

# **Bio-based building blocks for advanced photo-cure coating systems**

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## **ABSTRACT:**

Photo-curing, more specifically UV-curing technology is among the fastest growing advanced coating technologies and is rapidly expanding into a host of new application areas. Their growing acceptance is primarily driven by their environmentally friendly features, performance of these coatings, potential for enabling new products and economy. Despite these benefits, the materials used in the current photo-cure systems are predominantly derived from petrochemical sources making them unsustainable over the long term. Development of renewable resource-based alternate materials tailored for photo-cure applications is, therefore, very critical to future sustainable development of photo-cure coating technology.

This presentation highlights our research efforts in developing a platform of soybean oil-based value-added building blocks and demonstration of their suitability as alternative raw materials in advanced UV-curing coating compositions. A hyper-branched soy urethane acrylate (HSPU) has been developed and used as primary component of UV-curable composition. Coatings based on HSPU with varying acrylate content (using reactive diluent) and high bio-based content have been characterized and compared. Due to hyperbranched structure and large free volume in their inherent structure, they exhibited interesting properties for many potential industrial applications. Another group of soy-based derivatives - low viscosity and high-functionality acrylate monomers - have been designed and used as reactive diluent in conventional UV-cure formulation. The study demonstrates potential of these low odor and bio-based reactive diluents as partial or full replacement of conventional reactive diluents.

## **1. Introduction:**

Over the past few decades many advanced technologies in the field of printing inks and coatings have been commercialized, primarily to address environmental concerns and related regulations. Among these technologies are water-borne, high-solids, powder coatings and radiation curable coatings and inks. All these technologies have their own merits and challenges and hence depending upon end-use requirements of the products, have grown in different market segments.

Radiation curable coatings, and more specifically the UV-cure coatings, very clearly stand apart in terms of their low environmental impact, efficiency, low energy consumption and their ability to enable new products, when compared with other systems. These benefits are primary drivers for the growth of UV-curable systems both in the traditional as well as in the emerging new areas of applications. Despite these benefits, if we take a closer look at the supply chain of the materials used for UV-cure systems, it is evident that almost all of the materials used have fossil petroleum origin. This makes the current UV-cure systems unsustainable. For future sustainable development and environmental leadership we must reduce our dependence on petroleum-based resources and reduce carbon foot-print of UV-cure systems.

Bio-based materials, such as plant oils, are excellent renewable resources and using their chemical functionality they can be transformed into many different types of polymers and intermediates [1-6]. Our research group has focused on developing a platform of polymer building blocks derived

from soybean oil for coatings and related applications. [7-19] Polymeric and oligomeric materials used for UV-cure systems must meet stringent requirements of functionality, reactivity, viscosity, thermo-mechanical properties of their films, and cost for their successful deployment as film formers. In the present study we have designed, developed and demonstrated application of some novel soy-based oligomers and reactive diluents as alternative sustainable materials for UV-cure systems.

## **2. Experimental:**

### **2.1 Materials:**

Epoxy methyl soyate (EMS) (Vikoflex<sup>®</sup> 7010) and Epoxy methyl linseedate (EML) (Vikoflex<sup>®</sup> 9010), Dipropylene glycol diacrylate (DPGDA) (SARTOMER<sup>®</sup> SR-508) was procured from Arkema, USA. Epoxy acrylate oligomer (Rahn<sup>®</sup> 10-620/TM20) was supplied by Rahn USA corp., USA. Aliphatic urethane diacrylate (Ebecryl<sup>®</sup> 4833) used in this study was supplied by Cytec, USA. Toluene diisocyanate (TDI) was received from Bayer Material Science, USA. 2-hydroxyethyl acrylate (HEA) was procured from San Ester Corp. All the above materials were used as received. All other chemicals such as ethyltriphenylphosphonium bromide (ETPPB), triethylamine (TEA), acrylic acid (AA), methyl ether of hydroquinone (MEHQ), calcium oxide (ReagentPlus<sup>®</sup>), 48% aqueous solution of tetrafluoroboric acid (TFBA), dibutyltin dilaurate (DBTDL), toluene and methyl isobutyl ketone (MIBK) were purchased from Sigma Aldrich, USA. Toluene and MIBK were dried overnight over molecular sieve before use. Irgacure 184 and Irgacure 819, used as photoinitiators, were supplied by BASF, USA. Low carbon cold-rolled steel panels (type R) were purchased from Q-panel Lab products, USA.

### **2.2 Characterization methods:**

#### **FTIR Spectroscopy:**

The reactive diluents and oligomer synthesized in this study were characterized for their functional groups by FTIR spectroscopy in the mid operating range of 4000–400 cm<sup>-1</sup> using Bruker Tensor 27 FTIR analyzer. The representative spectra of %T (transmission) versus wave number are recorded. FT-IR spectroscopy has also been used to determine percent extent of conversion of acrylate groups during UV-curing process using peak-area method.

#### **Size exclusion chromatography:**

The reactive diluents and oligomer were also characterized for molecular weight using gel-permeation chromatography (GPC). A GPC system consisting of three Phenogel columns from Phenomenex (USA), PhenogelTM 5 $\mu$  50A, PhenogelTM 5 $\mu$  100A and PhenogelTM 5 $\mu$  500A, covering molecular weight range from 100 – 15000 g/mol; Viscotek VE 3580 RI detector and Malvern 270 Dual detector was used. Sample was dissolved in HPLC grade tetrahydrofuran (THF) (4 – 6 mg/ml). Sample injection volume was 100  $\mu$ L, flow rate of carrier solvent (THF) was 1.00 ml min<sup>-1</sup> and operating temperature was 45°C. The average molecular masses, Mn, Mw and polydispersity index were determined by software OmniSEC 4.7.

#### **Thermal analysis:**

The differential scanning calorimetry (DSC) analysis of cured films was performed using DSC Q 2000 from TA instruments, USA. 6 to 7 mg samples were accurately weighed in standard aluminium pan and scanning was done by ramping the temperature from –30 °C to 175 °C at a heating rate of 10 °C/min.

### **Gel content of the cured films:**

To evaluate crosslinking in the film, the gel content of the cured coatings was evaluated by immersing the accurately weighed free films (25mm×12.5mm) in methyl ethyl ketone (MEK). After 24 h of immersion, the films were dried in oven at 80 °C for 1 h and accurately weighed. The gel content (% by mass) was calculated as follow:

$$\% \text{ Gel content} = (W_g / W_f) \times 100$$

Where,  $W_f$  is the mass of the original dry film and  $W_g$  is the mass of the film after extraction with MEK.

### **Coating Properties:**

The cured coating films were evaluated for different mechanical properties such as adhesion (ASTM D 3359-02), impact resistance (ASTM D 2794 - 93), pencil hardness (ASTM D -3363 - 05) and Konig pendulum hardness (ASTM 4366-95). The dry film thickness of the coatings was measured by “micro-tri-gloss  $\mu$ ” instrument from BYK-Gardner, Germany. The solvent resistance was determined by double rub test using methyl ethyl ketone (MEK) as solvent (ASTM D 5402 - 06). It should to be noted that the pencil hardness reported refers to the hardest pencil that produced gouge in the film.

### **Tensile properties of cured films:**

The tensile properties of the cured free films (0.5 inch x 3 inch) were evaluated as per standard method (ASTM D 2370) at cross head speed of 0.2 inch per min and 2 inch of gauge length. Tensile properties of films are reported in table 7.

#### **2.2.1 Synthesis:**

#### **2.2.2 Synthesis of acrylated EMS (EMSHEAT) by trans-esterification of EMS with HEA**

In a three neck flask equipped with mechanical stirrer, thermo couple and heating mantle connected with temperature controller, 3 mole of HEA, 1 mole of EMS and MEHQ (0.5% by mass of HEA) were charged and heated to 120 °C. Calcium oxide, 1% by mass of EMS, which was calcined at 700 °C for 2 h prior to use was added to the reaction mass and reaction was carried out at 90 – 95 °C for 3 h. After completion of reaction, calcium oxide was allowed to settle, and the supernatant liquid mass was washed with distilled water and diethyl ether to remove excess HEA. 10% (W/W) solution of NaCl was used to assist better separation during washing. Diethyl ether was then evaporated in a rotary vacuum evaporator to obtaine the final product (EMSHEAT).

#### **2.2.3 Synthesis of reactive diluents: Soy – RD1, Soy – RD2 and Lin – RD3**

Reactive diluents Soy-RD1, Soy-RD2 and Lin-RD1 were prepared by acrylation of EMS, EMSHEAT and EML respectively using identical process. In a typical process for all the RDs prepared, molar excess of acrylic acid was used with one equivalent of oxirane compound. Acrylic acid was placed in a 3-neck flask equipped with mechanical stirrer, water condenser, thermocouple, and heating mantle connected with temperature controller to which 1% by mass of TEA was added. The reaction mixture was then heated to 100 °C and EMS/EMSHEAT/EML (as applicable) was added drop wise over a period of 1 h at 100 °C. The reaction was further continued until weight percent of oxirane oxygen (%OOC, ASTM D 1652 – 04) was reduced below 0.2%. After completion of reaction, the excess acrylic acid is removed by washing its diethyl ether solution with distilled water followed by washing with 5% (W/W) solution of sodium bicarbonate and finally by distilled water. Diethyl

ether is then removed in a rotary vacuum evaporator to obtain Soy-RD1, Soy-RD2 and Lin-RD-3 reactive diluents. The representative chemical structures of RDs are shown in figure-1.

The reactive diluents were characterized for saponification value (ASTM D 464 – 05), acid value (ASTM D 465 – 05) and viscosity (ASTM D 4287-00) by using cone and plate viscometer (Brookfield CAP 2000+). Their properties are presented in Table-1.

Table- 1 Typical Characteristics of RDs

Reactive diluent Identity	Average Functionality (Calculated)	Wt. per Acrylate (WPA), g. (Calculated)	Saponification Value (ASTM D 464)	Viscosity @25°C, (cP)	% Bio-based Content (Calculated)
Soy-RD1	1.14	349	301	206.3	84.7
Soy-RD2	2.12	206	360	103.3	74.9
Lin-RD1	1.47	290	320	464.1	81.1
DPGDA	2.00	121	463	10.0	0

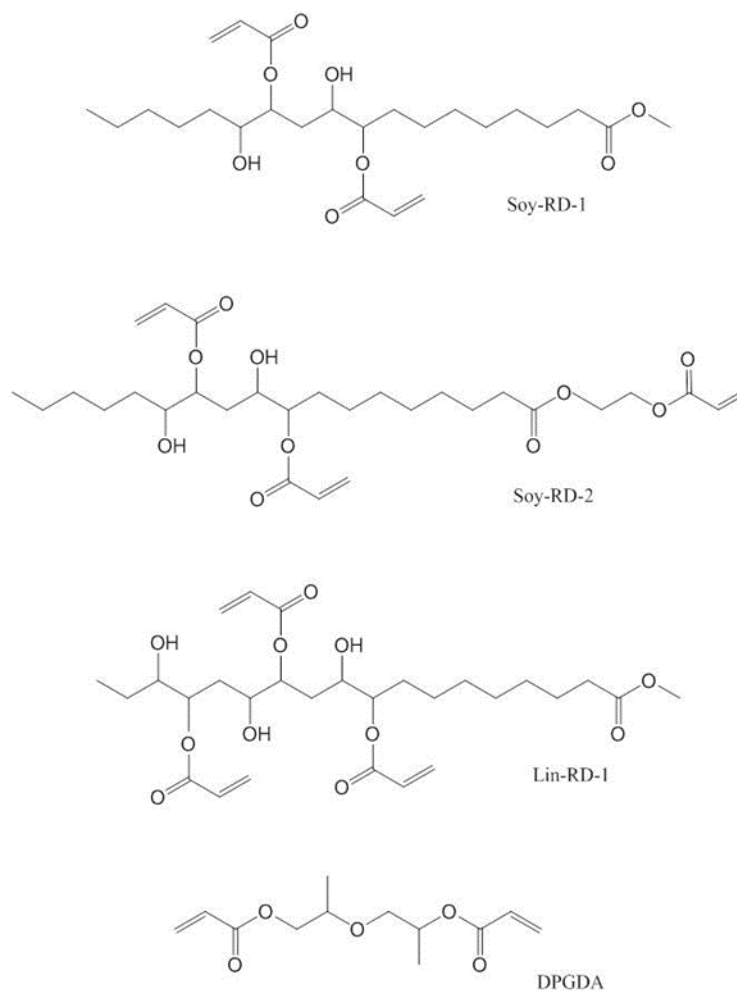


Fig. 1 Representative structures of reactive diluents used in the study

## 2.2.4 Synthesis of Hyper-branched soy-urethane acrylate Oligomer (Soy-UA)

Hyper-branched soy-urethane acrylate was synthesized by a series of steps shown below. All the intermediates were characterized to conform their structure before using them for the next step. A simplified reaction scheme is shown in Fig.2. In the first step EMSHEAT was synthesized from EMS as per the procedure shown above for reactive diluents. A hyper-branched soy-polyol was then synthesized from EMSHEAT by cationic ring opening polymerization through oxirane groups to yield a soy-polyol with pendent acrylate groups (EMSHEAT polyol). For the reason of simplicity, hyper-branched structure is not shown in Fig. 2. EMSHEAT (100.0 g) and 50 mg MEHQ were placed in three-neck flask equipped with mechanical stirrer, thermometer. The reaction mass is cooled to 7 -10°C using ice bath and 1g TFBA was added while stirring at 600 rpm. Ice bath was then removed and reaction was continued for 2 h at room temperature.

## 2.2.5 Synthesis of soy-urethane acrylate oligomer from EMSHEATP (Soy-UA)

In a 100 ml Erlenmeyer flask with a standard taper outer joint, 38.11 g (0.05 eq of hydroxyl) of EMSHEATP was accurately weighed and dissolved in 1:1 (w/w) mixture of toluene and MIBK to give 67% solid content in final composition. 200 ppm DBTDL was added as catalyst. The solution was cooled at 5 °C using ice-bath. To the cooled solution, 8.7 g (0.1 eq of isocyanates) TDI was added in 2 min under efficient stirring using magnetic stirrer. The reaction was continued for 2 h in ice cold water bath with gradual increase in temperature up to 20 °C. The reaction continued at 35-40 °C until the desired percent isocyanate content (% NCO) (ASTM D 2572-97) was reached to ensure complete reaction of hydroxyl groups of EMSHEATP. Subsequently, 5.8 g (0.05 eq hydroxyl) of HEA was added to the flask and reacted further at 35 – 40 °C until % NCO content was reached to 0%. Throughout the reaction care was taken to avoid moisture to come in contact with reaction mixture.

## 2.3 Preparation of coating composition

Two type of conventional coating systems, aliphatic urethane acrylate and epoxy acrylate, were studied with using different bio-based reactive diluents (Soy-RD1, Soy-RD2 and Lin-RD1) as well as with conventional petrochemical based reactive diluent (DPGDA). The coating compositions comprising of oligomer, reactive diluent are shown in Table-2 and 3. They are mixed with photoinitiator (4 phr, mixture of Irgacure 184: Irgacure 819, 80:20 by wt, used as 50% solution in acetone) under magnetic stirring for 10 min before application. Low-carbon cold-rolled steel panels (Q-panel, type R, 3"x 6"x 0.032") were cleaned with acetone and coatings were applied on it with wire bar applicator to give dry film thickness between 50-60 μ. Coatings were given flash off at ambient condition for 30 min and then cured with UV at energy density of 2500 mJ/cm<sup>2</sup>. Coatings were conditioned at ambient conditions for minimum 12 h before analysis.

## 3. Results and Discussion:

### 3.1. Design of soy-based reactive diluents:

Reactive diluents (RDs) are important components of UV-cure coating formulations. Besides their main roles of lowering viscosity of the compositions, they also significantly influence cure speed, cross-link density, and film shrinkage, among other factors [21]. One of the major concerns of conventional RDs is their unpleasant odor, skin irritancy and sensitization. Soy and linseed oil based reactive diluents prepared in the present study have been designed to overcome these challenges while maintaining good viscosity reduction characteristics. A series of reactive diluents have been prepared with different chemistry, varying chemical structure, and functionality. Fig.1 shows simplified chemical structures of RDs prepared for this study. The typical characteristics and their bio-based contents, as calculated by a following formula, are shown in Table-1.

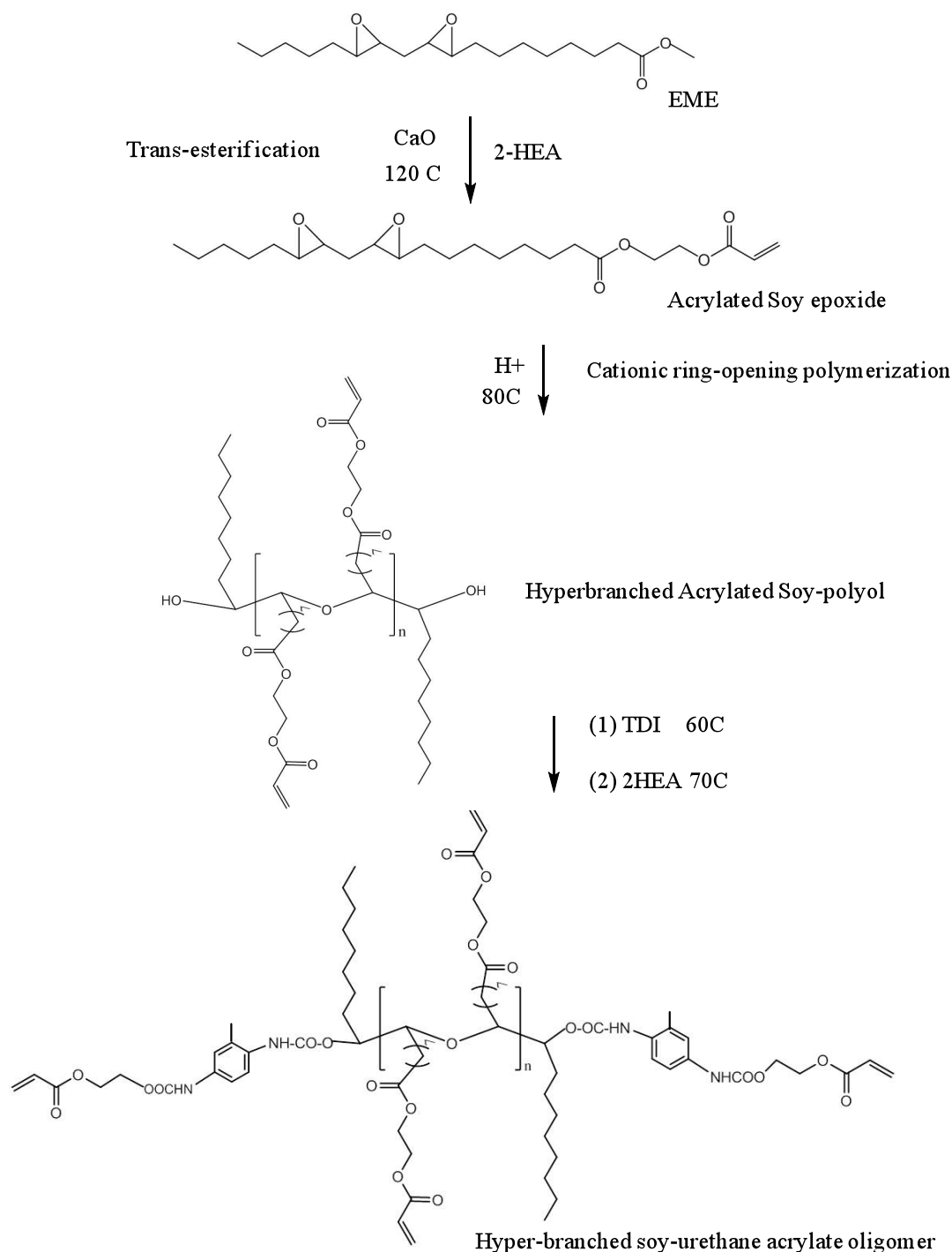


Fig.-2: Schematic representation of preparation of HSUA

### 3.2. Study of viscosity profile:

Viscosity reduction profile of RDs is very important, among many other factors, for their successful applications in UV-cure coatings and inks. In order to study viscosity reduction profile of bio-based RDs, two conventional oligomers, an epoxy acrylate oligomer (10-620/TM20 (Rahn, USA)) and an aliphatic urethane acrylate (EBECRYL 4833(CYTEC)), have been selected. Epoxy acrylate oligomer and aliphatic urethane acrylate

oligomers are referred to as EA and UA respectively, in the subsequent discussion. Their viscosity profiles are shown in Fig. 3. DPGDA, a conventional petro-based RD has also been used as reference RD.

As it is evident from the results that all the bio-based RDs can dissolve acrylate oligomers and their solutions were clear and free flowing, indicating their good compatibility. It is observed that the order of relative viscosity reducing potential of RDs is: DPGDA > Soy-RD-2 > Soy-RD1 > Lin-RD-1. This trend is observed with both EA and UA oligomers. In general, the viscosity reducing power of a RD is primarily dependent on the polarity of reactive diluents or solvents, among other factors. In case of RDs used in this study, the polar ester group would help solvate oligomer through polar-polar interaction and/or H-bonding interaction. The ester group contents are expressed as saponification numbers in Table-1; the higher the saponification number, the higher their ester group content. However, the results show interesting trend. As expected, DPGDA (sap. value =463) shows much greater viscosity reduction power compared to all other bio-based RDs. Among the bio-based RDs, Soy-RD-2 (Sap.value=360) shows the highest viscosity reducing power. Surprisingly, Lin-RD-1 (Sap. value = 320) shows much lower solvency compared to Soy-RD-1 (sap. Value =301) despite its higher ester content. We attribute this behavior to the internal H-bonding [21] resulting due to the proximity of the ester and hydroxyl group Lin-RD-1, as shown in Fig.4. While such H-bonding is possible in all the three bio-based RDs, it would be much more pronounced in Lin-RD-1 since it contains substantial fraction of linolenic ester, giving rise to product with three esters and three hydroxyl groups in proximity. Please note that Fig.1 shows only representative structures of the RDs and that they will be mixtures of compounds based on fatty acid compositions of the oil used. The greater internal H-bond formation potential of Lin-RD-1 is also supported by its higher viscosity (Table-1) compared to the other soy-based RDs. Soy-RD-2, that shows the best performance has lower –OH content (responsible for H-bonding) compared to Lin-RD-1 and greater ester content compared to Soy-RD-1.

It can be, therefore, inferred that in addition to the ester group content the chemical structure and viscosity of reactive diluents can significantly influence their viscosity reduction power for different oligomer types. Among the RDs studied, the Soy-RD-2 appears to have the best balance of chemical structure, polarity and viscosity and hence shows best viscosity reducing power.

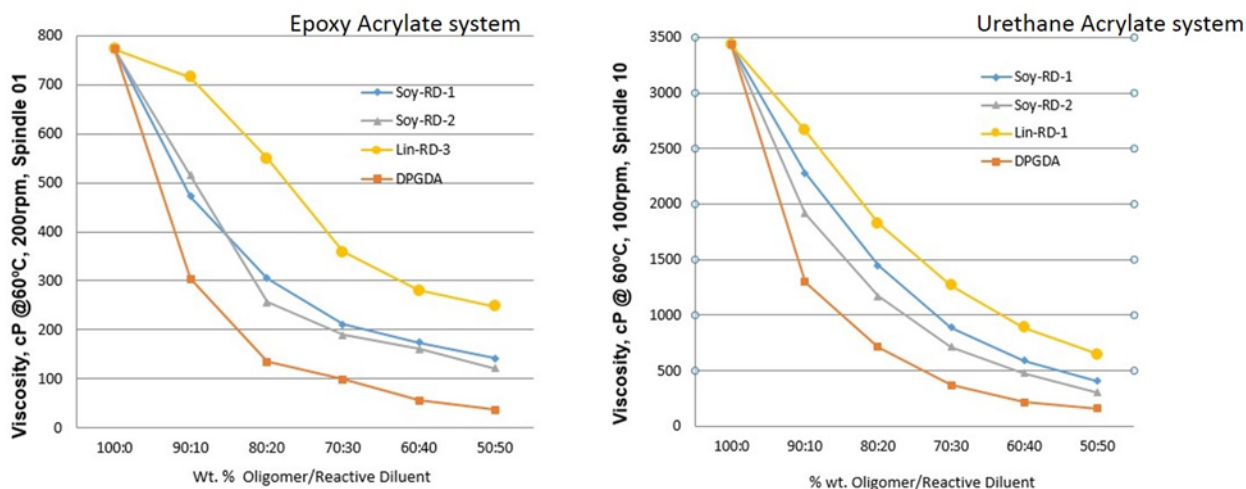


Fig. 3 Viscosity profile of different reactive diluents with Epoxy acrylate (left) and Urethane acrylate Oligomer (right).

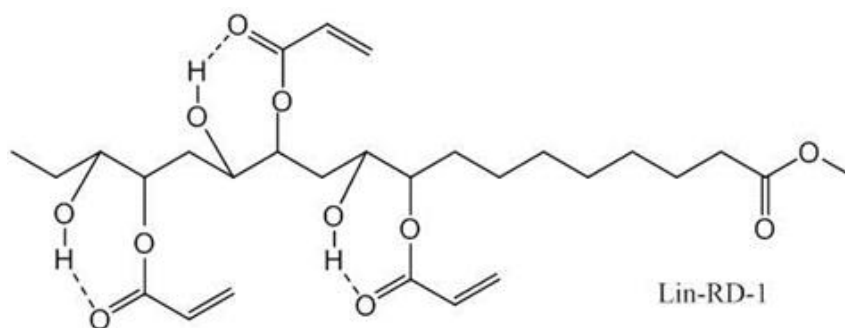


Fig. 4 A simplified structure of Lin-RD-1 showing probable H-bonding

### 3.3. UV-cured film properties:

UV-cure coatings were prepared from EA and UA oligomers and different RDs, in varying oligomer/RD ratio, to study the effect of RD type and amount on the film properties. Compositions using DPGDA, a conventional reactive diluent, were also prepared as reference. The results are presented in Table-2 and Table-3. In case of coatings based on EA oligomer (Table-2), all the films were clear and uniform with good adhesion. Epoxy acrylate is a “hard” oligomer and incorporation of bio-based RDs resulted in lowering of film hardness, as expected. The drop in hardness is much more pronounced with Soy-RD-1 due to its lower acrylate (WPA = 349) compared to other RDs. Lower acrylate content of Soy-RD-1 is expected to produce films with lower cross-link density and lower hardness. It is important, however, to note that Soy-RD-1 despite its lower acrylate content can still provide high solvent resistance (MEK-double rubs) when used at up to 50%.



Table- 2 Film properties of UV-cured Coatings\*, \*\*: EA / Reactive diluent system

Reactive Diluent Type	Oligomer/RD Ratio (by wt.)	Konig hardness (s)	Pencil hardness	MEK double-rub	Impact resistance(lb·in)	
					Direct	Reverse
Soy-RD-1	100:00	215.6	>5H	>200	20	<20
	80:20	177.8	H	>200	<20	<20
	70:30	147	H	>200	20	<20
	60:40	120.4	H	>200	20	<20
	50:50	86.8	F	>200	40	<20
	40:60	54.6	B	90	40	<20
Soy-RD-2	100:00	215.6	>5H	>200	20	<20
	80:20	184.8	4H	>200	20	<20
	70:30	161	4H	>200	20	<20
	60:40	133	4H	>200	20	<20
	50:50	93.8	2H	>200	20	<20
	40:60	63	4B	106	20	<20
Lin-RD-1	100:00	215.6	>5H	>200	20	<20
	80:20	233.8	4H	>200	<20	<20
	70:30	215.6	4H	>200	20	<20
	60:40	184.8	4H	>200	20	<20
	50:50	154	4H	>200	20	<20
	40:60	109.2	4H	>200	40	<20
DPGDA	100:00	215.6	>5H	>200	20	<20
	80:20	246.4	>5H	>200	20	<20
	70:30	239.4	>5H	>200	<20	<20
	60:40	236.6	>5H	>200	<20	<20
	50:50	232.4	>5H	>200	<20	<20
	40:60	229.6	>5H	>200	<20	<20

\* UV energy density = 2500 mJ/cm<sup>2</sup> \*\* Dry-film thickness = 50-55 microns

Table- 3 Film properties UV-cured Coatings\*, \*\*: UA / Reactive diluent system

Reactive diluent	Oligomer/RD Ratio (by wt.)	Konig hardness (s)	Pencil hardness	MEK double-rub	Impact resistance(lb-in)	
					Direct	Reverse
Soy-RD-1	100:00	53.2	4B	54	160	160
	80:20	37.8	4B	45	160	160
	70:30	22.4	4B	40	160	160
	60:40	14	3B	30	160	160
Soy-RD-2	100:00	53.2	4B	54	160	160
	80:20	25.2	4B	48	160	160
	70:30	19.6	4B	45	160	160
	60:40	16.8	B	40	160	160
Lin-RD-1	100:00	53.2	4B	54	160	160
	80:20	61.6	2B	120	160	160
	70:30	47.6	2B	70	160	160
	60:40	25.2	B	60	160	160
DPGDA	100:00	53.2	4B	54	160	160
	80:20	166.6	H	>200	40	120
	70:30	161	H	>200	40	60
	60:40	152.6	B	>200	20	<20

\* UV energy density = 2500 mJ/cm<sup>2</sup> \*\* Dryfilm thickness = 50-55 microns

### 3.4. Design of hyper-branched soy-based urethane acrylate oligomer (HSUA):

Oligomers used for UV-cure coatings must be carefully tailored to meet such diverse requirement as low viscosity, adequate functionality, faster cure response, compatibility with other components, ease of pigment dispersion and low cost. Further, the cured film must have balanced thermo-mechanical properties, low shrinkage, adequate cross-link density for chemical and solvent resistance, and good adhesion on a variety of substrates. These oligomer characteristics and the film properties can be achieved, in most part, by using innovative design strategies for oligomers. The hyper-branched soy-urethane acrylate oligomer (HSUA) in this study has been prepared from epoxidized methyl ester of soy fatty acids (EMS) as starting material, which is a commercially available soy derivative. A simplified reaction scheme is shown in Fig-2. While it is a common practice to esterify oxirane groups of EMS with acrylic acid to introduce UV-curable acrylate groups, we have used a different strategy involving trans-esterification of methyl ester groups with 2-hydroxyethyl acrylate (2-HEA). We have then utilized oxirane groups to build up higher molecular weight (oligomerization) by cationic ring-opening polymerization using an acid catalyst, to obtain hyper-branched oligomeric polyol. This polyol was then reacted with excess of di-isocyanate compound to prepare –NCO-terminated product that was then end-capped with 2-HEA to introduce additional acrylate groups. Using this unique strategy, we have been able to prepare soy-urethane acrylate oligomer with hyper-branched structure. The hyper-branching, though not shown in Fig. 2, will arise due to oxirane functionality of > 1 (~ 1.4) of EMS. We hypothesized that this HSUA with unique hyper-branched structure, uniform distribution of

acrylate groups along the oligomer, and some dangling chain ends would provide balance of such desirable properties as low viscosity, good cure response, uniform cross-link density, reduced shrinkage, and of course, high bio-based content. The characteristics of oligomer are shown in Table-4.

Table 4: Characteristics of HSUA

Properties	Value
Molecular Wt. (GPC) (Mn)	1576
No. Avg. Functionality (Calculated)	5.24
Viscosity (cPs) @ 25 °C	162.8 *
Wt. per acrylate (WPA) (Calculated)	301
% Bio-based content (calculated)	59.20%

\*Spindle No. 1, 750 rpm

### 3.5. UV-cure Coating compositions based on HSUA:

In order to validate our design strategy and to study the potential applications HSUA oligomer was evaluated in UV-cure compositions, with and without the use of reactive diluents. The compositions used for the study are shown in Table-5. UV-cured network of HSUA is expected to be “soft” and flexible by virtue of its hyper-branched structure, low acrylate density and aliphatic dangling segments which will provide low cross-link density and high free-volume. Therefore, in order to study the effect of increasing cross-linking a tri-functional TMPTA monomer has been used in varying proportion in the compositions studied.

### 3.6. UV-cured film properties for HSUA based coatings:

The properties of UV-cured coatings are reported in Table – 5 and 6. All the coatings were characterized for extent of curing by following acrylate group conversion as well as by determination of their gel contents (Table-6). Acrylate group conversion was calculated by peak area ratio method by measurement of characteristic FT-IR absorption peak area at around 810cm<sup>-1</sup>, before and after curing of the films. The FT-IR peak at ~1730 cm<sup>-1</sup> corresponding to carbonyl group was taken as reference, and % acrylate conversion was calculated by the following formula. [23]

$$\% \text{ Acrylate Conversion} = \frac{(A_{810} / A_{1730})_0 - (A_{810} / A_{1730})_t}{(A_{810} / A_{1730})_0} \times 100$$

Where  $(A_{810} / A_{1730})_0$  and  $(A_{810} / A_{1730})_t$  are relative absorbance of C=C bonds before and after curing, respectively. Gel contents were measured using method described earlier in Materials and Methods section. Coating HSUA100 shows very high acrylate conversion. In general, acrylate conversion in UV-cure coating significantly depends, among many factors, on free volume (Tg) of coatings [24,25]. The greater the free volume, the more is the relative mobility of the reacting species and hence greater the extent of reaction (% conversion). HSUA100 with low acrylate density has high free volume and hence high conversion. As can be seen in Table-6, with increasing TMPTA contents, the acrylate conversion drops since TMPTA has high acrylate density and would result in film with high cross-link density and reduced mobility of reactive species. Fig.5 shows DSC thermograms of UV-cured coatings. HSUA100 shows significantly lower Tg ( -9.3 °C, and another at 46.5°C), indicating high free volume and rubbery nature of this coating. With increasing high acrylate content TMPTA, Tg of the films increased to > 47 °C indicating “glassy” and highly cross-linked films. Gel content of coatings provide information about the components that are not connected with the network structure (gel) and their relative tendency to leach out during the test. [26-28]. The increase in gel contents of coatings in Table-6 with increase in TMPTA content is clearly due to the increase acrylate density of the

compositions. It is interesting to note that even though the acrylate conversion decreases with increasing TMPTA content, the networks formed become more complex and integrated showing decrease in gel contents.

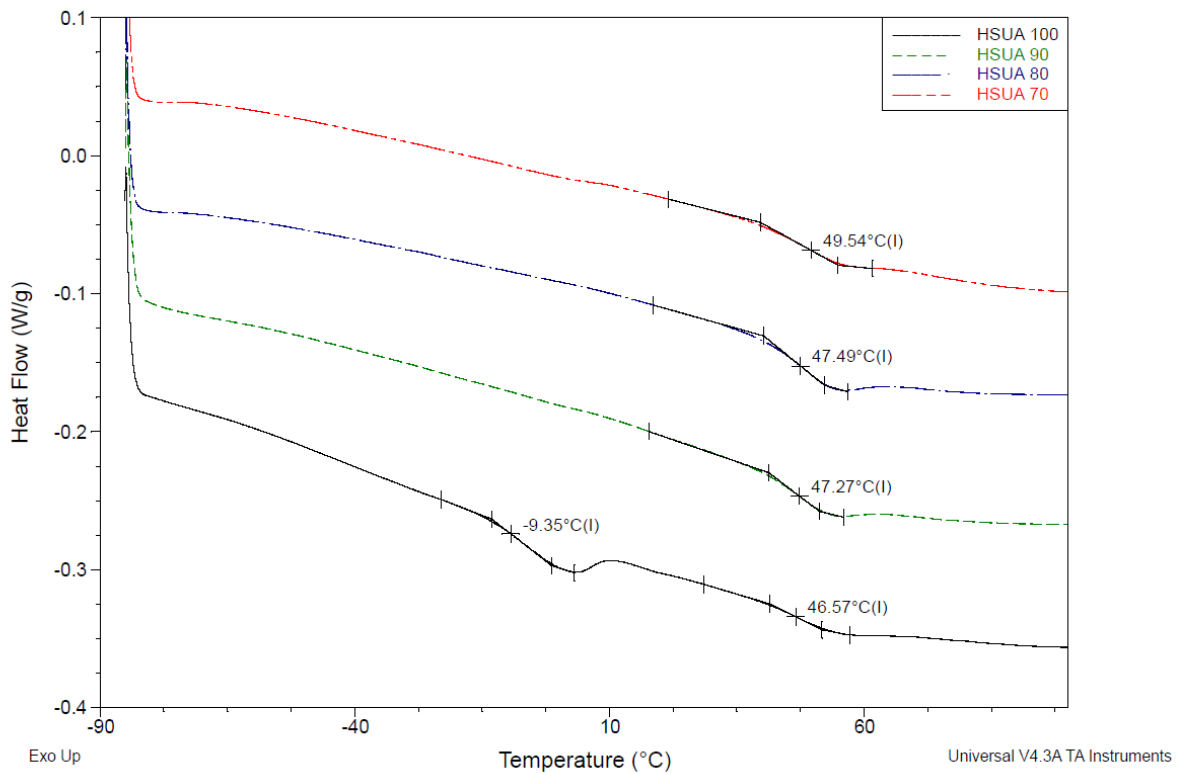


Figure 5: DSC thermograms of HSUA-based UV-cured films.

Table- 5 Film properties UV-cured Coatings\*, \*\*: HSUA / Reactive diluent system

Coating Code	HSUA/TMPTA Ratio (by wt.)	Pendulum Hardness Konig (s)	Pencil hardness	Cross-Cut Adhesion	Impact Resistance (lb-in)	
					Direct	Reverse
HSUA 100	100:00	36.4	< 5B	0B	160	160
HSUA90	90:10	64.4	4B	1B	40	20
HSUA80	80:20	88.2	B	3B	40	<20
HSPU70	70:30	113.4	H	3B	20	<20

\* UV energy density = 2500 mJ/cm<sup>2</sup> \*\* Dry-film thickness = 50-55μ

Table- 6 Film properties UV-cured Coatings\*, \*\*: HSUA / Reactive diluent system

Coating Code	HSUA/TMPTA Ratio (by wt.)	MEK Double-Rubs	Gel Content (%)	Acrylate conversion (FTIR) %
HSUA100	100:00	65	83.79	100.0
HSUA90	90:10	>200	83.84	97.3
HSUA80	80:20	>200	88.93	80.1
HSPU70	70:30	>200	90.36	77.1

\* UV energy density = 2500 mJ/cm<sup>2</sup> \*\* Dry-film thickness = 50-55 microns

Table-5 and 6 shows the properties of UV-cured coatings based on HSUA. As expected, the HSUA produced soft film and with increasing amount of TMPTA the film hardness increased progressively as evident from the Konig hardness and pencil hardness. This may be attributed to high free volume in the oligomer resulting from low cross-link density and the dandling fatty chain structure. The lower MEK resistance for HSUA100 and its significant improvement upon addition of TMPTA can also be explained based on free volume and cross-link density of their film, as stated above. It is also observed that incorporation of TMPTA increases film brittleness (lower impact resistance) and lowers adhesion. This can be due to the increase in cross-link density and volume shrinkage arising from tri-functional TMPTA monomer.

The tensile properties of UV-cured films of HSUA based coatings are shown in Table-7. HSUA100 showed much lower modulus, tensile strength and % elongation, typical of moderate functionality oligomers. With increasing TMPTA, significant increase in modulus and drop in %elongation was observed due to the formation of constrained network. Tensile strength results indicate formation of brittle network structure with increasing TMPTA contents. Overall, the HSUA oligomer designed in the present study can successfully be used in UV-cure coatings. By suitable choice of other co-oligomers and reactive diluents it is possible to customized properties of coatings for a target application, while maintaining high bio-based content of the final product.

Table 7: tensile properties of cured films of HSUA based coatings

Coating Code	Modulus (ksi)	Tensile strength (psi)	% Elongation at Break
HSUA100	32.7	1515.1	14.3
HSUA90	67.7	1031.4	2.3
HSUA80	129.4	1214.6	1.2
HSPU70	179.9	1199.0	0.8

#### 4. Conclusion:

In the present study soy-based building blocks suitable as components for advanced UV-cure coatings have been designed and developed. Two types of soy-derived materials – urethane acrylate oligomer and a series of reactive diluents – have been synthesized and studied as primary component and their blends with conventional petro-derived materials, in UV-cure coating formulations. The study of their film properties shows that these soy-based materials with high bio-based contents have significant potential for commercial

applications and presents an alternate sustainable raw material platform.

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