

DEVELOPMENT OF “SWEET” SOY-BASED, HIGH BIORENEWABLE CONTENT UV CURABLE COATINGS

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1. Introduction

The fast depleting petroleum reserve and the ever-increasing cost is attracting more and more serious attention to the industrial utilization of biorenewable raw materials in the chemical industry.^{1,2} Organic coatings are an important sector of the modern chemical industry. However, traditional coatings contain significant amount of organic solvents and other volatiles. The coatings industry has been identified as second only to the gasoline-automobile complex as the largest source of the VOC (volatile organic compound) pollutants that are responsible for excess ozone in the air.³ Driven by the rising raw material cost and the stricter environmental regulations, the coatings industry is transforming to a “greener” industry by incorporating more alternative renewable raw materials and cleaner technologies such as radiation cure, high solids, and waterborne coating technologies.^{4,5} Radiation cure coating technology including UV (ultraviolet) and EB (electron beam) cure is a green coating technology that has the capability to produce high performance coatings with high productivity, low energy consumption and extremely low VOC emission.⁶⁻⁸ It has been enjoying fast market growth since its introduction to the coatings industry.^{5,9} Utilization of biorenewable raw materials in the radiation cure coatings is a promising “green+green” solution to the challenges that the coatings industry is facing.

Bio-derived chemicals such as drying oils have a long history of being used as coating ingredients. Bio-derived chemicals have appealing features, including being environmentally benign and exhibiting short regeneration cycles which meet the demand of a sustainable chemical industry.² On the other hand, quality control, land uses, and logistic cost are potential issues in the industrial utilization of bio-derived chemicals. The intense research and development in the petroleum-based chemical industry since the early twentieth century has been providing the coatings industry with very cost effective, high quality raw materials over the past years. Thus, one major challenge in generating bio-based materials in order to substitute for their petrochemical-based counterparts is to match or even surpass the performance of petrochemical-based materials with competitive cost. Blending bio-derived ingredients into existing petrochemical-based formulations is an intuitive approach to utilize bio-derived chemicals. However, normally lower biorenewable content materials are produced in order to maintain the material performance, despite the fact that coating materials with high biorenewable content are highly desired. An alternative approach to obtain high biorenewable content, high performance materials is to custom-design and formulate the resin and coating system according to specific application needs based on the understanding of structure-property relationships of bio-derived chemicals. With this approach it is expected that the structural features and the related material properties of the bio-derived ingredients can be fully utilized in the formulations to achieve optimal material performance. At the same time, due to the limited availability of biorenewable raw materials on the current market, use of petrochemicals in

formulations is inevitable. These petrochemicals and their addition amount should be carefully examined in order to maximize their effect with lowest loading level. In addition to material performance, there are other important aspects to consider and explore in the development of high biorenewable content biobased materials. For example, it is desirable that the biobased materials disintegrate in the environment after use via mechanisms such as microorganism-induced anaerobic or aerobic degradation, without releasing harmful fragments.¹⁰ Consequently the degradation of these materials and the subsequent tracking and analysis of the released compounds are important research topics. On the other hand, from an application standpoint, the biobased materials must possess high enough durability throughout their service life time to withstand erosion in their service environment such as microorganism-induced deterioration, hydrolysis, and weathering etc. These aspects are critical research topics in addition to formulation and performance enhancement of high biorenewable content biobased materials.

Soybean is a major produce in the United States (US).¹¹ Soybean oil derived chemicals are important biorenewable materials in the coatings industry.^{12,13} Acrylated soybean oil (ASO) and epoxidized soybean oil (ESO) have been formulated into UV coatings but petrochemicals had to be incorporated into ASO or ESO in order to achieve better coating performance.¹⁴⁻¹⁷ Thus the biorenewable content was lower in these formulations. The softness of the fatty acid triglyceride backbone, and the lower reactivity for the mid-chain functional groups such as epoxies and acrylates are the main reasons for the inferior coating film properties.^{18,19} In order to develop soy-based, high performance UV curable coatings with high biorenewable content, the incorporation of highly effective petroleum-based crosslinkers, and biorenewable tougheners and reactive diluents into ASO was conducted in this work. Commercial hyperbranched acrylates (HBAs) were selected as the petroleum-based crosslinkers to co-photopolymerize with ASO. To our best knowledge, the use of highly functional hyperbranched acrylates in soy-based UV curable materials has not been reported. Owing to their unique branched molecular structures, hyperbranched acrylates exhibit low viscosity, high molecular weight and functionality, and lower photopolymerization shrinkage,²⁰ which are expected to significantly increase the properties of the UV curable, soy-based formulations. As to the biobased toughening monomers and reactive diluents, the “sweet” acrylated sucrose (AS) with varying acrylate functionality and acrylated tetrahydrofurfural (ATHF) were selected. Sucrose (chemical structure shown in Figure 1), commonly known as table sugar, is an abundant low cost biorenewable resource in US. The sucrose molecule possesses aliphatic ring structure and multiple hydroxyl groups. The aliphatic ring structure imparts balanced hardness and flexibility to the material, while the hydroxyl groups provide sites for chemical modification and intermolecular hydrogen bonding. AS can be synthesized through various routes including transesterification with methyl acrylates and methyl methacrylates.^{21,22} but the effect of AS as a toughening ingredient in UV curable coatings has not been investigated, despite that the unique molecular structure of AS may significantly alter the soy-based UV cured coating properties. Acrylated soybean oil has high viscosity, thus reactive diluents are necessary to lower the viscosity of ASO-based coating formulations. ATHF (structure shown in Figure 1B) is a derivative of furfural alcohol, a bio-derived chemical from a variety of agricultural by-products including corncobs, oat, wheat bran, sugarcane bagasse, and sawdust.²³ ATHF has ~ 70% biorenewable content, and has low viscosity and high solvency towards common acrylate oligomers and monomers. It is an ideal biorenewable reactive diluent for high biorenewable content soy-based coating formulations. The research progress towards the production of high performance and high biorenewable content soy-based UV curable coatings by incorporation of HBAs, ATHF and the “sweet” acrylated sucrose is discussed in this contribution.



Figure 1. Chemical structure of A. sucrose and B. acrylated tetrahydrofurfural alcohol.

2. Experimental

2.1 Materials used. Powderized sucrose was purchased from local grocery store. Methyl acrylate, potassium carbonate, tetrabutylammonium hydroxide, hydroquinone and phenothiazine were purchased from Aldrich. Ebecryl® 860 (ASO - acrylated soybean oil, 3.4 acrylate group per soybean oil molecule), Ebecryl® 168 and Ebecryl® 170 (UV curable phosphated acrylate adhesion promoter on metal) were kindly supplied by Cytec Industries Inc. Hyperbranched polyester acrylates CN2300 and CN2304 (abbreviated as A8 and A18 respectively, specifications shown in Table 1), and SR285, tetrahydrofurfural (ATHF), were kindly supplied by Sartomer Company Inc. Irgacure 2022 (PI), a 1:4 by weight photoinitiator blend of Phenylbis(2,4,6-trimethylbenzoyl)-phosphine oxide) and 2-Hydroxy-2-methyl-1-phenyl-1-propanone, was kindly supplied by Ciba Specialty Chemicals.

Table 1. Properties of hyperbranched polyester acrylates from Sartomer Company Inc.

Trade name	Abbreviation	Acrylate functionality	Acrylate equivalent weight (g/mol)	Surface Tension (mN/m @ 25 °C)	DMA T _g (°C)
CN2300	A8	8	163	32.6	96
CN2304	A18	18	96	32.6	181

2.2 Synthesis and characterization of acrylated sucrose (AS) and methacrylated sucrose (MAS).

The AS and MAS were synthesized in bulk following slightly modified procedures based on the procedures described in the literature.²¹ A typical procedure for the synthesis of acrylated sucrose is: powderized sucrose and tetrabutylammonium hydroxide were dried under 50 °C in vacuum oven overnight to remove water. 39.12 g sucrose was added into a 250 ml two-neck round bottom flask containing a Teflon-coated stir bar. Separately, 236.13 g methyl acrylate (three times in excess to sucrose), 1.38 g potassium carbonate, 2.75 g tetrabutylammonium hydroxide, 0.14 g hydroquinone and 0.14 g phenothiazine were pre-mixed in a beaker and added to the sucrose in the flask. The flask was connected to a condenser on one neck. A long needle was inserted into the flask through a rubber septum for dry air bubbling on the other neck. The reaction started by heating the flask in a silicone oil bath at 70° C. After designated reaction time, the reaction product mixture was diluted with acetone and the acrylated products were separated from the unreacted sucrose using vacuum filtration and acetone washing. The acrylated sucrose was recovered by removing acetone and excess methyl acrylate using rotary vacuum evaporation. The IR spectra were recorded with Thermo Scientific Nicolet 8700 Fourier Transform Infrared Spectrometer with detector type DTGS KBr. The mass spectra were obtained with an Applied Biosciences 4000 Q-Trap MS-MS equipped with a turbospray ion source.

2.3 UV curable coating formulation and characterization. The liquid coating formulation was simply prepared by adding and mixing all the ingredients in a vial, and gentle heating was used to help dissolution of the ingredients if necessary. For coating physical property tests, the liquid coatings were cast on aluminum Q-panels with a wire-wound drawdown rod to form a thin film with ~ 100 μm thickness, followed by UV curing using a Fusion LC6B Benchtop Conveyor with an F300 UVA lamp (UVA, irradiance ~ 1548 mW/cm², 2205/cm² measured by UV Power Puck® II from EIT Inc) in air. Typical curing protocol is 1 pass through the lamp with conveyor belt speed 10 feet/min. The coatings

were tested after being conditioned in ambient laboratory conditions for at least 24 hours. An automated surface energy measurement unit manufactured by Symyx Discovery Tools, Inc. and First Ten Angstroms was used to measure water contact angle on UV cured thin film materials. Three drops of water were used for each measurement, and the average contact angle and standard deviation were reported. Hardness testing was performed with a BYK Gardner pendulum hardness tester in König mode; the hardness was reported in seconds. Methyl ethyl ketone (MEK) double rubs were used to assess the solvent resistance of the cured coatings. A 26 oz hammer with 5 layers of cheesecloth wrapped around the hammerhead was soaked in MEK for rubbing. The number of double rubs taken to expose the substrate were recorded and reported. Falling weight direct impact testing was carried out according to ASTM D2794 with a 2 lb weight. The starting height was increased until the film was damaged and/or delaminated from the substrate, and the maximum height at which the film was intact was recorded. Tensile tests were performed using an Instron 5542 testing system (Instron Corp., Norwood, MA). ASTM D412-D dumbbell specimens were used. The strain rate was $0.2\% \text{ s}^{-1}$. Dynamic mechanical thermal analysis (DMTA) was performed using a TA Instruments Q800 DMA in rectangular tension/compression geometry. The analysis was carried out from $-50\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ at a frequency of 1 Hz and a ramp rate of $3\text{ }^{\circ}\text{C min}^{-1}$. T_g was obtained from the maximum peak in the $\tan \delta$ curves. Crosslink density (v_e) was calculated according to equation: $E' = 3v_eRT$, where E' value was determined in the linear portion at least $50\text{ }^{\circ}\text{C}$ greater than the T_g . DSC experiments were performed utilizing a TA Instruments Q1000 DSC with a heat-cool-heat cycle. The sample size was $\sim 5.0\text{ mg}$. Temperature was ramped from $-50\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ at $10\text{ }^{\circ}\text{C min}^{-1}$ in nitrogen.

3. Results and Discussion

3.1. Synthesis and characterization of acrylated sucrose and methacrylated sucrose. The synthesized acrylated and methacrylated sucrose (AS and MAS) are brown, highly viscous semi-solid materials. Unlike sucrose, which has poor solubility in most organic solvents, the AS and MAS exhibited good solubility in common organic solvents such as acetone, methanol, THF etc., as well as water. In addition, the AS and MAS showed good solubility in the reactive diluent ATHF. Generally, it was found that AS and MAS products obtained after longer reaction time had better solubility. FTIR and Mass Spectroscopy were used to characterize the synthesized AS and MAS. Figure 2 shows the FTIR spectrum of AS obtained after 6 hr reaction (AS6h) as an example. The appearance of the characteristic acrylate peaks at 807 and 1635 cm^{-1} indicates the attachment of acrylate group to the sucrose. Figures 3A and 3B show the mass spectra of AS obtained after 6 hr and 12 hr reactions (AS6h and AS12h) respectively; Table 2 lists the theoretical molecular weight calculation for acrylated sucrose with increasing acrylate functionalities. Molecular ion peaks with close molecular weight numbers shown in Table 2 were identified in the mass spectra for AS6h and AS12h, indicating the existence of AS with varying degree of acrylation in the product mixture. Also, it was noticed from Figures 3A and 3B that the acrylate functionality of the AS increased with increasing reaction time. In AS6h, five, six and seven acrylate functionalized sucrose oligomers were predominant; in AS12h, seven and eight acrylate functionalized sucrose oligomers were predominant. The Mass Spectroscopy results of AS6h and AS12h showed that the degree and distribution of acrylate functionality of the synthesized AS can be controlled by reaction time. Preliminary UV curing of synthesized AS and MAS were carried out. MAS exhibited poor photopolymerization reactivity, consequently only AS was chosen for formulation study.

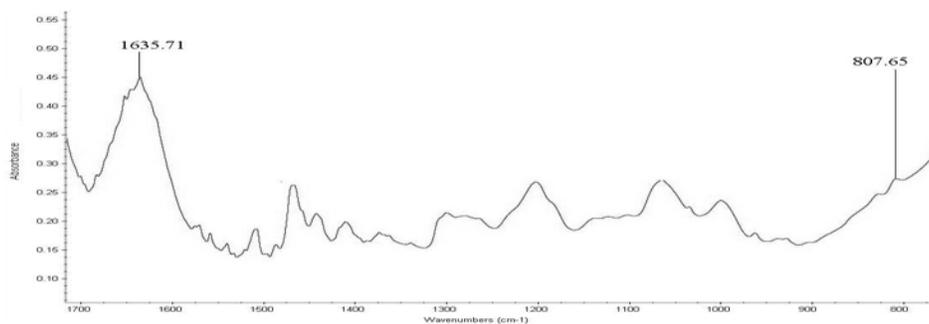
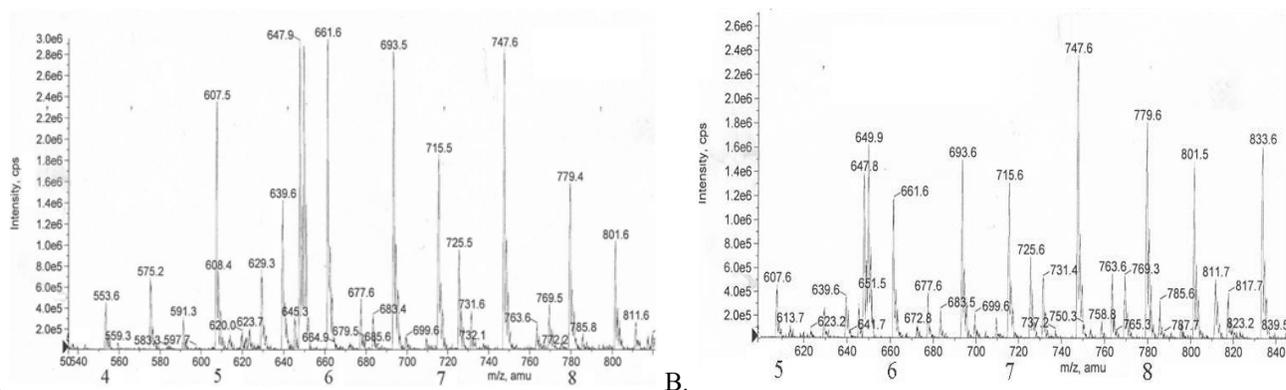


Figure 2. IR spectrum of AS6h showing the appearance of acrylate peaks at 1635 and 807 cm^{-1} .



A. Mass spectrum of AS6h, and B. AS12h.

Table 2. Molecular weight calculation for acrylated sucrose oligomers.

acrylate functionality	theoretical MW of AS	+17 (HO^-)	+23 (Na^+ , from the container glass etc.)
4	558.5	575.5	581.5
5	612.5	629.5	635.5
6	666.5	683.5	689.5
7	720.6	737.6	743.6
8	774.6	791.6	797.6

3.2. Formulation and characterization of soy-based UV curable coatings containing acrylated sucrose and hyperbranched acrylates. ASO is a highly viscous liquid. It can be UV cured in seconds by adding 3% wt. PI, but the formulation viscosity is too high for coatings applications. 20% wt. ATHF was added to the ASO and PI blend to achieve a reference formulation (Base) with applicable viscosity. To study the effect of AS and hyperbranched acrylates (HBAs) on the soy-based UV curable formulations, AS6h and AS12h, and A8 and A18 were added into the Base formulation, together with 5% wt. 1:1 blend of Ebecryl[®] 168 and 170 for adhesion enhancement on aluminum panels. The coating material performance of these formulations were tested and compared. The coating physical properties were first tested. Figures 4, 5, 6 and 7 show and compare the coating pendulum hardness, cross-hatch adhesion, impact resistance and solvent resistance respectively. Compared to the Base formulation, the addition of only 10% wt. HBAs significantly increased the coating hardness and solvent resistance. This enhancement is attributed to the incorporation of higher molecular weight multifunctional crosslinkers (HBAs) with higher glass transition temperatures and more rigid polyester backbones in the crosslinked ASO based coating films. The Base formulation has very poor adhesion on aluminum. Upon addition of HBAs and adhesion promoters, the coatings' adhesion was improved. The lower photopolymerization shrinkage of HBAs,²⁰ the acidic etching of the metal substrate by the adhesion promoters, and the

phosphonate complex formation between the metal and the adhesion promoters²⁴ were attributed to the improved adhesion. The addition of A8 didn't affect the coating impact resistance. On the other hand, A18 addition increased the impact resistance from 25 inch to 35 inch. The coating impact resistance is an overall evaluation of the coating adhesion, flexibility and toughness. The addition of more rigid A8 and A18 enhanced the coating adhesion due to lower photopolymerization shrinkage, however, the film flexibility didn't increase accordingly, which resulted in only slight increase in impact resistance.

In contrast to HBAs, the incorporation of 20% wt. AS6h and AS12h into the Base formulation generated more durable coating films, as evidenced by the much enhanced coating impact resistance. At the same time, decreased coating hardness and similar solvent resistance were found for the AS added formulations as compared to the Base formulation. These observations suggested that the AS6h and AS12h were acting as reactive flexibilizers in the soy-based coating formulations. Unmodified sucrose molecules have intensive intermolecular hydrogen bonding that results in hard, crystalline material.²⁵ Upon acrylation, as in the case of AS6h and AS12h, most of the hydroxyls in the sucrose were transformed into photo reactive acrylate groups. Thus hydrogen bonding in the AS was expected to be less intense. On the other hand, the five and six member aliphatic rings connected via an ether bond in the sucrose molecule possess balanced rigidity and flexibility. It can be predicted that crosslink network with such molecules would afford larger deformation via breaking of the hydrogen bonding and transformation of the acrylated sucrose molecule configuration under external forces before fracturing. Consequently, lower pendulum hardness but tougher coating films with much higher impact resistance were observed with AS addition. Negligible adhesion enhancement was found for the AS added samples. It is most probably due to the lower molecular weight of the AS molecules as compared to the HBAs, thus the photopolymerization induced shrinkage is still significantly high enough to affect the adhesion.²⁰ The combination of 10% wt. HBAs and 20% wt. AS6h or AS12h into the ASO-based formulations generated balanced coating performance. The coating hardness and impact resistance were in between the properties obtained by adding either the HBA or AS individually. However, it was noticed that the coating solvent resistance was not sacrificed and remained at over 400 double rubs even upon the addition of 20% wt. AS. Also, the coating adhesion for formulations with both HBAs and AS was higher than the formulations with either the HBAs or the AS individual addition, except for the formulation with 10% A18 and 20% AS12h. A synergistic effect between the HBAs and the AS seems to be present: The reactive nature of the AS helps to maintain the excellent solvent resistance obtained by addition of HBAs, while the relatively flexible AS may contribute to stress dissipation inside the coating during photopolymerization, leading to further enhanced adhesion after addition of HBAs. This synergistic effect will be further discussed when examining the coating thermal mechanical behavior.

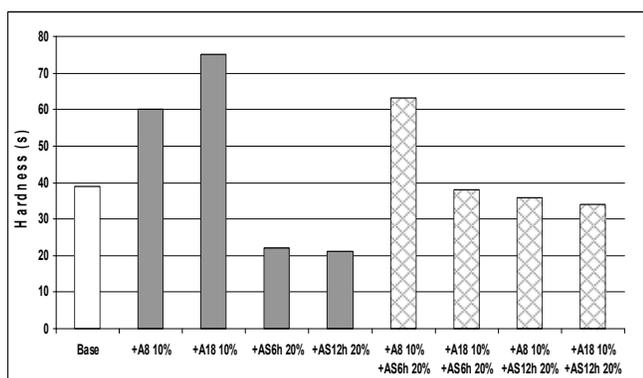


Figure 4. Coating pendulum hardness comparison.

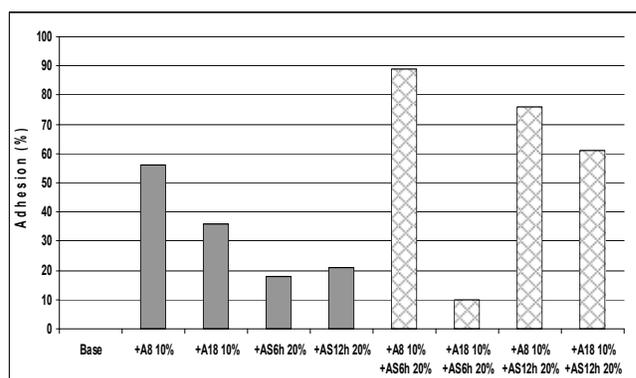


Figure 5. Comparison of coating adhesion to aluminum.

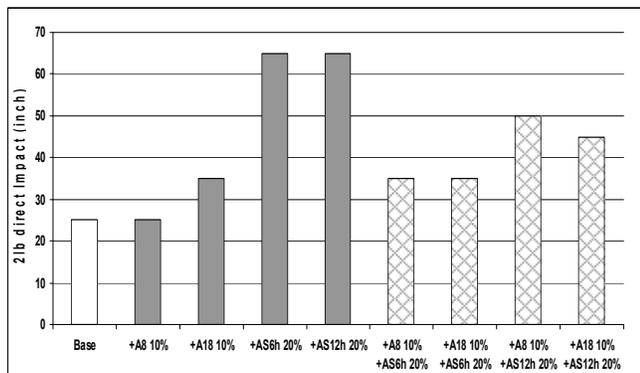


Figure 6. Coating impact resistance comparison.

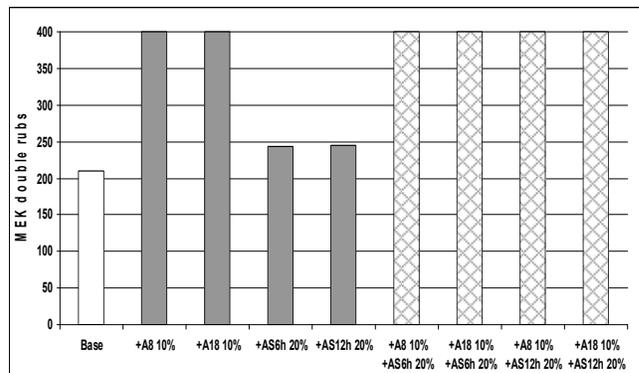


Figure 7. Coating solvent resistance comparison.

The synthesized AS6h and AS12h had good solubility in water. The effect of their hydrophilicity on the coating surface and bulk properties were evaluated by water contact angle measurements and water immersion test. Figure 8 shows that the coating produced from the Base formulation, which has over 75% wt. ASO, is hydrophobic with contact angle over 95 degree due to the hydrophobic nature of the crosslinked ASO network. Upon addition of HBAs, the coating contact angle decreased to around 85 degree, as a result of diluting the hydrophobic ASO network with relatively more hydrophilic polyester HBAs. When 20% wt. hydrophilic AS6h or AS12h was added respectively into the Base formulation, further decrement of the water contact angle was noticed, especially for the formulations containing AS6h, which is more hydrophilic due to the existence of higher number of residual hydroxyls. The combination of both HBAs and AS with ASO produced relatively hydrophilic coatings with water contact angles around 80 degree. Tap water immersion test was conducted to examine the stability of AS added, ASO based coating films in water. 10% or 20% wt. AS6h and AS12h were added to the Base formulation together with 10% wt. of A8 or A18. The formulations were applied onto bare aluminum panels, UV cured, and immersed in water for up to 7 days. Visual examinations of the coating films were conducted to evaluate the coating film stability in water. Figure 9 shows the images of the coating films taken after 7 days water immersion. For the coatings containing 20% wt. either AS6h or AS12h, the films delaminated from the bare aluminum panels after about 24 hours immersion. The stress generated from coating film swelling upon water absorption, and the reduced adhesion at the coating - substrate interface due to the replacement of water²⁶ were considered the major reasons for the quick delamination from the bare aluminum substrate. This observation confirms the high hydrophilicity of the coatings with high AS loading (20% wt.). With 10% wt. AS6h and AS12h addition, the ASO based coating films showed rather good stability in water after 7 days, as shown in Figure 9. All the other coating films adhered well to the bare aluminum panel, except for the formulation containing 10% wt. AS6h and 10% wt. A8, which showed slight delamination after 7 days. Most parts of the immersed coating films remained smooth, while certain spots on the clear films turned hazy due to water absorption. Generally, formulations containing 10% wt. AS6h had relatively lower resistance to water immersion versus the ones containing 10% wt. AS12h, which can be attributed to the higher -OH content in AS6h.

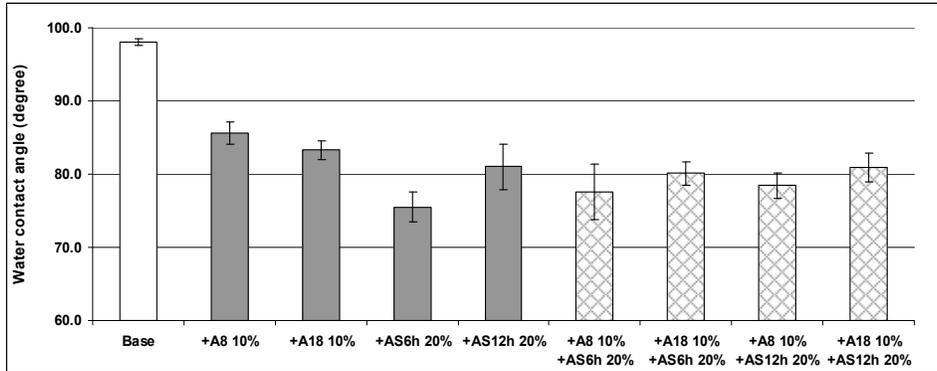


Figure 8. Water contact angle data for UV cured, soy-based coatings.

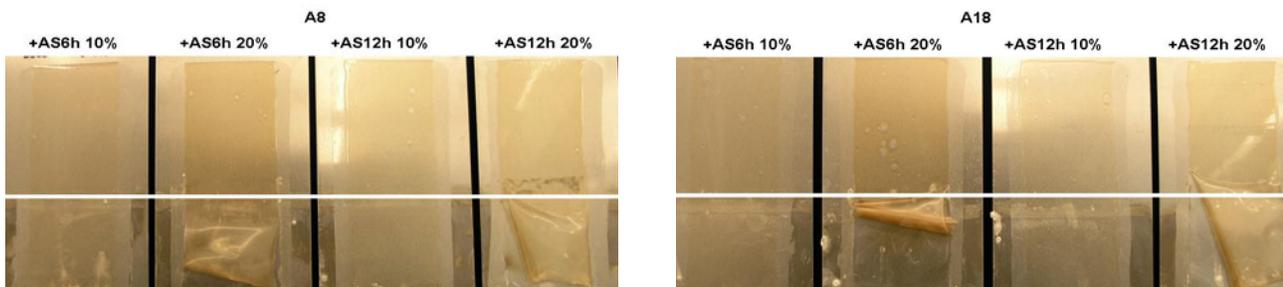


Figure 9. Coating film images after 7 days tap water immersion, the white line in the images shows the approximate location of water line during immersion.

The tensile modulus and elongation at break of the UV cured, soy-based coating films were obtained and the results shown in Figure 10. Compared to the Base formulation, significant coating modulus increment was achieved upon addition of HBAs, especially for the coatings containing A18, which has higher acrylate functionality and glass transition temperature than A8. The rigidity of the coating film increased accordingly as indicated by the lower elongation at break with A18 addition. When AS6h or AS12h was added to the Base formulation, the film modulus didn't change significantly, but the elongation at break increased by over 100%. The much enhanced elongation at break value is consistent with the observed much higher impact resistance upon AS addition, demonstrating the significant toughening effect of the AS in the UV cured soy-based coatings. A "mixing" effect was noticed for the formulations containing both AS and HBAs, as their modulus and elongation at break data were between the ones with only AS or HBA addition, showing balanced coating mechanical properties. The glass transition temperature and crosslink density of the soy-based coatings were obtained and calculated from DMTA as shown in Figure 11, and the overlap of the DMTA $\tan\delta$ curves is shown in Figure 12. The glass transition temperature of the Base formulation is around 20 °C, as a result of the softer, more flexible fatty acid triglyceride backbone of ASO. The polyester HBAs A8 and A18 have much higher glass transition temperatures than ASO due to the more rigid polyester backbone, higher molecular weight, and higher acrylate functionality. Upon individual A8 and A18 addition, the main glass transition temperature of the coatings increased to 25 - 30 °C. In addition, the glass transition peak broadened and extended to higher temperatures. The higher and broader glass transition in the two HBA-added UV cured coating formulations contributed to the higher hardness and modulus of the coatings films, indicating tougher crosslinked network formation. However, the crosslinking density for the two HBA added formulations (+A8 10% and +A18 10%) were lower than the Base formulation. The earlier photopolymerization induced vitrification of the higher functionality and higher molecular weight HBAs added formulations were considered the reasons for lower crosslink density.^{20,27} When only 20%

wt. AS6h or AS12h was added to the Base formulation, it was noticed from Figures 11 and 12 that the main glass transition of the crosslink network for these two samples didn't change significantly as compared to the Base formulation. However, a second transition appears as a shoulder peak of the main transition at higher temperature (about 80 °C). The second transition was attributed to the acrylated sucrose in the soy-based crosslinked coating network. The two transition peaks in the $\tan\delta$ curves indicates that there are two microphases^{28,29} in the crosslinked, acrylated sucrose-added UV cured coating films. The predominant phase is the crosslinked ASO, the second phase is the crosslinked acrylated sucrose oligomers. Due to the more rigid AS ring structure and intermolecular hydrogen bonding, the second phase has higher transition temperature. Since the second transition appears as a shoulder peak of the main transition peak in the $\tan\delta$ curves, it can be concluded that there is certain degree of compatibility or "phase mixing" between the ASO and AS phases,³⁰ largely owing to the chemical bonding formed between ASO and AS during the photopolymerization of the acrylate groups. The presence of two interconnected soft and hard micro phases resembles the micro phase separation in a typical polyurethane polymer, which exhibits excellent mechanical properties.^{30,31} The existence of micro phase separation in the AS added, ASO based crosslinked network explains in microscopic scale the observed significantly enhanced coating film impact resistance and tensile elongation at break. When both HBAs and AS were added into the ASO based formulation, it was first noticed from the $\tan\delta$ curves that the main transition peaks still appear at higher temperatures and are broader than the Base formulation, but the higher temperature transition peaks assigned to the AS phase were less distinct, indicating better compatibility between the ASO and AS. Hyperbranched polymers, owing to their hyperbranched molecular structure, have higher solubility and compatibility with other chemicals.^{32,33} Thus, the less distinct higher transition temperature peak is mostly probably due to the compatibilizer role the HBAs played in the ASO and AS added formulations. Despite improved compatibility, the less distinct micro phase separation, and the incorporation of more rigid, higher glass transition temperature HBAs generated coating films with lower impact resistance than the ones with only AS addition. With regard to other coating film properties such as tensile modulus and elongation, hardness, and impact resistance etc., a "mixing effect" was noticed that gives balanced coating properties. Higher crosslink density was found for both HBAs and AS added formulations as compared to formulations containing only HBAs or AS. This may be due to the apparent higher rubbery modulus, since higher photopolymerization conversion of the acrylate functional groups on HBAs and AS is less possible due to early vitrification in these formulations.^{20,27}

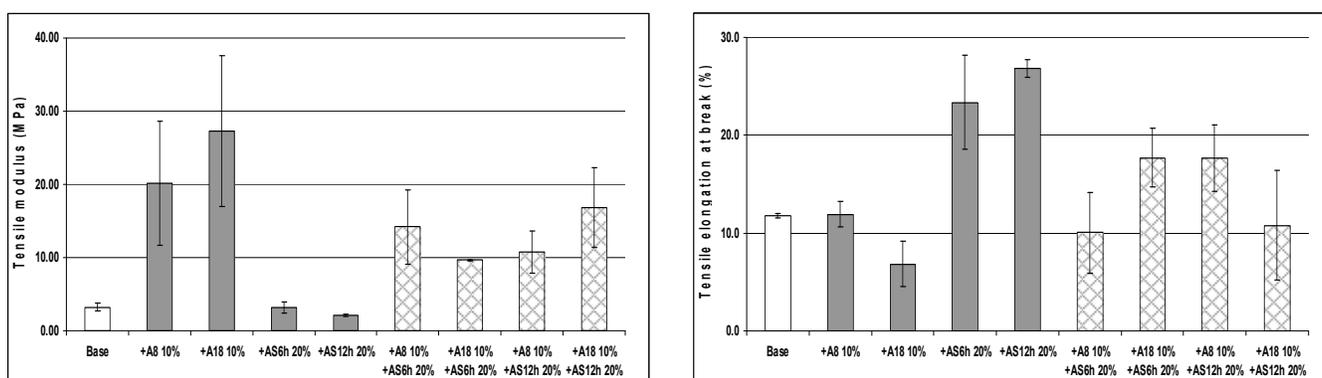


Figure 10. Tensile modulus and elongation for UV cured, soy-based coatings.

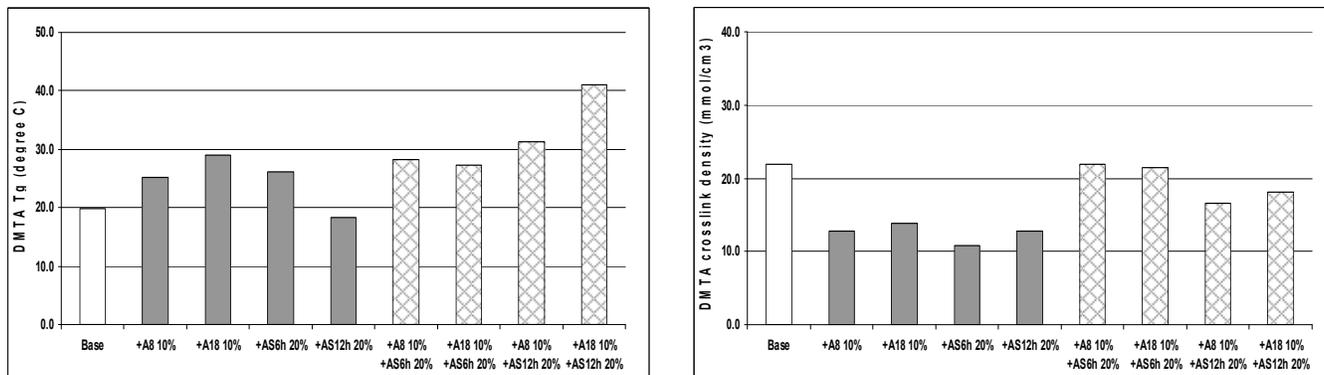


Figure 11. DMTA glass transition (main) and crosslink density for UV cured soy-based coatings.

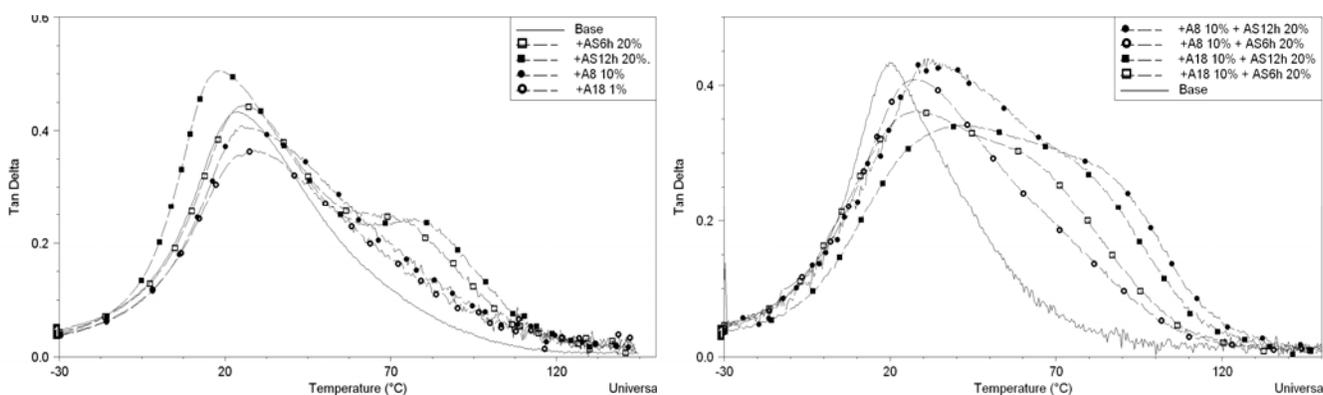


Figure 12. Overlap of DMTA tan δ curves for UV cured, soy-based coatings.

Thermal stability of the soy-based UV curable coatings was studied using Thermal Gravimetric Analyzer (TGA). The percent weight loss of the samples was plotted as a function of temperature and shown in Figure 13. All the samples showed a two step weight loss profile. The Base formulation showed major thermal decomposition between 250 to 400 °C, after which the sample continued to lose weight but at a slower rate, until at around 590 °C all the residual material burned off. When 10 wt. % HBAs were added to Base formulation, the weight loss profiles showed a similar major decomposition temperature range to the Base formulation, but at a little faster rate. After the major decomposition, the HBA-containing formulations exhibited slower decomposition rate versus the Base formulation, with more (about 5 wt. %) material left at the end of the TGA run. For 20 wt. % AS (AS6h or AS12h) and 10 wt. % HBAs (A8 or A18) added to the Base formulation, the major decomposition event started at a lower temperature around 200 °C, and the decomposition rate was much faster than other formulations without AS before 350 °C. This is due to the presence of sucrose in crosslinked networks, which starts thermal decomposition at ~ 186 °C and shows major weight loss at maximum rate between 233 to 300 °C.³⁴ After ~ 350 °C, the AS added formulations decomposed at a slower rate than the formulations without AS. Solid char formation as a result of the degradation of the sucrose components may be the reason for the slower rate of weight loss observed.³⁴

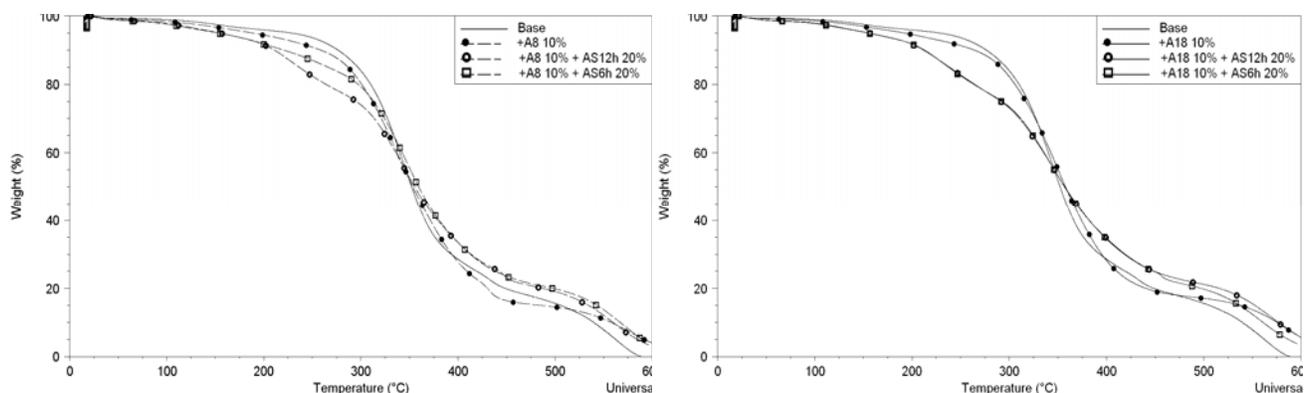


Figure 13. TGA weight loss curves.

The biorenewable content calculated in % wt. for the raw materials are 80%, 60%, 53% and 55% for ASO, ATHF, AS6h and AS12h respectively. The biorenewable content calculated for the soy-based, UV curable coating formulations studied is shown Figure 14. Acrylic acid is not counted as a bio-derived chemical in the calculations. When combining the HBAs and “sweet” AS as reactive toughening agents into the Base formulation, the biorenewable content of the modified formulations decreased by ~ 10-15% wt. to ~ 55 - 60 % wt., which is still reasonably high. On the other hand, the coating performance increased significantly, owing to the unique structural features of the HBAs and the AS discussed previously. Thus, the feasibility of producing soy-based, high performance UV curable coatings with high biorenewable content is demonstrated.

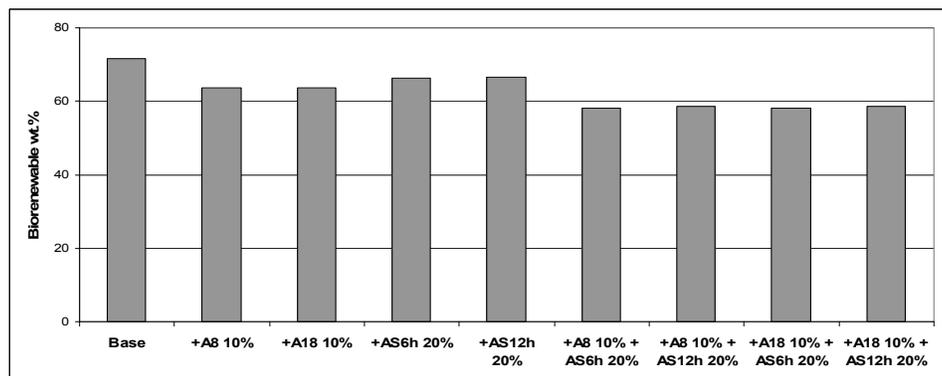


Figure 14. Biorenewable content in % wt. for the formulations studied.

4. Conclusions

Acrylated sucrose (AS) oligomers were synthesized and characterized using mass spectroscopy and FTIR. AS oligomers had good solubility in common organic solvents and acrylate reactive diluent. Acrylate functionality of AS increased with reaction time. Addition of higher T_g , polyester HBAs into the ASO-based, UV curable formulations increased the coating mechanical properties as well as glass transition temperature and tensile modulus, but decreased the crosslink density and tensile elongation. Addition of the “sweet” AS significantly enhanced the coating impact resistance and tensile elongation, which was attributed to the micro phase separation in the crosslinked coating films and the tougher structure of AS. High level of AS in the formulations resulted in high coating hydrophilicity and film delamination during water immersion. The combination of HBAs and AS in the ASO-based UV curable formulations produced “green” coatings containing ~ 60% wt. biorenewable ingredients with much enhanced and balanced coating properties.

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