# Highly Functional Acrylated Biobased Resin System
## for UV-Curable Coatings

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Interest in replacing petrochemical-based materials with biobased materials is increasing rapidly due to the rising costs of petrochemicals and greater awareness of issues around future sustainability. Triglycerides, the main component of plant oils, provide an attractive alternative to petroleum-based coating resins due to their abundance and low cost. The number of unsaturated functional groups in triglycerides is determined by the source of the oil and the composition of the fatty acids contained in the triglycerides. Due to their potential for oxidative crosslinking, unsaturated triglycerides have been used in alkyd resins that, for many decades, were the largest coating resin system in use. However, the unsaturation sites on the fatty acids can be chemically modified in various ways to make useful functional polymers. One method is converting the internal double bond into epoxy functionality. This oxirane ring can then be exploited further in many coatings technologies such as epoxy-amine and epoxy-anhydride crosslinking; converted into polyols for use in polyurethanes and melamine-formaldehyde cured systems; and acrylated for use in UV-cured systems.

The study of acrylated epoxidized vegetable oils (especially soybean oil) has been conducted intensively for its use in coatings, inks, adhesives, varnishes and more.[1-4] The excellent pigment wetting ability of acrylated epoxidized soybean oil (AESO) makes the resin a good option for printing inks; and the high reactivity of the acrylate double bonds provide sites for free-radical polymerization in the coating systems.[3,5] However, the drawbacks of using vegetable oil-based resins include poor properties such as softness of the film due to its low functionality and aliphatic backbone.
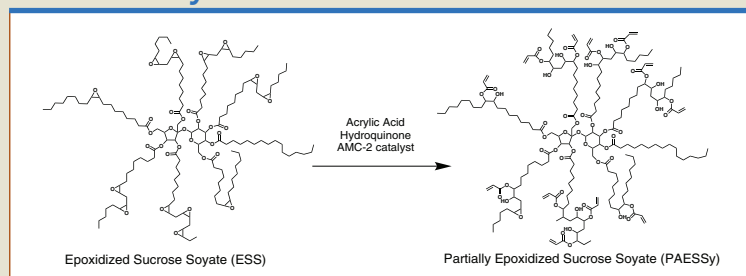
## FIGURE 1



**Biobased acrylated resin**

Epoxidized Sucrose Soyate (ESS) → Acrylic Acid Hydroquinone AMC-2 catalyst → Partially Epoxidized Sucrose Soyate (PAESSy)

## FIGURE 2



**Outline of the experimental scheme**

Degrees of Acrylation: Acrylated Epoxidized Soybean Oil (AESO) 4 acrylates/molecule | Low Acrylation ~ 50% (PAESSy 50) 6 acrylates/molecule | Medium Acrylation ~ 75% (PAESSy 75) 9 acrylates/molecule | High Acrylation ~ 90% (PAESSy 90) 11 acrylates/molecule

Types of Diluents: Methyl-ethyl ketone (MEK) | Isodecyl acrylate (IDA) | Hydroxy ethyl acrylate (HEA) | Hexane diol diacrylate (HDODA) | 50 : 50 HEA and HDODA
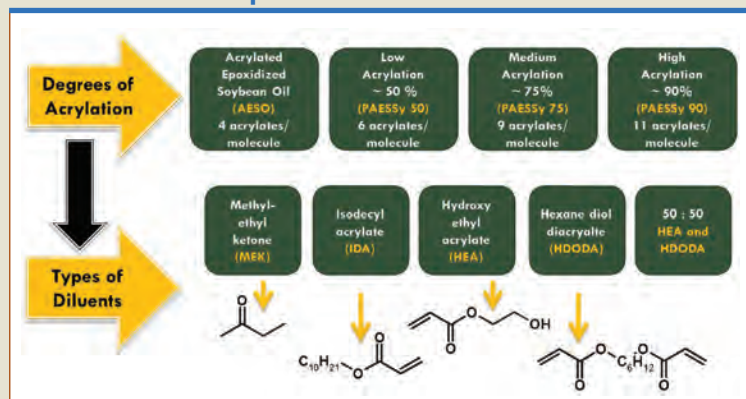
## FIGURE 3

### FTIR spectra of ESS and the acrylated resins in the range of 4,000-2,700 cm⁻¹
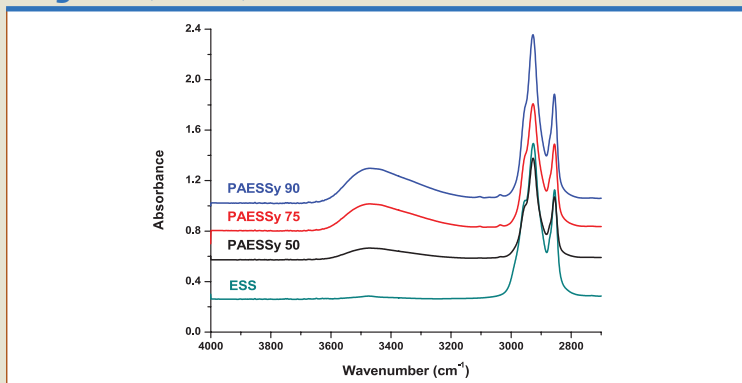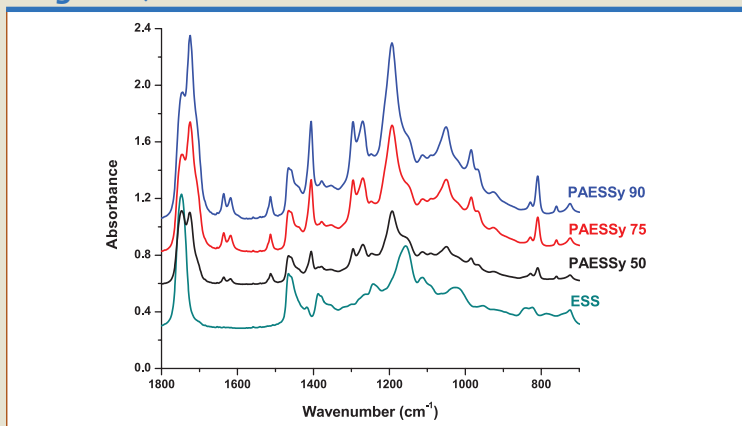


## FIGURE 4

### FTIR spectra of ESS and the acrylated resins in the range of 1,800-700 cm⁻¹



Petroleum-based chemicals may be blended with biobased resins to improve the properties, but then the biobased content is reduced.

An alternative renewable material with higher functionality for use in resins is the sucrose ester molecule. Sucrose ester is a molecule formed from sucrose and fatty acids of vegetable oils, where seven to eight of the hydroxyl groups have been esterified with the fatty acids of vegetable oils; thus, having 2-3 times more functionality compared to conventional triglyceride oils. Sucrose esters with low fatty acid substitution have been widely used as food emulsifiers and fruit coatings. The exploration of sucrose esters in the coatings industry is gaining popularity due to its high functionality, wide arbitrary hydrophilic and lipophilic balance (HLB), excellent physical properties, low viscosity, surface activity, low toxicity level and compositional flexibility. Similar to vegetable oils, the unsaturation present in the vegetable oil sucrose ester is

capable of being converted into epoxy groups and the synthesis of epoxidized sucrose ester resins has been reported in the literature.[6] These epoxy resins can have epoxy group functionalities ranging from 8 to 15 groups per molecule, depending on the vegetable oil used. Furthermore, a number of thermosetting systems based on epoxidized sucrose esters have been explored and have shown properties significantly superior to those based on triglycerides and comparable to their petroleum-based counterparts.[6-9] These exceptional performance properties are attributed to the high degree of crosslinking achieved as a result of the high functionality of the epoxidized sucrose ester resins and their derivatives.

In this research, a series of ultraviolet (UV)-curable resins were prepared from epoxidized sucrose soyate by the ring-opening reaction of the epoxy functionality in epoxidized sucrose soyate (ESS) with acrylic acid as shown in Figure 1. The final products have higher acrylate functionality than the corresponding soybean oil-based resin; thus, they can achieve higher crosslink density when cured. Furthermore, the acrylate functionality can be tuned by controlling the amount of acrylic acid used during the synthesis process. Curable-coatings formulations were prepared containing reactive diluents to reduce the viscosity. Structure-property relationships of the number of acrylate functional groups and types of diluents were investigated. Figure 2 shows the overall experimental scheme used in the study.

### Synthesis of Acrylated Biobased Resin

#### Synthesis Procedure

Highly functional acrylated biobased resins were prepared from the epoxy ring opening reaction of ESS

with acrylic acid. ESS was prepared as described previously.[6] The reaction was catalyzed by a chromium-based catalyst (AMC-2) obtained from Ampac Fine chemicals. This catalyst has been shown to promote the epoxy ring opening reaction with acids while minimizing epoxy homopolymerization and epoxy-hydroxyl reactions, which can lead to gelation. Furthermore, hydroquinone (a radical scavenger) was added to the reactor to avoid acrylate homopolymerization. Early homopolymerization or oligomerization of the resin by thermal means can lead to gelling.

ESS, hydroquinone (2.5% by weight) and chromium catalyst (1% by weight) were transferred into a reaction kettle equipped with a condenser, thermometer, addition funnel and mechanical stirrer. Acrylic acid was added dropwise to the kettle after the mixture reached a temperature of 90°C. This addition method was employed to better control the increase of both temperature and viscosity. The amount of acrylic acid depends on the desired degree of acrylation (either 50%, 75% or 90% by number of moles of epoxy). These resins will be called "partially acrylated epoxidized sucrose soyate" or PAESSy.

## FIGURE 5
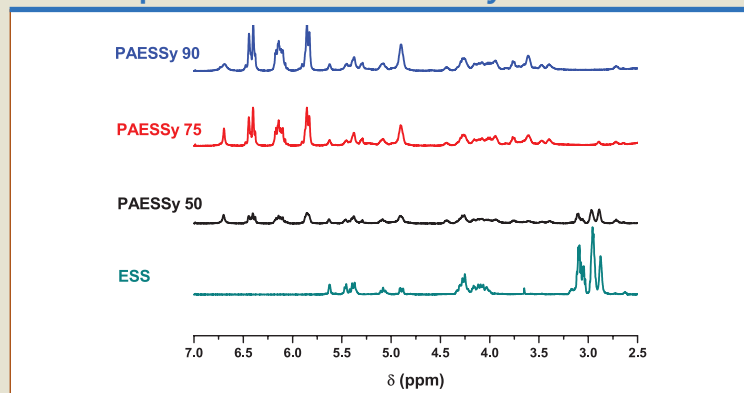
### $^{1}$H-NMR spectra of ESS and the acrylated resins
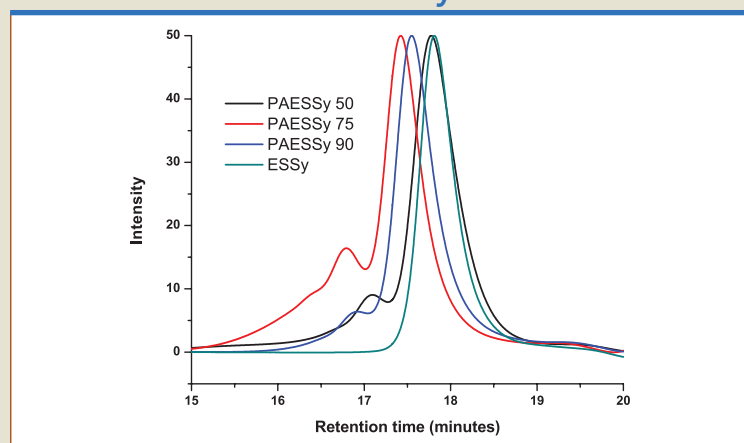


## FIGURE 6

### GPC curves for ESS and the acrylated resins



## TABLE 1

### FTIR Correlation Table

| Wavenumber (cm$^{-1}$) | Peak Assignment |
|---|---|
| 3,470 | Stretching for O—H of secondary alcohol (broad, medium) |
| 1,715 | Conjugation of C=O with $\alpha$, $\beta$ C=C (strong) |
| 1,636 | Stretching for C=C of HC=CH$_2$ (medium) |
| 1,406 | Scissoring for C=C of HC=CH$_2$ (medium) in plane CH$_2$ deformation |
| 1,300-1,150 | Stretching for C—O of esters (appear in three bands, the one in the 1,200cm$^{-1}$ is stronger than the others) |
| 1,070 | Stretching for C—O of C—C—OH secondary alcohol (medium) |
| 984 | Out-of-plane deformation |
| 810 | Out-of-plane deformation |

## TABLE 2

### Molecular weight for acrylated resins

| Resins | Molecular Weight (Mn) | | | |
|---|---|---|---|---|
| | Monomer | PDI | Oligomer | PDI |
| ESS | 2,400 | 1.15 | — | — |
| PAESSy 50 | 2,800 | 1.06 | 6,800 | 1.23 |
| PAESSy 75 | 4,000 | 1.06 | 8,700 | 1.12 |
| PAESSy 90 | 3,300 | 1.06 | 7,200 | 1.03 |

The reaction was carried out until the acid number of resins reached a value of below 15.

### Resins Characterization

Fourier-Transform Infrared (FTIR) and proton nuclear magnetic resonance spectroscopy were used to characterize the chemical composition of the resins. FTIR analysis was performed using a Thermo Scientific Nicolet 8700 FTIR spectrometer using a potassium bromide salt crystal. Proton-NMR was conducted on a JEOL-ECA (400 MHz) NMR spectrometer. The resin was dissolved in $CDCl_3$ and the data was processed using the Delta software package.

The acrylated biobased resins were successfully synthesized as seen in the FTIR and $^1$H-NMR spectra as shown in Figures 3-5. The FTIR peak assignments are listed in Table 1. Epoxy ring opening reaction was confirmed by the disappearance of the oxirane group peak at 823 cm$^{-1}$ in the FTIR spectra and at 3.00 ppm in the $^1$H NMR spectra. Furthermore, the multiple peaks of the acrylate group are shown in FTIR spectra at the following wavenumbers—3,470; 1,715; 1,636; 1,406; 1,295; 1,270; 1,193; 1,070; 984 and 810 cm$^{-1}$. In the $^1$H-NMR spectra, acrylate groups were shown by the peaks at = 4.90, 5.84, 6.12 and 6.43 ppm. Both FTIR and $^1$H-NMR spectra show a trend where the increasing extent of acrylation results in increased peak intensities. This observation further confirms the successful synthesis of the resins.

The molecular weight of the synthesized resins was characterized using a Waters 2410 Gel Permeation Chromatograph (GPC) with polystyrene as calibration standards. A 1%-sample solution in tetrahydrofuran was run with a flow rate of 1 mL/min. Figure 6 shows the GPC curves, while Table 2 lists the determined molecular weights. Each of the GPC traces for the acrylated resins shows a shoulder indicating the formation of higher molecular weight oligomers during synthesis. It is hypothesized that oligomer formation occurs from the reaction of the hydroxyl group generated from the acrylic acid-epoxy reaction reacting with another epoxy group. Further optimization of the catalyst and reaction conditions might reduce the occurrence of this side reaction.

### Coatings Formulations with Reactive Diluents

The viscosities of the acrylated epoxidized sucrose soyate resins are high mainly due to the high number of hydroxyl groups present. The addition of reactive diluents to the coating formulations was necessary to reduce the viscosity for easier application. Several reactive diluents with different acrylate functionalities were explored to observe their effect on coatings properties. The diluents chosen are isodecyl acrylate (IDA), 2-hydroxyethyl acrylate (HEA) and 1,6-hexanediol diacrylate (HDODA). In addition, coatings were formulated with the solvent methyl ethyl ketone (MEK) to evaluate the properties

## TABLE 3

### Viscosity of acrylated resins and their blends with diluents

| Resin Types | Viscosity (mPa·s) | | | | | |
|---|---|---|---|---|---|---|
| | Resins | Solvents/Diluents | | | | |
| | | MEK | IDA | HEA | HEA:HDODA (1:1) | HDODA |
| AESO | 35K | 750 | 2,600 | 2,600 | 2,800 | 2,700 |
| PAESSy 50 | 54K | 1,000 | 4,800 | 8,300 | 5,600 | 5,000 |
| PAESSy 75 | 103K | 3,000 | 12K | 11K | 12K | 12K |
| PAESSy 90 | 731K | 1,700 | 12K | 10K | 12K | 9,200 |

## FIGURE 7

### Conversion of acrylated resins with HDODA diluent determined by RTIR (820-800 cm⁻¹)
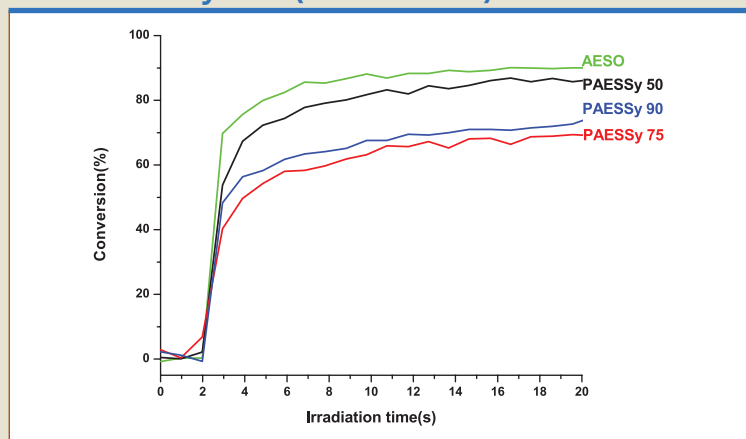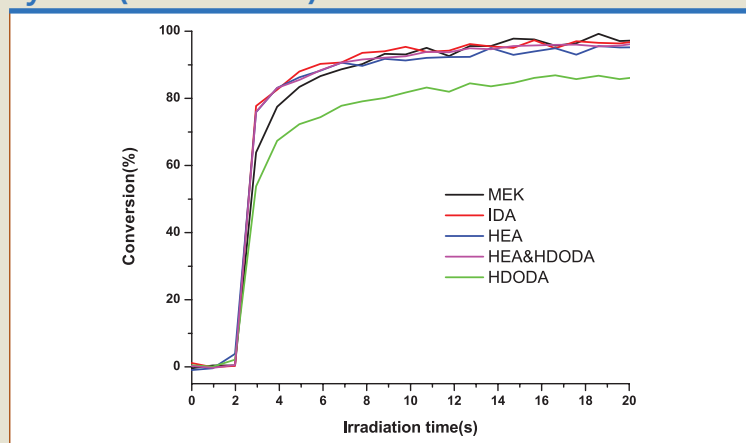


## FIGURE 8

### Conversion of PAESSy 50 with diluents determined by RTIR (820-800 cm⁻¹)



of the acrylated resins having no acrylate functional diluent. The coating formulations contained resins, diluents and photoinitiator in a weight ratio of 4:1:0.25. The photoinitiator used was Darocure 1173 by Ciba (2-hydroxy-2-methyl-1-phenyl-propan-1-one). In addition, formulations with acrylated epoxidized soybean oil (AESO) from Cytec were also used for comparison.

The viscosities of the resins and their formulations were measured using an ARES Series Rheometer with parallel plate geometry at a shear rate of about $0.200 \pm 0.0100$ s⁻¹ and the results are shown in Table 3. Acrylation of ESS yields hydroxyl groups that increase the viscosity largely due to hydrogen bonding. This trend can be seen in the AESO, PAESSy 50, PAESSy 75 and PAESSy 90 resins. As the number of acrylate groups increase, there are more hydroxyl groups present in the resin and, therefore,

the viscosity increases dramatically. In addition, the formation of higher molecular weight oligomer (as seen in the GPC traces) can also lead to high viscosity. The addition of diluents or solvent resulted in lower viscosity due to the decrease in the polymer-polymer interaction forces which was overcome by the polymer-diluent interactions. The viscosity did not vary significantly as the reactive diluents were varied. However, the MEK formulation had the lowest viscosity among all due to its hydrogen bond accepting ability as well as low density.

## Photopolymerization Kinetics

### Real Time Infrared (RTIR) Spectroscopy

The conversion profiles for the photopolymerization of acrylated systems with different degrees of acrylation and various diluents were determined using RTIR spectroscopy. The measurements were made using a Thermo Scientific Nicolet 8700 RTIR spectrometer equipped with a Lesco Super Spot MK II fiber optic UV light with an irradiance of 50 mW/cm⁻² at the sample. The sample was equilibrated at 25°C for 30 seconds and then irradiated with the UV light for 90 seconds. The decrease of the area of two peaks that correspond to the unsaturation of functional groups were monitored—810 cm⁻¹ (C=C out of plane deformation) and 1,636 cm⁻¹ (C=C stretching for HC=CH₂).

Conversion profiles of the systems based on 810 cm⁻¹ peak are shown in Figures 7 and 8. Similar results were observed for the 1,636 cm⁻¹ peak and are not shown. All of the systems cure rapidly and reach final conversion within several seconds. The final conversion of acrylate groups ranges from approximately 60% up to 90%. The number of acrylate groups in the system influenced the final conversion of the formulations. As seen in Figure 7,

higher numbers of acrylate groups result in lower conversion due to earlier vitrification of the network resulting in limited ability of acrylate groups to diffuse and react with an active free radical. The PAESSy 75 and 90 show similar results. PAESSy 75 has a slightly lower conversion than PAESSy 90, perhaps due to the higher amount of higher molecular weight (and higher functionality) oligomer.

Figure 8 shows the effect of the diluents on the photopolymerization of the systems containing PAESSy 50. HDODA has the lowest conversion of all systems since it has more acrylate groups and will reach vitrification sooner than the systems with monoacrylate diluents. It is interesting that there is no significant difference in the photopolymerization of the systems with either MEK or the monoacrylate diluents. Also, the ultimate conversion is fairly high considering that the acrylated resin has an average functionality of six acrylates per molecule. Perhaps the flexible nature of the fatty acid backbone allows for reasonable mobility of the acrylate groups during the photopolymerization.

### Photo-Differential Scanning Calorimetry (Photo-DSC)

The reaction kinetics was further characterized using a Q1000 DSC from TA Instruments outfitted with a photocalorimetry accessory, which measures the time taken to achieve maximum conversion. Coating formulations with a weight of 5-15 mg were equilibrated at 25°C and exposed to UV irradiation for five minutes with a light intensity of 40 mW/cm$^{-2}$. AESO showed the shortest time to reach maximum conversion in the range of three seconds, while the high acrylate functionality of sucrose soyate-based polymers are in the range of 7-13 seconds. The shortest time was

observed with PAESSy 90 MEK system, while the longest was PAESSy 90 HEA. There was no significant difference in the polymerization induction time or enthalpy of polymerization between the PAESSy resins. AESO systems have much shorter time to reach maximum peak of polymerization, which was suggested due to its low viscosity; thus, the molecular chain has a higher mobility and is able flow in order to react with each other and polymerize.

### Coating Properties

To form coatings, the formulations were applied on cleaned and degreased steel, glass and pine wood panels using a drawdown bar film applicator at an approximate dry film thickness of 40 μ. The coatings were cured by exposure to UV irradiation for 20 seconds using a Fusion LC6B Benchtop Conveyer with an F300 Lamp of intensity ~1,180 mW/cm$^2$ as determined by a UV Power Puck II from EIT Inc.

## FIGURE 9

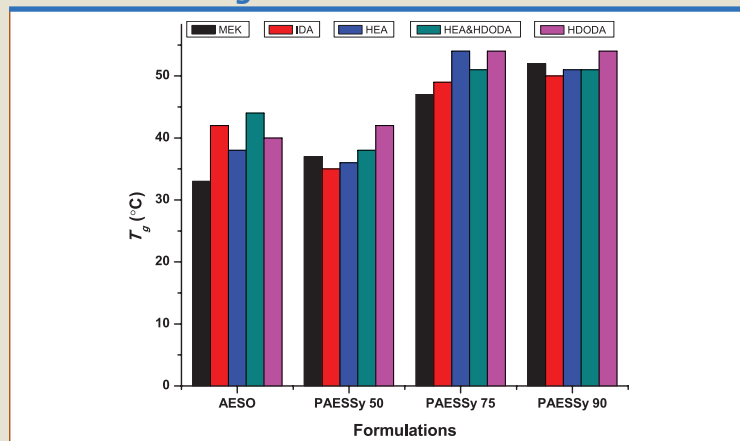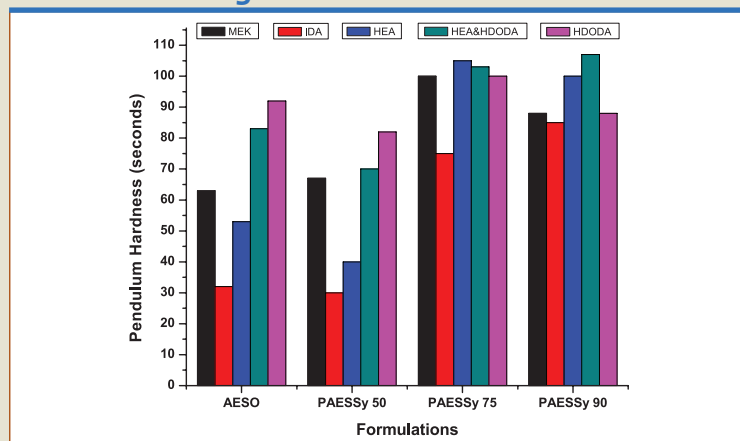### Glass transition temperatures ($T_g$) of acrylated biobased coatings



## FIGURE 10

### König pendulum hardness of acrylated biobased coatings

The glass transition temperature, $T_g$, is an important property of polymers, as it allows one to predict the behavior of the coating film. The $T_g$ of a thermosetting polymer is related to both the backbone composition and crosslink density of the polymer. In this experiment, the $T_g$ of the samples was determined using a Q1000 DSC from TA instruments where they were heated from -70 to 150°C with a heating ramp of 30°C/min. Figure 9 shows the $T_g$ values, while Figure 10 shows the pendulum hardness of the coatings. For the AESSy systems, an increase in $T_g$ was observed as the degree of acrylation was increased, which is attributed to the higher functionality and crosslink density of the resins. The different diluents used did not affect the $T_g$ significantly since they were only used in small amounts. The $T_g$ values for the coatings based on AESO are similar to those based on PAESSy 50, while the coatings based on the resins with higher levels of acrylation have higher $T_g$ values.

The chemical resistance of the films was assessed using MEK double rubs. All coating systems have MEK double rubs values of higher than 400, with the exception of the IDA formulations which has values ranging from 100 to 300. The long carbon side chain of IDA was suggested to be the source of crosslink defects where it acts as a dangling chain.

The coatings were also subjected to a steel wool abrasion evaluation where coating thickness loss after 100 double rubs with steel wool was evaluated. Most of the coatings showed a thickness loss of less than 10%, while the IDA-containing coatings had the highest loss at ~40%.

The hardness of the coatings generally increases as the degree of acrylation of the PAESSy resins increases (Figure 10) and is also dependent on the reactive diluent used.

However, the influence of the diluent is less significant for the coatings using the resins with the higher degree of acrylation, with the exception of IDA. The coatings made with the higher degree of acrylation PAESSy resins have significantly greater hardness than the coatings based on AESO. Similar to the observation in the MEK double rubs test, IDA formulations show inferior performance compared to the others

Crosshatch adhesion was conducted following ASTM D3359. Adhesion of all coating films on the steel substrate was poor (0B), while adhesion for all of the coatings on the pine wood substrate was excellent (5B). As illustrated in the photo-DSC data, the acrylated epoxidized formulation had a rapid curing induction time. Due to the shrinkage in volume from the liquid phase into a solid phase (van der Waals interspacing into covalent bonds) in a short period of time coupled with the high surface energy of the metal substrate, the films delaminate easily from the metal surface. For a porous and less rigid substrate such as wood, the liquid coating is able to better penetrate into the substrate and adhere better due to a mechanical interlocking mechanism.

## Conclusions

The synthesis of novel acrylated, highly functional resins from epoxidized sucrose soyate having various degrees of acrylation has been carried out by ring-opening reaction of ESS with acrylic acid. Oligomerization was observed with the resins with a higher extent of acrylation, PAESSy 75 and PAESSy 90. Coatings formulations cure rapidly with ultimate conversion a function of the resin system's degree of acrylation. The use of monofunctional diluents result in higher overall conversion during photopolymerization. Due to the high crosslink density of the photopolymerized coatings,

the coatings are hard and have good chemical and abrasion resistance. While the use of acrylic acid in the resin synthesis, as well as the use of acrylate diluents, reduces the overall biobased content of the systems, it should be noted that several processes for the synthesis of acrylic acid using renewable raw materials are being explored. Further work in our laboratories is in progress to further optimize the resin synthesis; reduce the viscosity of the systems; and further evaluate the structure-property relationships. ◗

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