**The exploration of Michael-addition reaction chemistry to create high performance, ambient cure
thermoset coatings based on soybean oil**

Adlina Paramarta and Dean C. Webster*

Department of Coatings and Polymeric Materials

North Dakota State University

Fargo, ND 58108-6050

Abstract

Using Michael addition crosslinking technology, thermoset coatings were prepared from acrylated epoxidized sucrose soyate (AESS) and amine crosslinkers. AESS was synthesized from sucrose soyate, which is the sucrose ester of soybean oil fatty acids and has an average of about 12 functionalities per molecule. Due to the high functionality of AESS and fast reactivity of the amine crosslinkers, the coatings can be cured at ambient temperature (21 °C) in a relatively short period of time yielding good coatings properties. When AESS was reacted with 4'4'-methylene bis(cyclohexylamine), the acrylate group conversion was determined by FTIR to be up to 90%. It was also found that the type of solvent used in the coatings formulation affected the film formation and thus the coatings properties. The addition of 1,6-hexanediol diacrylate diluent in the formulations resulted in softer and lower T_g coatings. Using a trifunctional amine such as diethylene triamine, coatings could be prepared without the addition of any catalyst. Overall, thermosets made from AESS Michael crosslinking technology provide a highly bio-based coating system with good hardness and chemical resistance.

Keywords: Coatings, Michael addition reaction, acrylated epoxidized sucrose soyate, ambient cure coatings

* Corresponding author: Address: PO Box 6050, Dept 2760, Fargo, ND 58108 Ph: 701-231-8709; email: dean.webster@ndsu.edu

1. Introduction

Michael addition is a reaction between a nucleophile (Michael donors) and an activated olefin (Michael acceptor) to produce a covalent bond between the Michael donor and acceptor. The general reaction scheme is shown in Scheme 1. The Michael addition reaction has been employed as a versatile tool in the synthesis of linear, graft, hyperbranched, dendritic and network polymers for a wide range of applications such as coatings, adhesives, bio-medical/pharmaceutical, and specialty chemicals [1-11].

Scheme 1. General reaction mechanism of Michael addition

The use of the Michael addition reaction for crosslinking in the coatings industry has been gaining more attention recently. This popularity is motivated by the following benefits. First, the reaction only requires mild conditions to achieve high conversion with favorable reaction rates, and thus coatings can be cured at ambient temperature. The reaction rates can be controlled by the selection of monomer precursor, catalyst system, and solvent [12-15]. Second, there are no volatile by-products of the reaction, thus eliminating or minimizing the amount of volatile organic compounds (VOCs). Lastly, there are a wide range of commercially available chemicals that can be used as reactants and catalysts. Common functional groups used as Michael donors include acetoacetates, amines, thiols and phosphines. There are more options of functional groups that can be used as Michael acceptors, which include acrylate esters, acrylonitrile, acrylamides, maleimides, alkyl methacrylate, and α,β -unsaturated aldehydes. Even though it is often not necessary to add a catalyst to accelerate the reaction, a catalyst may be added to ensure that the reaction reaches high conversion; the catalyst can be either a base (hydroxide, amine, alcohol, etc) or an acid (p-toluene sulfonic acid, sulfuric acid, bis(trifluoromethanesulfon)imide, etc.). Mather et al. have presented a thorough review discussing the use of a wide variety of those precursors for polymer macromolecular design for many applications [12].

The use of Michael addition technology for coatings applications has been explored since the 1980s [1, 13, 16-19]. Yet, there are many concerns to be addressed in order for this reaction to be widely applied for coatings applications. First, this reaction can proceed fairly fast at room temperature and thus coatings formulations may have a somewhat short pot life or working time. Recently, Brinkhuis et al. addressed this concern by using a novel blocked catalyst and kinetic control additive system [20]. The system consists of the reversible blocking of a strong base catalyst with dialkylcarbonate. The strong base reacts with the carbonate to form carbonate anions, which have low reactivity to initiate the

Michael addition reaction and thus results in a long pot life in the container. Upon application, the large surface area shifts the equilibrium to trigger the catalyst de-blocking and thus initiates the reaction. Unfortunately, this reversible catalyst blocking system produces alcohol as a by-product. Another cause of the limited use of the Michael addition reaction in the coatings industry is due to limited options for highly functionalized resins and/or crosslinkers to create thermoset coatings with good hardness and chemical resistance. The most commonly used functional groups reported for Michael addition curing are acetoacetate and acrylate esters. Often, appropriate blends of di-, tri-, and tetra- acrylates must be used to achieve good performance [8, 10, 19].

Recently, Webster et al. invented a highly functionalized acrylate resin based on epoxidized sucrose soyate (ESS) [21]. Epoxidized sucrose soyate is an epoxy resin derived from the sucrose ester of soybean oil fatty acids [22-24]. This epoxy resin has an average of 12 functional groups per molecule, and, when crosslinked, has been shown to offer excellent mechanical properties in coatings and composites applications [25-35]. The ESS resin can be modified into an acrylate resin through ring opening of the epoxy using acrylic acid; the reaction is shown in Scheme 2. The synthesis of AESS is a fairly straightforward, one-pot synthesis process with very high conversion requiring no further purification. The number of acrylate groups can be tuned by controlling the amount of acrylic acid used during the synthesis process. The use of this highly functionalized acrylate resin for UV-curable coatings has been shown to yield improved performance compared to an acrylate functional resin based on soybean oil [28]. Using this AESS resin for Michael addition crosslinking can be beneficial due to its high functionality which can lead to a high crosslink density. Furthermore, the use of AESS will also potentially increase the sustainability of the materials since it is a 75+% bio-based resin.

Scheme 2. Representative structures showing the acrylation of epoxidized sucrose soyate

Thus, the goal of this work was to explore the feasibility of using the AESS resin to produce high performance, ambient cured coatings using Michael addition crosslinking. Structure-property relationships of the coatings system were studied based on the variation in the acrylate-to-amine ratio, type of amine crosslinker used, and the use of a reactive diluent. The properties evaluated include mechanical coatings properties and thermal properties. For comparison, a coatings system derived from acrylated epoxidized soybean oil (AESO) was also prepared.

2. Experimental Scheme

2.1. Raw Materials

Acrylated epoxidized sucrose soyate (AESS) resin was synthesized from epoxidized sucrose soyate (ESS), with 90% of the epoxy groups being converted into acrylate groups. The synthesis and characterization of ESS and AESS resin is presented in previous publications [24, 28]. Ethyl 3-ethoxypropionate (EEP) was provided by Eastman Chemical Co. 4'4'-Methylene bis(cyclohexylamine) (PACM) was provided by Air Products. Diethylene triamine (DETA), m-xylylene diamine (MXDA), and p-toluene sulfonic acid monohydrate (pTSA) were obtained from Sigma Aldrich. 1,6-Hexanediol diacrylate was provided by Sartomer. Ethanol was obtained from Alfa-Aesar. The structures of the chemicals used in this work are illustrated in Figure 1.

Figure 1. Structures of the chemicals used in this work. AESO structure is representative.

2.2. Coatings formulation

AESS was first dissolved in a variety of solvents, and air bubbles in the mixture were removed by sonication. Then, amine crosslinker and pTSA catalyst were added to the mixture. The mixture was stirred using a spatula for 1 minute, and then applied onto 7.62 x 15.24 x 0.051 cm (3 x 6 x 0.020 in) cold rolled steel panels pretreated with iron phosphate (Bonderite 1000 [™] obtained from Q-panel) and 10.16 x 15.24 x 0.081 cm (4 x 6 x 0.032 in) glass panels using a draw down bar at 150 μ m (6 mils) wet film thickness. The panels were then forced-cured in the oven at 80°C for 45 minutes. For ambient-cured coatings, the coatings were set aside on the laboratory bench at 21°C to cure for 1 week prior to evaluation of properties.

Structure-property relationships of the coatings were studied based on compositional variation in the functional group molar ratio, amount of reactive diluents used, type of amine crosslinker, and curing method. The compositions of these coatings formulations are summarized in Table 1.

Table 1. Coatings formulation compositions

No.	Acrylate Resin	Amine Crosslinker	Acrylate-to-Amine Molar Ratio	Diluents (HDDA) Amount (mol %)	Cure Process
1	AESS	PACM	1 : 1	0	Forced
2	AESS	PACM	1.5 : 1	0	Forced
3	AESS	PACM	2 : 1	0	Forced
4	AESS	PACM	3 : 1	0	Forced
5	AESS	PACM	1.5 : 1	25	Forced
6	AESS	PACM	1.5 : 1	50	Forced
7	AESS	PACM	1.5 : 1	75	Forced
8	AESS	DETA	1.5 : 1	0	Forced
9	AESS	MXDA	1.5 : 1	0	Forced
10	AESO	PACM	1.5 : 1	0	Forced
11	AESS	PACM	1.5 : 1	0	Ambient

2.3. Viscosity and gel-time study using rheometer

An ARES Series Rheometer was used to measure the viscosity of the resin system and determine the gel time of the coatings formulation. Parallel plate geometry was used and the gap between the plates was set to be 1 mm. For viscosity measurements, the sample shear rate was 0.1 to 100 Hz, and the reported value was taken from an average of 3 measurements at 10 Hz. Then, for gel time determination, the formulations were sheared at 0.1 Hz, and storage modulus, loss modulus, and

viscosity values were monitored. Gel time was determined when storage modulus value was equal to loss modulus value or when the viscosity value increased dramatically.

2.4. Drying time determination

The drying times of the coatings were determined using a BK Drying Recorder. The results were analyzed using ASTM D5895. Four stages were determined: Stage 1 corresponds to set-to-touch time, stage 2 corresponds to tack-free time, stage 3 corresponds to dry-hard time, and stage 4 corresponds to dry-through time.

2.5. Chemical analysis using FTIR spectroscopy

Fourier-transform infrared (FTIR) spectroscopy was performed using a Thermo Scientific Nicolet 8700 FTIR spectrometer using a potassium bromide salt crystal. FTIR analysis was used to determine the conversion of the acrylate group in the AESS after the curing process. The conversion is determined from the decrease in the area of three peaks that correspond to the unsaturation of the functional groups: 810 cm^{-1} (C=C out of plane deformation), 1407 cm^{-1} (C=C scissoring of HC=CH₂ (medium) in-plane CH₂ deformation 1637 cm^{-1} (C=C stretching for HC=CH₂).

2.6. Coatings characterization

The dry film thickness on steel substrates was measured using a Byko-Test 8500 coatings thickness gauge; the reported value is the average and standard deviation of 10 points of measurement on the panel. The hardness of the coatings was determined using König pendulum hardness and pencil hardness following ASTM D4366 and ASTM D3363, respectively. Flexibility was measured using conical mandrel bend test (ASTM D522) and reverse impact (ASTM D3794). Adhesion was measured using the cross-hatch adhesion method (ASTM D3359). Solvent resistance was determined through the methyl ethyl ketone (MEK) double rubs test, where a MEK-saturated cheese cloth was wrapped on a hammerhead and then rubbed against the coatings surface back and forth until coatings failure was observed. Solvent resistance may indicate the degree of crosslinking of the thermoset. The specular gloss was measured using BYK Gardner Micro-Tri-Gloss Gloss Meter at 20°, 60° and 85° following ASTM D523.

2.7. Thermal analysis

The thermal properties of the cured coatings were analyzed through differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). DSC experiments were performed using a TA Instruments Q2000 DSC. The glass transition temperature, T_g , of free films were determined using a heat-cool-heat method, and the reported value was taken from the inflection point during the heating cycle. Free film samples of 10 mg were exposed to a heat-cool-heat cycle from -80 to 250 °C with 30

°C/min heating (or cooling) ramp. DMA experiments were performed using a TA Instruments Q800 DMA. Coatings films were cut to have a width of 5 mm and 15 mm in length. The sample was heated from -50 to 150 °C with 3 °C/min heating ramp at 1Hz frequency and 0.1% strain. Furthermore, a preload force of 0.01 N was used and force track was set to 125%.

2.8. Soxhlet extraction

Soxhlet extraction of the coatings was performed to determine the gel fraction of the thermoset network. About 0.3 g of cured samples was folded inside filter paper, which then was inserted into an extraction thimble in a Soxhlet extraction apparatus. The extraction process was conducted with acetone as a solvent, and samples were extracted for 17 hours by acetone at reflux. After the process was completed, the wet residual samples were dried in the oven at 120 °C for 1 hour. The gel fraction was calculated from the ratio of sample weight after and before the Soxhlet extraction.

3. Results and Discussion

3.1. Aza-Michael addition reaction overview

A Michael addition reaction involving nitrogen-donor functionality is often referred as an aza-Michael addition. Since the amine can act as both the donor agent and base, the addition of catalyst is often not necessary. In this research, highly functionalized AESS resin was reacted with an amine crosslinker to form a thermoset network, and the reaction was catalyzed using a Bronsted acid, p-toluene sulfonic acid monohydrate in ethanol. The catalyst was added to ensure a high conversion of functional groups. In the case of an acid-catalyzed reaction, the acid coordinates with the unsaturated olefin and activates the receptor. This coordination increases the reactivity of the acrylate by increasing its electrophilicity [36-39]. The reaction mechanism and chemical structures of the raw materials are depicted in Scheme 3.

R₁, R₂ = highly functionalized acrylate resin

R = aliphatic, cycloaliphatic and aromatic crosslinker

Scheme 3. Reaction between acrylate groups in AESS and amine

As shown in Scheme 3, primary amines can react with two equivalents of acrylate to form tertiary amines. The reaction of amine hydrogen with the acrylate functionality tends to follow second order kinetics based on the concentration. Yet, the addition of acrylate to the formed secondary amine may affect the overall reaction kinetics as the reaction proceeds. The reactivity of 1° amine vs. 2° amine is highly dependent on the electronic and steric environment of the amine [40]. Generally, 2° amines are more nucleophilic than 1° amines and are therefore more reactive, yet the steric hindrance of the surrounding environment often causes the slow addition of 2° amines. In the case of linear aliphatic amines having low steric hindrance on the 2° amine such as n-methylenediamine, the reactivity sequence of multi-functional amines was observed to be 2° amines (original) > 1° amine >> 2° amines (formed). Yet, for linear aliphatic amines having high steric hindrance on the 2° amine such as n-hexylethylenediamine, the reactivity sequence changes to 1° amine > 2° amine (original) > 2° amine (formed). For a similar reason, the addition to the 2° amine (formed) tends to be significantly slower due to the high steric hindrance of the polymer backbone [40].

3.2. Solvent selection

Before going into more detail into the Michael reaction between AESS resin and amine crosslinker, it is important to note that the AESS resin has an extremely high viscosity (1.30×10^6 mPa.s) due to the high number of hydroxyl groups in the resin. Thus, in order to be easily applied as coatings, the resin viscosity must be reduced by the addition solvent and/or diluents. The solvent or diluent should be compatible with the formulation components. Furthermore, the solvent should evaporate at an appropriate rate during the curing process. If diluents are used, the addition of diluents should not affect the mechanical properties dramatically. The range of the viscosity for easy application was targeted to be below 1000 mPa.s.

Several solvents were screened to determine their suitability in reducing the viscosity of the AESS resin as well as their influence on coatings properties, as shown in Table 2. Solvents were added to produce 75% wt. solids coatings formulations. The solvents evaluated included methyl ethyl ketone (MEK), methyl iso-butyl ketone (MIBK), tert-butyl acetate (TBA), ethyl-3-ethoxypropionate (EEP), hexane (HEX) and cyclohexanone (CHX). These solvents were selected based on the following criteria: polarity, boiling point, and regulatory issues (i.e., VOC exempt). In this experiment, 4,4'-methylene bis(cyclohexylamine) (PACM) was used as the crosslinker. Coatings formulations were prepared with acrylate to primary amine equivalent ratio of 1.5:1, and pTSA catalyst at 5% by mole of 1° amine. Coatings were prepared by drawdown and were cured at 80 °C for 45 minutes. Coatings characterization was performed one week after being cured.

Table 2. Effect of solvent on coatings made using AESS cured with PACM.

Solvent	AESS + Solvent Properties		Coatings Properties		
	Soluble	Viscosity (mPa.s)	Appearance	König Hardness (s)	MEK double rubs
MEK	Yes	770 ± 160	Trapped bubbles (small size)	75	200
MIBK	Yes	660 ± 70	Trapped bubbles (small size)	48	325
CHX	Yes	2940 ± 280	Defects throughout	20	75
TBA	Yes	1260 ± 20	Trapped bubbles (bigger size)	50	325
EEP	Yes	790 ± 30	Minimal amount of bubbles	109	>400
HEX	No	-	-	-	-

The addition of solvent reduces the viscosity of the resin due to a decrease in the polymer-polymer interaction forces, dominated by the hydrogen bonding, which was overcome by the polymer-solvent interactions. As expected, AESS was not soluble in non-polar solvents such as hexane; and thus the AESS-HEX coating formulation was not prepared. AESS is fairly miscible with ketone- and ester-based solvents. The decrease in the viscosity depends on the polarity of the solvent. With the ketone-based solvent, due to similar structures of MEK and MIBK, the decrease in the viscosity is similar. The symmetrical chemical structure of the CHX causes the molecule to be less polar than MEK and MIBK, and thus the viscosity of the AESS-CHX system is higher. Then, comparing TBA and EEP solvents, EEP is more polar than TBA due to its ethoxy group and thus the decrease in the viscosity was observed to be greater. Even though the viscosity of AESS-CHX and AESS-TBA was out of the target range, coatings formulations were still prepared.

Initially, it was thought that the addition of PACM to the formulation would reduce the viscosity further since its viscosity is fairly low (80 mPa.s @25 °C). However, after the addition of amine and catalyst, the viscosity increases immediately to the range of 2000+ mPa.s for MIBK and EEP. This increase in the viscosity thus did not allow air bubbles introduced in the mixing process to escape quickly enough during application, and thus resulted in trapped bubbles in the cured coatings. The size of the bubbles in the cured coatings is affected by the boiling point and the solubility of the solvent. For the TBA system, the size of the bubbles was observed to be the largest compared to the other systems. It is thought that the solvent was not quite miscible in the AESS-PACM mixture, and thus tended to result in larger trapped bubbles in the cured coatings.

As seen in Table 2, the coatings properties based on AESS-PACM with different solvents are fairly good with the exception of the CHX system. The CHX-containing coating is fairly soft and not well crosslinked as indicated by MEK double rubs. Furthermore, this coating formulation had a longer pot-life than the other systems. Typically, the formulations would gel in the vial an hour after mixing, yet the

CHX system did not. It is known that ketones may react with primary amines to form imine and water, and this reaction is reversible [41]. Since CHX has a comparatively higher boiling point compared to MEK and MIBK, it does not evaporate as quickly and is expected to bind more with amine as an imine. Thus, there are less amine functional groups available to react with AESS, resulting in poor solvent resistance for the coating.

Overall, the most optimum coatings were obtained with EEP with excellent pendulum hardness and MEK double rubs. The slow evaporation rate of EEP balances the quick reactivity of the AESS-amine reaction, resulting in a minimal amount of bubbles trapped in the cured coatings. Based on these observations, EEP was chosen to be the solvent for further experimentation.

3.3. Effect of stiochiometry

As shown in the previous section, initial thermoset coatings made from AESS-PACM were successfully prepared and the excellent MEK double rubs data is an indication that the coatings are cured and have good solvent resistance. To confirm that the reaction did occur at the molecular level, FTIR spectroscopy analysis of the coatings formulations and cured coatings was carried out. Furthermore, it is necessary to study the impact of the molar ratio of acrylate to 1° amine on the properties of the materials. In this part of the study, AESS was crosslinked with PACM and the reaction was catalyzed using pTSA catalyst.

3.3.1. Functional group conversion

Figure 1 shows the FTIR spectra of 2 different coating systems before and after curing: AESS-PACM with a range of acrylate to 1° amine ratios and AESS with pTSA catalyst without any PACM. It can be observed in the spectra that there is a decrease in the acrylate group concentration shown by a decrease in the intensity of the C=C bond at 1637 cm^{-1} (C=C stretching for $\text{HC}=\text{CH}_2$), 1406 cm^{-1} (C=C scissoring for $\text{HC}=\text{CH}_2$), and 810 cm^{-1} (C=C out of plane deformation). By calculating the change in the peak area of those C=C peaks before and after curing, the acrylate group conversion can be estimated. It is important to note that peak deconvolution was performed to obtain a more accurate determination of the peak area. For liquid coatings formulation, peak fitting was carried out using a Voight calculation, while a Gaussian peak fit calculation was used for the solid cured coatings. The results of the calculations are shown in Table 3.

As seen in Table 3, the acrylate conversion decreases as the acrylate-to-1°amine molar ratio is increased, and the pattern can be observed with every C=C peak. The conversion ranges from 90% to 40%, which seems to be fairly low for a thermoset system. However, it is important to note also that

even though complete conversion was not achieved after curing at 80 °C for 45 minutes, the coated surfaces were tack-free.

Figure 1. FTIR spectroscopy of coatings with 2:1 molar ratio of acrylate to 1° amine (using PACM amine) and coatings with no PACM amine (AESS+pTSA catalyst)

Table 3. Acrylate conversion by FTIR spectroscopy with different equivalent ratios

Acrylate-to-1° Amine	Decrease in the peak area (%)		
	1637 cm ⁻¹	1406 cm ⁻¹	810 cm ⁻¹
1 : 1	86.4	96.6	93.0
1.5 : 1	67.5	87.0	82.3
2 : 1	53.6	71.5	69.3
3 : 1	63.8	50.2	44.5
No Amine	32.1	50.1	17.6

Coatings were prepared using PACM

While preparing the formulations, it was found that the mixture of AESS and pTSA catalyst, without the presence of PACM amine, gelled in the container 6 hours after it was mixed. This unexpected observation suggested that the hydroxyl groups in the AESS resin might be able to react with the acrylate groups. To verify this hypothesis, AESS resin was mixed with pTSA catalyst (2.45%wt.) and then

cured in the oven at 80 °C for 45 minutes. Then, the same FTIR analysis was conducted. As shown in Figure 1 and Table 3, characterization by FTIR spectroscopy further showed that the hydroxyl and acrylate groups decreased after curing at 80 °C for 45 minutes. Furthermore, the coating film from the AESS-pTSA system was found to have 100 MEK double rubs, which shows that the coating was fairly well crosslinked. The crosslinking between acrylate and 2° hydroxyl group in the AESS resin may signify two possible scenarios. First, without the presence of amine or other crosslinker, the AESS resin may react with itself to form a polymer network. In the presence of amine or other crosslinker, however, this reaction becomes a secondary reaction. Looking back at Figure 1, it can be observed that there were no significant changes in the area of the OH peak at 3300 cm^{-1} , which indicates that the amount of this secondary reaction may be very minimal.

Scheme 4. Possible reaction of AESS self-crosslinking

3.3.2. Gel time and dry time

In the previous experiment, AESS-PACM coatings formulations were cured at an elevated temperature to accelerate the curing reaction. However, these systems have sufficient reactivity to be cured at ambient temperature, and it will be shown later that the properties of the oven-cured and room temperature-cured coatings do not differ significantly. In this section, the gel time and dry time of the AESS-PACM coatings at ambient temperature ($\sim 23\text{ }^{\circ}\text{C}$) were studied as a function of the acrylate to 1° amine molar ratio and the results are shown in Figure 2 and Table 4.

The gel time of the coatings was determined using a rheometer at 23 °C. At the gel point, the molecular network is undergoing a transition from liquid to solid, and thus the storage modulus value (G') is equal to the loss modulus value (G'') and the viscosity (η) increases dramatically. As seen in Figure 2 and Table 4, the gel time increased as the acrylate to 1° amine molar ratio was increased. The results from $G'=G''$ value and η agree with each other as they follow the same pattern, and the gel time values are in the same range. It is interesting to observe that despite the fact that the gel times of the four formulations were different, the G' or G'' values at the gel point are approximately the same at 2.32 kPa.

Then, as expected, the viscosities of the formulations at 90 minutes are very different; they increased as the molar ratio was increased.

Figure 2. Rheological properties of AESS-PACM with different acrylate to 1° amine molar ratios

Table 4. Gel time and dry time of thermoset coatings with different equivalent ratios

Acrylate-to-1° Amine	Gel Time (min)		Dry Time (hour:min)			
	G' = G''	η increase	Set-to-touch	Tack free	Dry-hard	Dry-through
1 : 1	18	22	0:20	0:30	5:30	>12:00
1.5 : 1	28	33	0:35	0:50	2:00	5:25
2 : 1	48	52	1:05	1:25	2:45	5:50
3 : 1	71	76	1:30	1:45	3:45	6:10

Coatings formulations were prepared using PACM

The dry times of the coatings formulations of AESS-PACM with different molar ratios were also determined using a BK drying time recorder. The recorded drying behavior values listed in Table 4 are an average of 6 different measurements. As observed with the gel time values, increasing the molar ratio resulted in slower drying times up to the tack free time. Yet, surprisingly, the dry-hard and dry-through

times of the 1:1 coatings system were much slower compared to the other coatings systems, which implies that the molecular network was built up at a slower rate after a certain point. Furthermore, after 12 hours, the 1:1 coatings are still soft and can be easily scratched. Overall, this observation indicates that fast tack-free time or gel time does not necessarily imply a fast through dry time.

3.3.3. Coatings properties

In order to further understand the impact of the acrylate-to-amine molar ratio on the AESS-PACM coatings, it is important to conduct thermal and mechanical coatings characterization. Thermal characterization was conducted using differential scanning calorimetry (DSC) to obtain the glass transition temperature, T_g , and residual heat of polymerization. Dynamic mechanical analysis (DMA) was used to obtain the T_g and storage modulus values. Mechanical coatings characterization includes determinations of hardness, solvent resistance, adhesion, and flexibility. The results are shown in Figure 3 and Tables 5 and 6.

First, in the DSC curves in Figure 3, the T_g of the coatings obtained from the first heating cycle is lower than that obtained in second heating cycle. However, a small exothermic peak in the first heating cycle was observed, indicating the occurrence of some additional curing. It is predicted that during the first heating cycle, polymer network rearrangement and further curing occur simultaneously, thus causing the increase in the observed T_g in the second heating cycle. The T_g by DMA was determined at the temperature where the tan delta maximum occurred. The obtained T_g value from both DSC and DMA show a similar pattern. The T_g value of coatings with acrylate to 1° amine molar ratio of 1:1 and 1.5:1 are fairly similar. Increasing the molar ratio results in a decrease in the T_g value. The storage modulus values at 25 °C values decrease as the acrylate to 1° amine was increased, which indicates that the coatings became softer and more flexible. The storage modulus value in the rubbery region at $T_g+60^{\circ}\text{C}$ is often used to indicate the crosslink density of the coatings. The highest modulus was obtained for coatings with acrylate to 1° amine molar ratio of 1.5:1.

Coatings mechanical properties in Table 6 show that there is no significant difference in the hardness and T_g of the coatings with 1:1 and 1.5:1 molar ratio, similar to what was observed with the T_g values. Yet, surprisingly, the chemical resistance of the 1:1 molar ratio system is lower compared to the 1.5:1 system. This observation was predicted due to the cracking defects that appeared in the 1:1 system, which was caused by fast gelation at the surface. Furthermore, this appearance of cracks caused the coatings to have lower specular gloss. Increasing the molar ratio resulted in softer coatings, which agrees with the findings of the thermal analysis.

To summarize, the system with 1.5:1 molar ratio showed good properties compared to other molar ratios with fairly high conversion, good gel time thus workable condition, excellent hardness, flexibility and chemical resistance. Thus, this formulation was chosen as a control system for further study involving variation in the diluents, amine crosslinker, acrylate resin, and the curing process.

Figure 3. The DSC first and second heating cycle of coatings with different acrylate to 1° amine ratios

Table 5. Thermal properties of the coatings

System	No.	Sample	DSC analysis		DMA analysis		
			T_g Cycle 1 (°C)	T_g Cycle 2 (°C)	T_g by $\tan \delta$ (°C)	E' @ 25°C (MPa)	E' @ $T_g+60^\circ\text{C}$ (MPa)
Acrylate-to-Amine Ratio*	1	1:1	15.4	37.8	45.8	1037	5.87
	2†	1.5:1	29.2	36.9	43.4	714	6.28
	3	2:1	22.6	26.8	35.9	304	4.62
	4	3:1	5.4	16.3	28.5	92	4.35
HDDA Amount*	2†	0 mol %	29.2	36.9	43.4	714	6.28
	5	25 mol %	26.6	26.7	33.1	298	4.40
	6	50 mol %	15.3	15.3	19.1	21	4.54
	7	75 mol %	-0.8	2.4	16.0	13	6.31
Amine X-linker	2†	PACM	29.2	36.9	43.4	714	6.28
	8‡	DETA	21.4	28.4	39.9	489	15.74
	9	MXDA	20.8	20.6	38.2	516	11.78
Acrylate Resin*	2*	AESS	29.2	36.9	43.4	714	6.28
	10	AESO	-2.7	1.1	13.8	8	2.94
Cure Process*	2*	Forced	29.2	36.9	43.4	714	6.28
	11	RT	39.3	36.6	38.6	581	8.65

*Coatings were formulated using PACM crosslinker and pTSA catalyst

†Formulation used as control: using PACM crosslinker (1.5:1 molar ratio)

‡No catalyst was added

Table 6. Mechanical Properties of the Coatings

System	No.	Sample	DFT	König	Pencil Hardness		MEK DR	Rev. Impact	Adhesion	Mandrel Bend (%)	Gloss			Gel Fraction (%)
			μm	(sec)	Gouge	Scratch		kg-m (inch-lb)			20°	60°	85°	
Acrylate- to-Amine Ratio	1	1:1	64±17	108	6H	3B	250	1.15 (100)	2B	>28	85	123	81	93.6
	2†	1.5:1	62±14	105	9H	B	>400	0.92 (80)	2B	>28	109	132	100	91.6
	3	2:1	57±9	52	7H	2B	275	1.15 (100)	3B	>28	120	135	100	92.9
	4	3:1	58±11	21	7H	4B	100	0.92 (80)	3B	>28	116	128	101	92.5
HDDA Amount	2†	0 mol %	62±14	105	9H	B	>400	0.92 (80)	2B	>28	109	132	100	91.6
	5	25 mol %	53±8	59	8H	2B	175	0.46 (40)	0B	28	88	113	97	92.2
	6	50 mol %	44±11	20	3H	4B	50	0.92 (80)	3B	>28	107	139	98	93.7
	7	75 mol %	48±10	14	2H	4H	100	1.15 (100)	4B	>28	77	133	85	95.3
Amine X- linker	2†	PACM	62±14	105	9H	B	>400	0.92 (80)	2B	>28	109	132	100	91.6
	8‡	DETA	52±5	56	5H	HB	225	1.15 (100)	2B	28	64	109	77	
	9	MXDA	50±4	82	9H	B	>400	1.38 (120)	4B	>28	88	117	86	94.1
Acrylate Resin	2*	AESS	62±14	105	9H	B	>400	0.92 (80)	2B	>28	109	132	100	91.6
	10	AESO	43±8	12	B	8B	75	1.15 (100)	4B	>28	143	149	97	93.2
Cure Process	2*	Forced	62±14	105	9H	B	>400	0.92 (80)	2B	>28	109	132	100	91.6
	11	RT	57±10	107	8H	F	>400	0.69 (60)	0B	>28	88	113	97	90.4

*Coatings were formulated using PACM crosslinker and pTSA catalyst

†Formulation used as control: using PACM crosslinker (1.5:1 molar ratio)

‡No catalyst was added

3.4. Structure-property relationships

Further studies were then carried out to explore the properties of coatings made using reactive diluents and different amines. Then, the obtained properties were compared with a system derived from a similar, but much lower functionality, bio-based acrylate resin, acrylated epoxidized sucrose soyate (AESO). It is important to note that all of the coatings were cured at 80 °C for 45 minutes to accelerate the experimental time. Therefore, it is also necessary to compare the properties of oven-cured coatings with ambient-cured coatings. The complete thermal and mechanical coatings properties are listed in Tables 5 and 6. Overall, all of the coatings were observed to have good flexibility with >28% elongation and to be highly crosslinked with >90% gel fraction.

One method to adjust the viscosity of the formulations is by blending the AESS resin with a reactive diluent such as 1,6-hexanediol diacrylate (HDDA). Therefore, a series of AESS-HDDA blends was prepared and coatings formulations were made. HDDA was added to the formulations such that the amount of acrylate functionalities due to HDDA was 25%, 50%, and 75% by mol. Adding low molecular weight difunctional acrylate into the formulation may cause plasticization as observed in the lower hardness and T_g of the thermoset networks. Furthermore, looking at the DMA results, the storage modulus values at temperatures well above T_g for systems with 75% of HDDA and without HDDA are fairly similar. This observation indicates that the approximate crosslink density of the network system is fairly similar, and thus the properties of the networks are largely dependent on the backbone of the network rather than on the crosslink density.

Variation in the amine crosslinker composition results in different coatings properties. First, it is important to mention that catalyst was not added to the formulation with diethylene triamine (DETA). It was found that if catalyst was added to the formulation, the system gelled within a few minutes of mixing, thus making the application process difficult. This rapid gelation was predicted due to the presence of the 2° amine. Recall in the previous section, unhindered 2° amine is more reactive than a 1° amine. The order of reaction rate was predicted to be 1° amine > 2° amine > 2° amine (formed). Since gelation was obtained very quickly, it is expected that high conversion of functional groups might be limited as the network is locked in place, and thus inferior MEK double rubs were observed. However, surprisingly, the storage modulus values of the DETA system at a temperature well above T_g is comparatively higher than PACM system.

Comparing coatings derived from AESS and AESO, it can be clearly seen that the AESO-based coating is significantly softer and has a lower T_g despite a similar acrylate equivalent weight between AESS and AESO at 310g/mol. However, the key difference between the resins is the much higher number of

functional groups per molecule in the AESS. This higher functionality leads to a higher crosslink density resulting in higher T_g and hardness.

Finally, coatings properties for the system cured at ambient temperature are compared with those cured at elevated temperature. It was found that the properties are not significantly different with similar values of hardness, flexibility and T_g .

4. Conclusion

The Michael addition reaction was successfully utilized to produce thermoset coatings derived from AESS and amine crosslinker. FTIR spectroscopy of the coatings before and after curing indicates that the reaction is capable of reaching up to 90+% conversion of acrylate. Furthermore, it is suggested that AESS is able to undergo self-crosslinking from the reaction of acrylate and hydroxyl groups. Yet, in the presence of amine crosslinker, this reaction might be occurring, but to a minimal extent. A fast gelation time can be reached with a formulation having a 1:1 molar ratio of acrylate to 1° amine, and it can be prolonged by increasing the molar ratio. However, fast gelation times can cause cracking and incomplete reaction and thus lead to inferior chemical resistance. The thermal and mechanical coatings properties with different amounts of diluents and different amine crosslinkers were also evaluated. The addition of diluents into the system resulted in coatings that are softer, while the presence of 2° amine in the DETA causing the system to gel very fast and thus did not require the addition of catalyst. In sum, this preliminary study has shown that the aza-Michael reaction of a highly functional acrylated resin can be used as a viable coating binder system that cures rapidly at ambient conditions and can yield coatings having good solvent resistance, as well as good hardness and flexibility.

Acknowledgement

The authors would like to thank the National Science Foundation and North Dakota EPSCOR program for the funding under grant number IIA-1355466.

5. References

- [1] Noomen A. Applications of Michael addition chemistry in coatings technology. *Progress in Organic Coatings*. 1997;32:137-42.
- [2] Rector FD, Blount WW, Leonard DR. Applications for Acetoacetyl Chemistry in Thermoset Coatings. *Journal of Coatings Technology*. 1989;61:31-7.

- [3] Mather BD, Miller KM, Long TE. Novel Michael Addition Networks Containing Poly(propylene glycol) Telechelic Oligomers. *Macromolecular Chemistry and Physics*. 2006;207:1324-33.
- [4] Ferruti P, Marchisio MA, Duncan R. Poly(amido-amine)s: Biomedical Applications. *Macromolecular Rapid Communications*. 2002;23:332-55.
- [5] Tomalia DA, Naylor AM, Goddard WA. Starburst Dendrimers: Molecular-Level Control of Size, Shape, Surface Chemistry, Topology, and Flexibility from Atoms to Macroscopic Matter. *Angewandte Chemie International Edition in English*. 1990;29:138-75.
- [6] Bielinska A, Kukowska-Latallo JF, Johnson J, Tomalia DA, Baker JR. Regulation of in vitro Gene Expression Using Antisense Oligonucleotides or Antisense Expression Plasmids Transfected Using Starburst PAMAM Dendrimers. *Nucleic Acids Research*. 1996;24:2176-82.
- [7] Tomalia DA, Baker H, Dewald J, Hall M, Kallos G, Martin S, et al. Dendritic macromolecules: synthesis of starburst dendrimers. *Macromolecules*. 1986;19:2466-8.
- [8] Moszner N, Rheinberger V. Reaction behaviour of monomeric β -ketoesters, 4. Polymer network formation by Michael reaction of multifunctional acetoacetates with multifunctional acrylates. *Macromolecular Rapid Communications*. 1995;16:135-8.
- [9] Klee JE, Neidhart F, Flammersheim H-J, Mülhaupt R. Monomers for low shrinking composites, 2. Synthesis of branched methacrylates and their application in dental composites. *Macromolecular Chemistry and Physics*. 1999;200:517-23.
- [10] Dammann LG, Gould ML. Liquid uncrosslinked Michael addition oligomers prepared in the presence of a catalyst having both an epoxy moiety and a quaternary salt United States: Ashland Inc; 2004.
- [11] Roy R, Laferriere CA. Michael addition as the key step in the syntheses of sialyloligosaccharide-protein conjugates from N-acryloylated glycopyranosylamines. *Journal of the Chemical Society, Chemical Communications*. 1990:1709-11.
- [12] Mather BD, Viswanathan K, Miller KM, Long TE. Michael addition reactions in macromolecular design for emerging technologies. *Progress in Polymer Science*. 2006;31:487.
- [13] Clemens RJ, Rector FD. A comparison of catalysts for crosslinking acetoacetylated resins via the Michael reaction. *Journal of Coatings Technology*. 1989;61:83-91.
- [14] Bickel CL. The Addition of Malonic Esters to an Acetylenic Ketone. *Journal of the American Chemical Society*. 1950;72:1022-3.
- [15] Connor R, McClellan WR. THE MICHAEL CONDENSATION. V*. THE INFLUENCE OF THE EXPERIMENTAL CONDITIONS AND THE STRUCTURE OF THE ACCEPTOR UPON THE CONDENSATION. *The Journal of Organic Chemistry*. 1939;3:570-7.

- [16] Witzeman JS, Nottingham WD. Transacetoacetylation with tert-butyl acetoacetate: synthetic applications. *The Journal of Organic Chemistry*. 1991;56:1713-8.
- [17] Marsh SJ. Acetoacetate chemistry—crosslinking versatility for high-solids coatings resins. *American Chemical Society Division of Polymer Chemistry: American Chemical Society*; 2003. p. 52-3.
- [18] Clemens RJ, Hyatt JA. Acetoacetylation with 2,2,6-trimethyl-4H-1,3-dioxin-4-one: a convenient alternative to diketene. *The Journal of Organic Chemistry*. 1985;50:2431-5.
- [19] Tung CC. Recent advances in isocyanate free coatings. *Surface Coatings Australia*. 1999;10-5.
- [20] Brinkhuis R, Schuttyer J, Thys F, Wolf ED, Buser T, Kalis J, et al. Taming the Michael Addition reaction. *European Coatings Journal*. 2015;34-40.
- [21] Webster DC, Sengupta PP, Chen Z, Pan X, Paramarta A. Highly functional epoxidized resins and coatings. *United States Patent Office. US: NDSU Research Foundation*; 2015.
- [22] Monono EM, Bahr JA, Pryor SW, Webster DC, Wiesenborn DP. Optimizing Process Parameters of Epoxidized Sucrose Soyate Synthesis for Industrial Scale Production. *Organic Process Research & Development*. 2015;19:1683-92.
- [23] Monono EM, Webster DC, Wiesenborn DP. Pilot scale (10 kg) production and characterization of epoxidized sucrose soyate. *Industrial Crops and Products*. 2015;74:987-97.
- [24] Pan X, Sengupta P, Webster DC. Novel biobased epoxy compounds: epoxidized sucrose esters of fatty acids. *Green Chemistry*. 2011;13:965-75.
- [25] Pan X, Sengupta P, Webster DC. High biobased content epoxy-anhydride thermosets from epoxidized sucrose ester of fatty acids. *Biomacromolecules*. 2011;12:2416-28.
- [26] Pan X, Webster DC. Impact of Structure and Functionality of Core Polyol in Highly Functional Biobased Epoxy Resins. *Macromolecular Rapid Communications*. 2011;32:1324-30.
- [27] Pan X, Webster DC. New Biobased High Functionality Polyols and Their Use in Polyurethane Coatings. *ChemSusChem*. 2012;5:419-29.
- [28] Paramarta A, Pan X, Webster DC. Highly functional acrylated biobased resin system for uv-curable coatings. *Radtech Report*. 2013:26-32.
- [29] Nelson T, Galhenage T, Webster D. Catalyzed crosslinking of highly functional biobased epoxy resins. *J Coat Technol Res*. 2013;10:589-600.
- [30] Nelson T, Masaki B, Morseth Z, Webster D. Highly functional biobased polyols and their use in melamine-formaldehyde coatings. *J Coat Technol Res*. 2013;10:757-67.
- [31] Nelson TJ, Bultema L, Eidenschink N, Webster DC. Bio-Based High Functionality Polyols and Their Use in 1K Polyurethane Coatings. *Journal of Renewable Materials*. 2013;1:141-53.

- [32] Kovash CS, Pavlacky E, Selvakumar S, Sibi MP, Webster DC. Thermoset Coatings from Epoxidized Sucrose Soyate and Blocked, Bio-Based Dicarboxylic Acids. *ChemSusChem*. 2014;7:2289-94.
- [33] Ma S, Webster DC. Naturally Occurring Acids as Cross-Linkers To Yield VOC-Free, High-Performance, Fully Bio-Based, Degradable Thermosets. *Macromolecules*. 2015;48:7127-37.
- [34] Ma S, Webster DC, Jabeen F. Hard and Flexible, Degradable Thermosets from Renewable Bioresources with the Assistance of Water and Ethanol. *Macromolecules*. 2016;49:3780-8.
- [35] Paramarta A, Webster DC. Bio-based high performance epoxy-anhydride thermosets for structural composites: The effect of composition variables. *Reactive and Functional Polymers*. 2016;105:140-9.
- [36] Wabnitz TC, Spencer JB. A General, Brønsted Acid-Catalyzed Hetero-Michael Addition of Nitrogen, Oxygen, and Sulfur Nucleophiles. *Organic Letters*. 2003;5:2141-4.
- [37] Wabnitz TC, Yu J-Q, Spencer JB. Evidence That Protons Can Be the Active Catalysts in Lewis Acid Mediated Hetero-Michael Addition Reactions. *Chemistry – A European Journal*. 2004;10:484-93.
- [38] Wabnitz TC, Yu J-Q, Spencer JB. A General, Polymer-Supported Acid Catalyzed Hetero-Michael Addition. *Synlett*. 2003:1070-2.
- [39] Vedejs E, Gingras M. Aza-Claisen Rearrangements Initiated by Acid-Catalyzed Michael Addition. *Journal of the American Chemical Society*. 1994;116:579-88.
- [40] Wu, Liu Y, He, Chung, Goh. Effects of Chemistries of Trifunctional Amines on Mechanisms of Michael Addition Polymerizations with Diacrylates. *Macromolecules*. 2004;37:6763-70.
- [41] Carey FA. Reaction with Primary Amines: Imines. *Organic Chemistry*. 4th Edition ed. Boston, MA: McGraw-Hill College; 2000. p. 672.