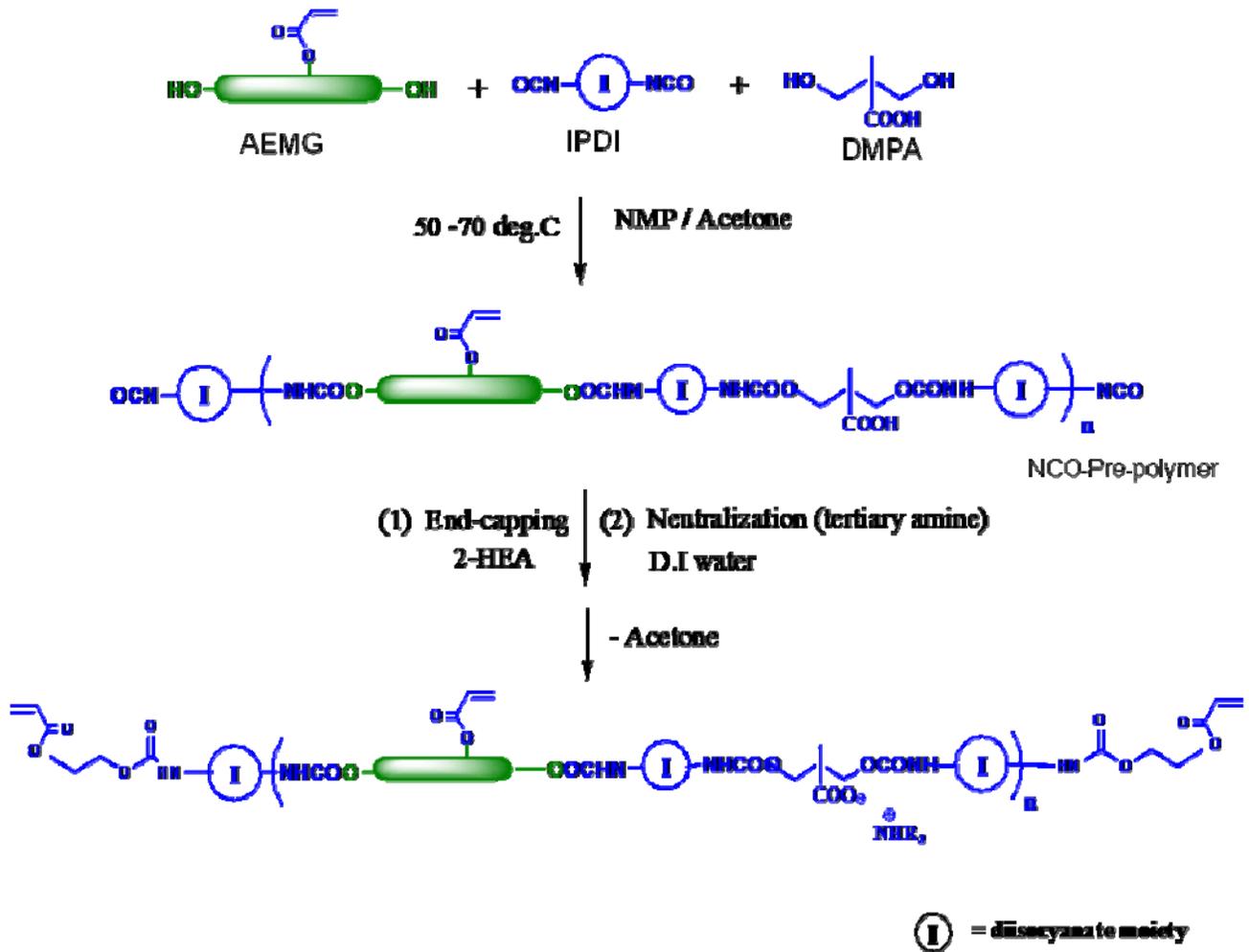

Fig. 3   Simplified general reaction scheme for synthesis of UV-PUD

Coating Application and Curing

The composition for ESO based system (cationic cure) were prepared by mixing ESO and GPTMS in appropriate wt. ratios (see Table-1). Photoinitiator Irgacure-250 and sensitizer ITX were incorporated by first dissolving into a small quantity of acetone and then thoroughly mixed with ESO+GPTMS mixture. All coatings were applied to approximately 2 mil dry film thickness, onto mild-steel panels 6" x 4"x 0.032", procured from Q-Panel. The PUD based compositions were prepared by addition of free radical photoinitiator Darocure-1173. Coatings

were applied to the substrates by manual draw-downs with a # 22 Mayer rod. A Fusion UV system with a D-bulb was used for UV-curing. All UV-curing was done at 40 feet/min. Using a Compact Radiometer from UVPS, the energy density measured was 2100 mJ/cm^2. S and for nano composite systems 2800 mJ/cm^2 for PUDs.

Results and Discussion:

Cationic-cures system:

Table-1 shows coating compositions of cationically curable system based on ESO and GPTMS in varying proportions. These compositions contain two distinct set of functionality – oxirane and silane, in varying amounts. The bio-based content for all the compositions has been calculated by the following formula.

$$Bio\text{-}based\ Content\,(\%) = \frac{Amount\ of\ bio\text{-}based\ carbon}{Amount\ of\ bio\text{-}based\ carbon\ +\ Amount\ of\ fossil\ carbon} \times 100$$

The photoinitiatiator I-250 is a photolabile superacid that generates super acid (Bronsted acid) when exposed to UV radiation of appropriate wavelength and intensity. The super acid initiates cationic polymerization (curing) of oxirane compounds (ESO and GPTMS) by well known reaction mechanism, leading to formation of croslinked network [9-13]. Recently Croutxe-Barghorn et al. has shown that silane finctional compounds can be UV-cured in presence of cationic photoinitiators[11]. It has been shown that in presence of photo-generated strong acid silanes and organo-silanes can undergo rapid hydrolysis, utilizing ambient moisture, to form silanols. The silonals thus formed are condensed to form siloxane (silica) network. Thus, irradiation of a system consisting of oxirane and organo-silane functional compounds, in presence of cationic photoinitiator, would lead to the formation of cross-linked network by two distinctly different reaction mechanism (dual-cure), resulting into formation of complex organic-inorganic hybrid nano-composite coatings. In the ESO /GPTMS system studied, we have systematically varied functional group contents to study their effect on final film properties. Composition EN 82 contains ESO and n-propyltrimethoxysilane (NPTMS), in place of GPTMS. NPTMS does not contain oxirane functionality but has only silane functionality. This composition is included to study the effect of film properties on the nature of organic-inorganic cross-linked materix. In this later case, due to the absence of oxirane functionality in NPTMS, the two networks formed by ESO and NPTMS would not be interconnected and hence are expected to have different performance.

The UV-cure reaction has been characterized by monotoring functional groups of the systems by FT-IR spectroscopic technique. Fig.4 (a) shows a representitive FT-IR spectra for uncured liquid composition and Fig.4 (b) shows UV-cured film (ATR mode). The depletion of absorption peaks at 844 cm^{-1} corresponding to oxirane groups is due to the cationic crosslinking through oxirane-oxirane reaction. The depletion of –Si-O-C- peak at 1069cm^{-1} and emergence of broad peaks in 1000 – 1140 cm^{-1} region corresponding to -Si-O-Si- clearly shows the formation of siloxane network. Thus, the study clearly shows the concomitant hydrolysis and condensation of silane compounds during cationic polymerization of oxirane functional groups, resulting into simultaneous formation of organic-inorganic hybrid nanocomposite films.

Table-1   **Coating Compositions of Cationic –cure systems ***

Composition Code	ESO Wt.%	GPTMS Wt. %	NPTMS	No. Avg. Oxirane functionality	% Bio-based Content
EG 100	100	0	0	4.2	84.64
EG 91	90	10	0	3.21	78.37
EG 82	80	20	0	2.59	71.72
EG 73	70	30	0	2.17	64.65
EG 64	60	40	0	1.86	57.21
EG 55	50	50	0	1.63	49.22
EN 82	80	20	20	4.2	79.01

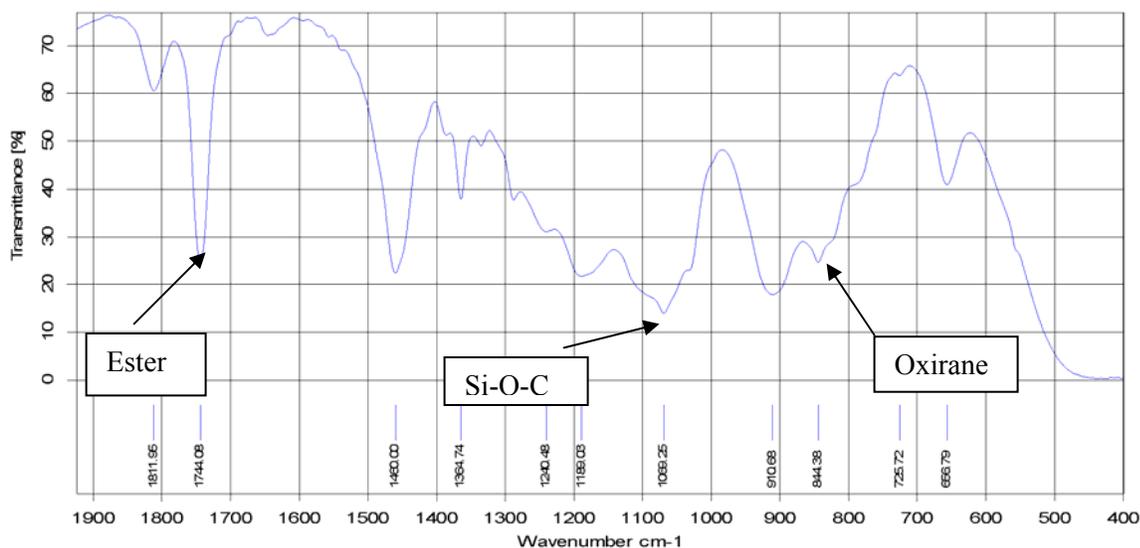*All composition used I-250 (3.0% by wt.) and ITX (0.6% by wt.), photoinitiator/ synergist system.
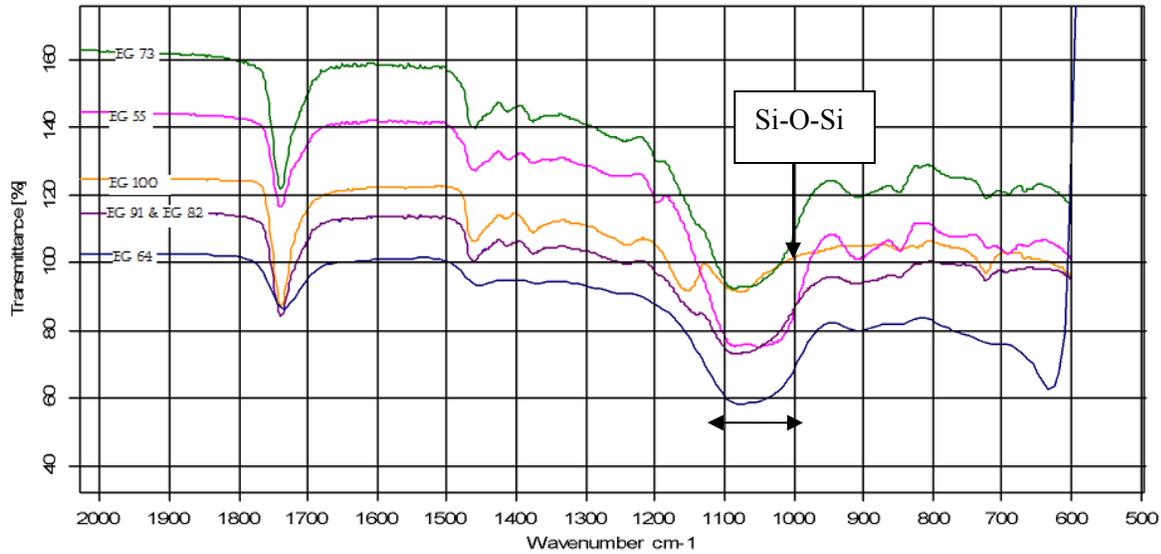

Fig.4 (a) FT-IR of uncured sample

Fig.4 (b) ATR IR of cured samples

Table-2   Film properties of cationic-cure coating systems.

Composition code / Properties	EG 100	EG 91	EG 82	EG 73	EG 64	EG 55	EN 82
% ESO	100	90	80	70	60	50	80
% GPTMS	0	10	20	30	40	50	20
Bio based Contnet %	84.6	78.4	71.7	64.7	57.2	49.2	79
Koenig Hardness (s)	47.6	53.2	54.6	60.2	70	75.6	43.4
MEK double rubs	0	125	200	300	300	300	50
Cross Hatch Adhesion	0B	5B	5B	5B	5B	5B	3B
Impact strength (D/R) (lbs. x inch)	80/80	80/80	80/80	80/80	80/80	80/80	80/80
Pencil Hardness	B	5H	7H	8H	8H	9H	H
% Gel Content	95.13	96.6	98.08	97.37	98.64	97.91	79.65
Water contact angle, (°)	51.5	67.8	69.9	76.3	77.7	76.4	62.9

Coating Properties:

Table-2 shows various properties of cationically cured films of a series of coating compositions. EG100 is based on only ESO and no silane. In general, compositions containing GPTMS show much improved overall coating performance. As GPTMS content increases (compositions EG 100 through EG55), both pencil hardness and Koenig hardness increases due

to the increased cross-linked density of the films. It should be noted that GPTMS has three –Si-O-Me groups per molecule and can form potentially three cross-links. MEK double rub test essentially provide information about cross-link density of the films. As can be seen from Table-2, as expected, MEK double rub numbers increase with increasing GPTMS, clearly showing increased cross-link density of siloxane network. All the films except EG 100 show excellent adhesion. Poor adhesion of EG 100 may be due to very soft nature of the film that has poor mechanical integrity.

It is interesting to compare ESO/GPTMS systems with EN82 (based on NPTMS). NPTMS, due to its lack of oxirane functionality, is expected to form hybrid silica network that is *not* chemically connected with ESO network. This is expected to affect a number of film properties. As comparison of film properties of EG 82 and EN 82 show significant difference in hardness, and solvent resistance. The poor solvent resistance (MEK double rub numbers) clearly indicates reduced crosslink density, mainly due to the cross-linked networks that are not chemically connected. The substantially lower gel content of EN 82 clearly supports our argument. Thus, in addition to absolute cross-link density, the formation of chemically connected network structure is essential for improved film properties. The water-contact angles of all the coatings have been reported in Table-2. The results indicates that in general, with increasing GPTMS content, the coating surfaces tend to become more hydrophilic, as indicated by reducing water contact angle. This can be attributed to both increasing hydrophilic silica content (polar) and reducing oil content (non-polar). In case of EN82, the higher contact angle (comparable to that of EG100 despite having lower oil content) may be due to the presence of dangling n-propyl chains of NPTMS having lower surface free energy oriented at the coating-air interface. Such orientation can result into reduced surface free energy.

Differential mechanical analysis:

The DMA thermograms for cationically cured coatings are shown in Fig.5. Fig. 5(a) clearly shows that with increasing silane content from 0% to 50%, storage modulus of films increases, due to increase in cross-link density arising from siloxane structure. Table-3 shows modulus of various films in the rubbery region. It is interesting to note that for sample EN82, the one with non-oxirane containing silane, the storage modulus is significantly lower than its oxirane -containing counterpart (sample EG82). This clearly demonstrates the effect of chemically connected network (in EG 82) on storage modulus of the film. Thus, besides merely the formation of two simultaneous networks, their interconnection is found to be an important factor governing their mechanical properties.

A comparison of peaks of Tan δ plots (Fig. 5(b)), which is a measure of Tg of the films, provide interesting information. Film without any silane (EG100) has significantly lower Tg compared to those with silane. Further, there is no appreciable difference in Tgs of films with varying amounts of silane. Therefore, it appears that glass transition is primarily governed by the organic matrix. Sample EG64 shows two Tan δ peaks, indicating micro-phase separation. Broadening of Tan δ peaks with increasing silane content of the composition indicates increasing phase heterogeneity of the nano-composite films.[14]
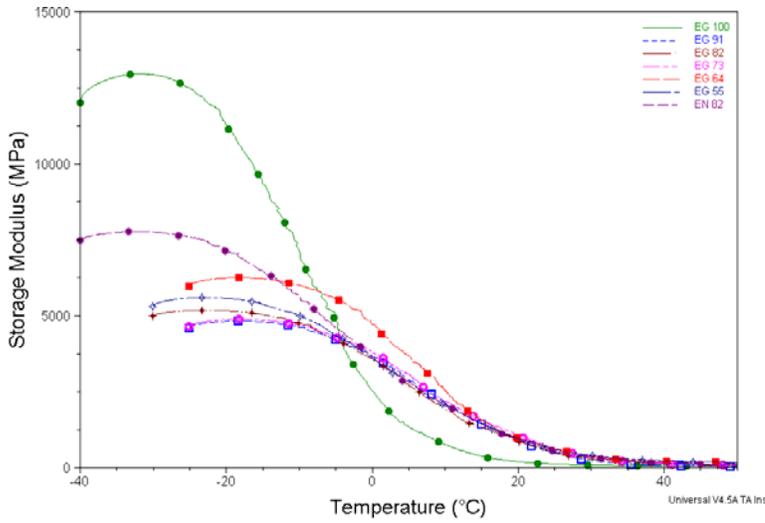
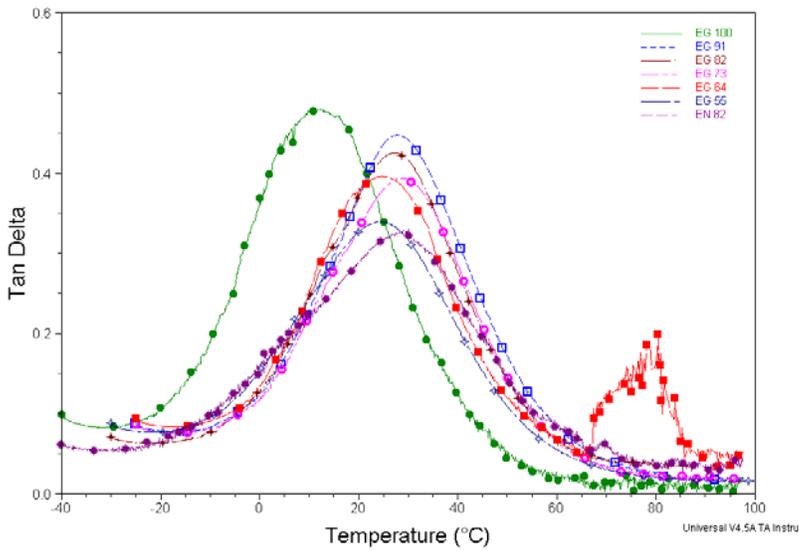Fig. 5 (a) Storage Modulus of all cured coatings

Fig. 5 (b) Tan Delta of all cured coatings

Table-3   Results of DMA of nano-composite films

Properties	EG 100	EG 91	EG 82	EG 73	EG 64	EG 55	EN 82
Storage Modulus (Mpa) at 30°C , above Tg)	80.36	230.11	286.3	253.8	389	401.5	175.1
Tan δ (°C)	12.08	27.97	27.26	28.68	24.61, 78	23.44	28.78

UV-Curable Polyurethane Dispersion:

Acrylated Soy-monomer and UV-curable Polyurethane dispersions (UV-PUDs)

A novel soybean oil-based acrylate functional polyol – acrylated epoxidized soy-monoglyceride (AEMG)- has been synthesized and characterized. Epoxidized soy-monoglyceride (EMG), an intermediate for synthesis of AEMG was prepared by glycerolysis of ESO in presence of basic catalyst, under relatively lower temperature of 160 °C, as compared to glycerolysis of soybean oil. Miscibility of glycerol with ESO permits low temperature transesterification. Reaction conditions were optimized to derive product without any loss of oxirane functionality. Acrylation of EMG was carried out by direct esterification with molar excess of acrylic acid. By optimization of reaction conditions and EMG / acrylic ration, it was possible to prepare acrylated product without appreciable oligomerization through oxirane-oxirane reaction. Table-4 shows characteristics of AEMG prepared for the study.

Synthesis of UV-PUD: Three UV-PUDs, differing primarily in acrylate content (weight per acrylate) and molecular weight were synthesized, as shown in Table-5. UV-PUD-X 1.5 is prepared from isocyanate prepolymer (NCO index =1.5) by chain extension with ethylenediamine. Chain extension leads to very high molecular weight and lower acrylate content. UVPUD-EC 1.5 and UVPUD-EC 1.4 are prepared from NCO-prepolymers (NCO index =1.5 and 1.4 respectively), by end capping with 2-HEA. Thus these two PUDs have lower molecular weight and higher acrylate content. All UVPUDs have comparable bio-based content.

Table-4 Characteristics of AEMG

Property	Value
Viscosity (Poise, 25°C)	149 Poise
Iodine value	73.0
Hydroxyl # (mgs of KOH)	395.0
Acid # (mgs of KOH)	1.0
Acrylate Eq. wt.	347
Degree of acrylation	0.99
Degree of etherification	0.01
Axylate Functionality	1.35
Hydroxy functionality	3.35

Table-5 Composition and characteristics of UV-PUDs

Properties	UV-PUD - X 1.5	UV PUD - EC1.5	UV PUD - EC1.4
NCO/OH (Pre-polymer)	1.5	1.5	1.4
DMPA content (% by wt.)	7.1	7.08	7.4
NMP Content (% by Wt.)	7.2	7.23	7.2
% AEMG by wt.	31.05	28.32	29.9
Mean Particle size (nm)	40	22.4	32
Weight per Acrylate (Calculated)	1134.45	540	529
Bio-based Content % (based on NVM)	26.69	23.90%	25.40%

Coatings based on UV-PUDs were formulated and applied onto the steel panels. Table-6 presents properties both un-cured as well as UV-cured films. After application and 20 min. flash-off time, all UV –PUDs were dry-to-touch. This is a very important property from the stand point of their industrial application since this allows easy handling of coated parts before UV-cure. Also, applications on 3D objects with shadow areas for UV-curing can also be benefit since in the shadow area, even without UV-curing, films would have reasonable good resistant properties.

As can be seen from Table-6, all the coatings significantly improve in hardness and solvent resistance (MEK double-rubs) after UV curing. This is due to the formation of cross-linking through acrylate double bonds upon UV-exposure. The slight reductions in impact resistance of UV-cured films indicate reduced flexibility due to increased cross-link density.

Comparisons between the cured films of three UVPUD films show that UV-PUD X 1.5 has lowest hardness and solvent resistance. This is attributed to the lower acrylate content and hence lower cross-link density. UV-PUD EC-1.5 and UV-PUD-EC-1.4 differ slightly in molecular weights; with former having lower molecular weight. The slightly better film properties of UV-PUD-EC-1.4 may be due to its higher molecular weight.

DSC thermograms of UV-PUDs are presented in Fig.6. As expected, the UV-PUD-CE 1.5 shows highest Tg probably due to greater hard segment content. A comparison between the two end-capped UV-PUDs, the one derived from lower molecular wt. prepolymer (UV-PUD-EC-1.5) shows lower Tg compared to its higher molecular weight counterpart.

Table-6   Film Properties of UV-PUDs

Film Properties	UV-PUD -X 1.5		UV-PUD -EC 1.5		UV-PUD -EC1.4	
	Before cure	After cure *	Before cure	After cure *	Before cure	After cure *
Pendulum Hardness (koenig, s)	70	82	110	225	120	233
Pencil Hardness	3H	4H	B	5H	B	6H
Impact Resistance (D/R) (lbs. x inch)	50/50	40/30	120/100	100/80	120/100	100/80
Adhesion (cross-hatch)	4B	4B	5B	5B	5B	5B
MEK double -rubs	0	50	0	75	0	75

*D-bulb, 2800 mJ/cm^2. S
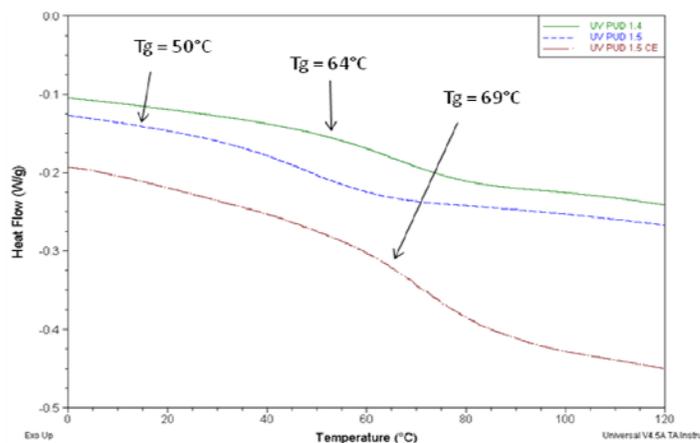
Fig. 6   DSC thermogram of UV-PUDs
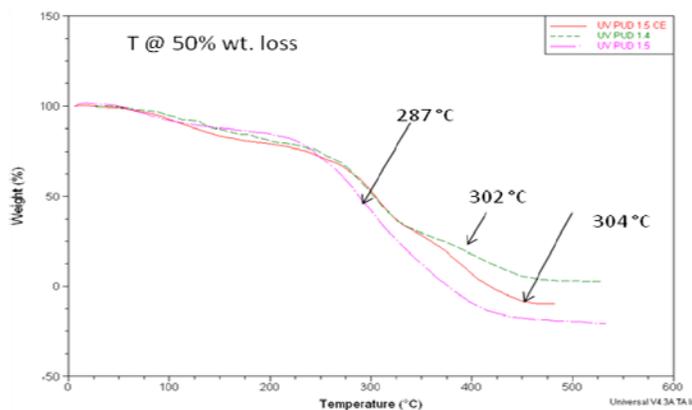
Fig.7   Thermogravimetric analysis of UV-PUDs

Thermogravimetric analysis of UV-PUDs reveals that all the cured films of UV-PUDs show good thermal stability. It appears that the temperature at 50% wt. loss is affected by molecular weight of polymer and their cross-link density.

Conclusion:

Novel UV-curable compositions based on renewable materials – soybean oil - have been reported. A very unique chemistry to derive bio-nano-composite coatings by UV-cure mechanism and concomitant UV induced sol-gel process has been reported. These nanocomposite coatings, with high bio-based content show very interesting properties and have great potential for commercial exploitation. UV-curable PUDs have been prepared from an soy-derived acrylate monomer. It is possible to design UV-PUDS with varying molecular weights and acrylate functionality to derive coatings with wide range of properties. The coatings developed in this study have substantial bio-based content and hence have reduced carbon foot print and environmental impact.

Acknowledgement:

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