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Effect of a fluoroalkyl-functional curing agent on the wettability, thermal and mechanical properties of hydrophobic **biobased** epoxy coatings

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Abstract

Over the past several decades, producing materials from fossil-based sources has become a serious problem because such action continues to contribute to global warming and contamination of the ecosystem. Thus, it is highly desirable to address this issue through producing functional materials via green chemistry such as the use of renewable compounds. In this paper, the preparation of hydrophobic coatings based on isosorbide, a derivative of polysaccharides, is reported. The inherently hydrophilic thermoset derived from isosorbide was made hydrophobic through the use of the hydrophobic curing agent F8815. The influence of the F8815 concentration on the decomposition temperature, glass transition temperature and storage modulus of the biobased samples was explored using TGA, DSC and DMA, respectively. The results showed that, despite of its poor mechanical and thermal properties, incorporation of F8815 served to improve the thermal and mechanical properties of the isosorbide-based

polymers. Deconvolution analysis of FTIR spectra and SEM images provided insightful information on the participation of F8815 in the polymer network.

Keywords: hydrophobic coatings; isosorbide; biobased; epoxy polymer;

1. Introduction

Fossil sources are non-renewable sources that have been exploited not only as basic materials for energy generation but also as starting compounds/intermediates for the synthesis of other chemicals. The historical dependence of society on these kinds of sources has contributed to global warming and pollution of the environment. To overcome these problems, researchers are motivated to replace fossil-based raw materials with renewable feedstocks in the design and synthesis of their materials. Epoxy polymers have received a special attention since it is known that approximately 90% of epoxy resin production comes from a non-renewable compound, Bisphenol A (BA) [1, 2]. BA is a harmful chemical as it can attack the endocrine system [3, 4]. Therefore, great effort is required to transform the current epoxy technology into an eco-friendly technology, especially in the substitution of biobased resins for BA-based epoxy resins.

Superhydrophobic and hydrophobic materials are able to repel water, and thus could be potentially useful for anti-corrosion [5-7], self-cleaning [8-10], and anti-icing [11-13] applications. Based on dynamic and static water contact angle (WCA) measurements, superhydrophobic coatings have $WCA > 150^\circ$ (and CA hysteresis $< 10^\circ$), and hydrophobic coatings have $150^\circ > WCA > 90^\circ$ [14, 15]. Although the type of curing agents affects the wettability of diglycidyl ether of BA (DGEBA), DGEBA is naturally hydrophilic when cured with traditional curing agents such as diethylenetriamine ($WCA = 79 \pm 2^\circ$) [16]. Thus, designing epoxy-based hydrophobic coatings requires chemical modification in the epoxy formulation. Two approaches have been successfully used to prepare hydrophobic epoxy polymers. One is an intrinsic method that involves the modification of the epoxy resin and/or curing agent by attaching hydrophobic units [17, 18]. The other is extrinsic, mostly applied in superhydrophobic polymers, which consists

of modifying the surface and/or the bulk of the film using additives that are not necessarily chemically bonded to the polymer network [19, 20].

Although various researches have been reported on the preparation of epoxy superhydrophobic coatings, little work has been done on the preparation of superhydrophobic and/or hydrophobic polymers using **biobased** epoxies [21-24]. In fact, not all the potentially useful bio-epoxies have been explored for the design of hydrophobic coatings [2, 25]. Isosorbide, or 1,4:3,6-dianhydro-D-glucitol, is a compound that can be obtained from polysaccharides [26]. It is a candidate for preparing bio-epoxy resins. So far, little work has been carried out on preparing hydrophobic bio-epoxies; only one report **has been** published in the preparing hydrophobic bulk polymers from the isosorbide [27]. **The intrinsic method** in which a hydrophobic isosorbide resin was prepared by chemically attaching benzoyl groups to the isosorbide structure **was utilized**. The isosorbide-based thermoset with the best properties showed a T_g and water uptake of 136°C and 1.28 wt %, respectively. However, there has been no report on the use of bio-epoxy resin to synthesize hydrophobic coatings.

The preparation of hydrophobic polymer-based films from isosorbide following a simpler methodology **is reported here**. A commercially available hydrophobic oligosiloxane, Dynasylan® F8815 (abbreviated as F8815), was employed **at various concentrations** to react with the hydrophilic isosorbide resin [28]. The thermal, mechanical and wettability properties of the resulting coatings were studied.

2. Experimental Section

2.1. Materials

Isosorbide (Dianhydro-D-glucitol 98%) and epichlorohydrin 99% were obtained from Sigma Aldrich. NaOH pellets (grade AR) and acetone were obtained from Schedelco and

A.P.C. Chemical Industries, respectively. Dynasylan® F 8815 was obtained from Evonik Industries. All materials were used as received without further purification.

2.2. Synthesis of isosorbide-based resin.

Isosorbide epoxy resin was prepared in a similar way as reported elsewhere [28]. A mixture of isosorbide and epichlorohydrin was heated to 145°C and kept under reflux in an Argon atmosphere. Subsequently, aqueous NaOH solution (50% w/w) was added dropwise into the mixture. The system was maintained for 4 hours under the same conditions to allow the reaction to complete. During the reaction with NaOH, water was progressively extracted by using an inverted Dean-Stark apparatus. The molar ratio of isosorbide to epichlorohydrin to NaOH was 1: 10 : 2. Then, the mixture was filtered to remove particles which were washed with acetone. Finally, the product was isolated by rotary evaporation at 60°C and 80 mbar. The resin was viscous and light yellow.

2.3. Synthesis of hydrophobic isosorbide-based coatings.

Isosorbide resin (1.0g) was dispersed in 0.4 g of water with magnetic stirring for 30 minutes. Then, different amounts of F8815 was added into the isosorbide mixture and was magnetically stirred for 24 hours. Different mixtures were prepared by adjusting the mass ratio of isosorbide resin to F8815 to be 1 : 0 (denoted as iso_{net}), 1 : 0.25 (S0.25), 1 : 0.5 (S0.5), 1 : 1 (S1), 1 : 2 (S2) and 0 : 1 (F8815). The samples were cured in an oven at 70°C for 1 hour, and then at 180°C for 24 hours; the heat rate from 70°C to 180°C was 0.61 °C/min. Spin-coating and drop-casting were used to prepare samples on glass substrates. Spin-coated samples were prepared at 4000 rpm for 30s using a conventional spin coater. The drop-casted samples were prepared by manually spreading the dispersion onto the substrate before curing.

Spin-coated samples were used for the measurements of surface energy and water contact angle. The drop-casted samples were carefully peeled off and used for thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FT-IR) and dynamical mechanical analysis (DMA).

2.4. Characterization

The NMR spectra of isosorbide resin were recorded with a Bruker AV 300 Spectrometer at 300 MHz for ^1H NMR and 75 MHz for ^{13}C NMR.

Epoxy index of isosorbide resin was measured by adapting the methodology reported elsewhere [29].

A field emission scanning electron microscope (FESEM 7600F) was employed to analyze the morphology of the polymer film operated at 5kV. Polymer films were coated with a thin layer of golden before the analysis.

A TGA Q500 (TA Instruments) was used for the TGA in a temperature ramp mode from room temperature to 600°C at 10°C/min under nitrogen flow (60.0 mL/min). The tests were performed on an alumina crucible supported on a platinum pan. The quantity of the samples was around 13-16 mg. Three measurements of each sample were carried out and the results were analyzed using the software TA Universal Analysis.

A (heat flux) DSC Q10 (TA Instruments) was used for the DSC performed in standard aluminum pans containing samples weighting around 13-17 mg. The pans were heated from -50°C to 200°C at 10°C/min under nitrogen flow (50 mL/min). For each sample, three measurements were taken. For the liquid mixtures, the DSC was performed in hermetic pans containing samples with a weight around 1.20 to 2.7 mg. The pans were heated from -50°C to 200°C at 10°C/min under nitrogen flow (50 mL/min). The analysis of the DSC data was performed by the software TA Universal Analysis.

Fourier-transform infrared (FTIR) spectroscopy of the peeled off samples (backside) were done using a FTIR MIR/NIR Frontier (Perkin Elmer) in an attenuated total reflectance (ATR) mode. The wavelength range of the analysis was from 4000-600 cm^{-1} , with 32 scan accumulations and with a resolution of 4 cm^{-1} . Baseline correction of data was carried out by the software Spectrum (PerkinElmer).

An OCA 20 goniometer (Dataphysics) was used to evaluate the static contact angles of a 5 μL droplet of DI water, ethylene glycol and n-hexane deposited on films. At least three measurements were obtained for each sample at room temperature. The surface energy calculations were done in accordance to the OWRK method [30-32] through the software SCA 20 (Dataphysics).

DMA of the film samples was performed in a DMA Q800 (TA Instruments) in a controlled strain mode with 15 μm in amplitude. All the samples were rectangular and subjected to a tension strain. The width of the samples was 3-6 mm for samples with thickness higher than 0.5 mm or 2-3 mm for samples with thickness between 0.5-2 mm. The samples were heated from -20°C to 180°C twice consecutively, and the data of the second heating was analyzed with the software TA Universal Analysis. At least two samples were measured for each composition.

3. Results and discussion

3.1. Characterization of the precursors

The successful preparation of an epoxy resin from isosorbide was confirmed by FTIR (Figure 1). The absorbance peak at 907 cm^{-1} of the isosorbide resin was assigned to the vibration of the epoxy rings that confirms the epoxidation of the isosorbide. According to the titration method, the epoxy index of the resin was 0.42. In addition, isosorbide resin showed two peaks at 1072 and 1018 cm^{-1} that are attributed to the C-O stretching vibration

characteristic of ethers. As reported in the literature [28], this epoxy resin is composed of a mixture of epoxy oligomers instead of a single epoxy monomer. The oligomer nature of the isosorbide resin was confirmed by the results of ^1H (Figure S1, supplementary material) and ^{13}C NMR (Figure S2).

On the other hand, isosorbide resin was able to cure without the participation of any curing agent. Figure 1 shows the FTIR spectrum of this thermoset (iso_{net}). Two main characteristics were observed in its spectrum in relation to the spectrum of isosorbide resin. First, it did not possess any epoxy ring band at 907 cm^{-1} . Second, a small peak at 1727 cm^{-1} , attributed to the carbonyl group, appeared. This indicates that the epoxy groups were consumed during the heat treatment and they have participated in the crosslink reactions. The crosslinking might be originated from the reaction between the free hydroxyl groups in the isosorbide resin and the epoxy groups (Figure S3) [33]. On the other hand, the appearance of carbonyl groups of epoxy-amine polymers has been reported before and was attributed to thermal oxidation [34]. Therefore, based on the observations that epoxy groups were consumed and that carbonyl group were produced, it is confirmed that iso_{net} has been cured and aged at the same time during the heat treatment.

The hydrophobic curing agent, F8815, was also examined by FTIR (Figure 2). The results confirm that F8815 possesses three functional groups (fluoroalkyl, aminoalkyl and silanol groups, illustrated in Figure S4). The presence of the fluoroalkyl groups was proved by the bands at 1241 and 1206 cm^{-1} that are attributed to the C-F stretching, and the weak band at 696 cm^{-1} ascribed to the CF_2 scissoring [35]. Moreover, it is worth mentioning that F8815 has only primary amino groups as proved by the pair of peaks at 806 and 776 cm^{-1} (NH_2 bending, inset) [36], and the relative strong band at 1639 cm^{-1} (NH_2 stretching). F8815 can be used to produce hydrophobic coating by curing itself (F8815_c , Figure 2).

The most apparent difference between the FTIR spectra between F8815_c and F8815 lies with the reduction in the intensity of the silanol groups in F8815_c. This reduction is expected since the silanol groups are the reactive groups, and through the polymerization reaction F8815 turns into F8815_c.

3.2. Characterization of the biobased coatings

The effect of adding F8815 on the hydrophobicity of the isosorbide-based films was studied by measuring the corresponding water contact angles (WCA) and apparent surface energies (Table 1). First, F8815_c was confirmed as a hydrophobic polymer because of its higher WCA (110.63°) and lower apparent surface energy (10.88 mJ/m²) than the sample without any hydrophobic curing agent, iso_{net}. The latter is hydrophilic as demonstrated by its low WCA (52.60°) and high apparent surface energy (45.27 mJ/m²). Nonetheless, isosorbide resin became hydrophobic when mixed with F8815. All samples containing F8815 were hydrophobic exhibiting WCA higher than 100° and apparent surface energies below 14 mJ/m². Therefore, F8815 is confirmed to be an effective hydrophobic curing agent.

The hydrophilicity of the iso_{net} is attributed to the exposure of the hydrophilic ether and hydroxyl groups that can interact with water through hydrogen bonds. These ether and hydroxyl groups not only come from the original isosorbide resin but also from the epoxy ring-opening reactions (crosslink reactions) [37] that generates more ether and hydroxyl groups. In contrast, the hydrophobicity of the isosorbide-based samples containing F8815 was achieved due to the presence of fluoroalkyl groups on the film surface.

The thermal properties of the biobased samples were studied by TGA (Figure 3). The results show that there was a weight loss in the beginning of the heating process for all the biobased samples except for F8815_c. This weight loss was attributed to the water

desorption, which implies that the hydrophobic coatings are still able to absorb a small amount of water from **ambience**. **The water sorption was also confirmed by DSC results as shown in Figure S5.** Therefore, our results **indicate that** it is possible to have **a hydrophobic coating** with certain amount of water sorption. The hydrophobicity of films occurs at much larger **length** scale in comparison with that of water sorption (nano or sub-nanoscale). In fact, as reviewed in the literature [38], water sorption of epoxy polymers can be understood from two different **points** of views. **One considers** that water can diffuse into the polymer matrix due to the available free space (free volume). The other believes that water can penetrate into the polymer network due to the polar groups free to form intermolecular bonds. We believe that both crosslink density and the surface polarity of the films **are** responsible for the water sorption. Regarding the polarity of the hydrophobic **biobased** polymers, it seems that the hydrophobic chains of F8815 were not able to hide completely the polar groups (such as the hydroxyl groups formed during curing) of the isosorbide matrix.

To investigate **the effect of F8815 content on** the thermal properties of the isosorbide-based polymers, **the polymers were dried first before the analysis**. From TGA thermographs, it was noted that water has been removed from the polymers at 200°C. Thus, 200°C was chosen as the reference temperature to calculate the decomposition temperatures (T_d), defined at 5% weight loss, as shown in Figure 4. F8815_c has the lowest T_d while all the **biobased** samples have a higher T_d . The low T_d of F8815 is associated to its poor crosslink density. However, despite its weak thermal resistance, F8815 contributed to the increase of the T_d of S0.25 and S0.5 in relation with iso_{net}. Nevertheless, augmenting the concentration of F8815 in the polymer can cause a detrimental effect on the T_d , as shown in the T_d of S1 and S2. The amount of F8815 has a nonlinear effect on the T_d of the samples, in which the highest T_d were exhibited by S0.25 and S0.5.

To explore the influence of F8815 on the glass transition temperature (T_g), the DSC thermographs of the samples were obtained. The results were measured after heating consecutively three times from -50°C to 200°C in order to dry the samples. The data of the third heating are shown in Figure 5. F8815_c exhibited the lowest T_g , which can be attributed to the combined effect of its low crosslink density and the flexible silicon chains. In addition, the T_g profile resembles the T_d curve, proving the nonlinear trend of F8815 found on T_d results (Figure 4). This study finds that despite its inherently weak thermal properties, F8815 is able to improve the thermal properties of iso_{net} through cross-linking reactions, as proved in S0.25, S0.5 (maximum value achieved) and S1 samples.

On the other hand, the addition of F8815 also affects the thermomechanical properties of the biobased samples as shown in the DMA results. The DMA results shown in Figure 6 corresponds to the second heating (the first heating was used to dry the samples). Due to the complications in preparing a free-standing film, F8815_c was not tested. The results proved again F8815 content has a non-linear trend of influence on the storage modulus (E') of the samples. The highest E' was obtained by S0.5 and the minimum by S2.

Combining results of T_d , T_g and E' , there is a clear optimal thermal and mechanical properties of the hydrophobic coating with sample S0.5. One possible explanation is that a stoichiometric reaction has been achieved when the mass ratio of isosorbide resin to F8815 is 1 : 0.5. As a result, S0.5 is able to achieve the maximum crosslinking density, and further increment in F8815 concentration will cause the segregation of F8815 that acts as a plasticizer. The plasticization effect caused by an unreacted reagent can be inspected by calculating the enthalpy of polymerization (ΔH_p) [39]. In this technique, the curve of ΔH_p versus concentration of a reagent will be the maximum when its concentration equals the concentration at the maximum of DSC curves. The decrease in the T_g and ΔH_p after the maximum values is interpreted as a result of an unreacted reagent.

Following this theory, ΔH_p for various samples were calculated. The results in Figure 7 show that the ΔH_p increases as the amount of F8815 increases but no maximum was observed. This observation can be explained by the fact that isosorbide resin and F8815 can polymerize alone. In other words, even if isosorbide resin and F8815 were not mixed in a stoichiometry ratio for the epoxy-amino reaction, the ΔH_p would continue to increase as F8815 can polymerize by itself through the condensation reaction of silanol groups. Thus, it was not possible to confirm any stoichiometry reaction in the current study.

FTIR spectroscopy was carried out to investigate the crosslink reactions between the isosorbide resin and F8815 (Figure 8). Similar to the FTIR spectrum of iso_{net} (Figure 1), the spectra of the hydrophobic biobased samples did not show the appearance of the epoxy band at 907 cm⁻¹, signifying that the epoxy groups reacted completely during the curing treatment. Moreover, the presence of F8815 in the hydrophobic samples (S0.25, S0.5, S1 and S2) was confirmed by the characteristic bands of CF₂ scissoring (696 cm⁻¹) and the amino bands (NH₂ bending, 808 and 780 cm⁻¹).

According to the Beer Lambert law [40], the absorbance of a substance, A, is directly proportional to its concentration:

$$A = \varepsilon cl, \quad (1)$$

where ε , c and l stand for absorption coefficient (l mol⁻¹ cm⁻¹, specific for each frequency), molar concentration (mol l⁻¹) and path length of radiation, respectively. Therefore, a simple relationship between the absorbance and the concentration of a functional group can be achieved if the path length of radiation is the same for the samples analyzed. Since it is difficult to know the penetration length of the radiation, the absorbance of the functional groups studied was normalized by the absorbance of a reference band [33, 40, 41].

In order to study the reaction between the epoxy group and amino group, the integrated absorbance (band area) of the two NH_2 bending bands was calculated (Figure 9a). These bands were selected for this analysis since they facilitate the identification of primary and secondary bands. As proved in literature [36], primary amines are characterized by possessing two bands for the NH_2 bending mode, while secondary amines possess only one band for the NH bending vibration. In contrast, the single stretching NH_2 band at 1639 cm^{-1} does not have this advantage. Therefore, it was not used for this study. On the other hand, the analysis of the carbonyl group band was also carried out (Figure 9b). This is because the carbonyl groups appeared in all the isosorbide-based samples, and therefore, it plays a role in the thermal and mechanical properties.

Because the carbonyl groups originate from the isosorbide structure, its absorbance was normalized by a reference band that belongs purely to isosorbide (968 cm^{-1}). Similarly, the amino group absorbance was normalized by a reference band that belongs to F8815 only (697 cm^{-1}). The reference band of isosorbide was fitted from ~ 978 to $\sim 955\text{ cm}^{-1}$ by using a Gaussian-Lorentz Cross model. The reference band of F8815 was obtained by deconvoluting the region from ~ 717 to $\sim 680\text{ cm}^{-1}$ into two bands by using a Gaussian function. For the analysis of the NH_2 band at 808 cm^{-1} , the region between 857 and 795 cm^{-1} was deconvoluted into three Gaussian curves. The NH_2 band at 780 cm^{-1} was extracted by deconvoluting the absorbance band between 795 to 756 cm^{-1} into two Gaussian curves for both the hydrophobic samples and the hydrophilic sample iso_{net} . Because in the same region iso_{net} also possesses the band at 780 cm^{-1} , the 780 cm^{-1} absorbance of the hydrophobic samples was corrected by subtracting the corresponding 780 cm^{-1} absorbance of isosorbide. In the case of the carbonyl group, the deconvolution was performed in the region between 1780 and 1560 cm^{-1} using three Gaussian curves.

The integrated absorbance of the amino and carbonyl bands are shown in Figure 10. Interestingly, the intensity of the amino bands at 808 and 780 cm^{-1} were almost the same for sample S0.5 and were different for the other samples (S0.25, S1 and S2). This very close similarity in the absorbance of the two amino bands of S0.5 resembles the original intensity of the amino bands of F8815, therefore, suggesting that almost no primary amino groups **have** reacted with epoxy groups.

In contrast, the unequal absorbance of the two amino bands of the other samples suggested a more complete reaction of the amino groups with the epoxy resins. In this case, the low intensity of 808 cm^{-1} band in comparison with that of 780 cm^{-1} band **suggests** that primary amino groups **have started the reaction but not been** consumed totally. Furthermore, since the consumption of the primary amino groups leads to the creation of secondary amino groups, the band absorbance of secondary amino groups should also increase. **This is proven** by the increase in the band absorbance at 780 cm^{-1} . It is worth mentioning that secondary amino groups can continue **to react** to form tertiary amines, in which no bending NH_2 bands **would** appear. Thus, the band at 780 cm^{-1} may also represent the concentration of **the formed** tertiary amino groups. The results also suggest that as the concentration of F8815 increased, the amino groups reacted with epoxy groups to a greater degree (with exception of S0.5).

In relation with the carbonyl absorbance (Figure 10b), it is clear that the $\text{C}=\text{O}$ concentration of S0.5 was the highest among the hydrophobic coatings. Therefore, when comparing **among hydrophobic coatings only**, S0.5 contained the highest concentration of carbonyl groups and was the least reactive to amino groups (highest NH_2 concentration left after curing). In addition, the $\text{C}=\text{O}$ concentration of S0.5 was close to that of iso_{net} , which suggests that S0.5 is similar to iso_{net} in its chemical properties. This is reasonable since S0.5 **has** the largest amount of NH_2 groups unreacted (**as it behaves like the iso_{net}**).

With exception of S0.5, the C=O concentration decreased as the concentration of F8815 increased. This trend was similar to that of the NH₂ concentration, in which the NH₂ concentration left after curing decreased as F8815 concentration increased. Consequently, augmenting the concentration of F8815 favored the reaction between amino groups and epoxy groups, while hindered the formation of C=O.

Overall, the FTIR results suggest that F8815 might have not completely reacted with isosorbide resin in S0.5 due to the high content of primary amino groups left after curing. In contrast, the F8815 in the other hydrophobic coatings (S0.25, S1 and S2) had a better participation in its reaction with epoxy groups from isosorbide resin. Therefore, FTIR results find it invalid to reply on the stoichiometry reaction to explain the trend found in the T_d, T_g and E' curves. A new hypothesis can be proposed to explain the nonlinear effect of F8815 concentration on the thermal and mechanical properties based on the polymer entanglement and molecular rigidity. Since originally the precursors (isosorbide resin and F8815) were oligomers, chain entanglements are expected to occur during the mixing process. Moreover, the rigid and flexible oligomer chains of isosorbide resin and F8815, respectively, must also play a role in the properties. The concentration of carbonyl groups might also contribute to the rigidity of the polymer and should be taken into consideration.

Therefore, as F8815 concentration increased, the isosorbide resin chains were reinforced by the oligosiloxanes, increasing the intermolecular interactions. For S0.25, the polymer entanglement was not only held by intermolecular interactions but also through covalent bonds from the epoxy and amino reaction. The same explanation can be given for the improved properties of S0.5 over S0.25. However, in S.05 the polymer entanglement was mainly maintained by intermolecular bonds since FTIR results showed high content of NH₂ groups after curing. Nevertheless, the S0.5 seemed to have better a molecular rigidity due to its high concentration of carbonyl groups (Figure 10b). Therefore, the best

properties found in S0.5 can be attributed to the best balance between the rigidity of isosorbide resin and C=O, and the flexibility of the oligomer chains F8815 in the formation of polymer entanglements. As the content of F8815 increased further (S1, S2), the flexibility of the oligosiloxanes became more evident. That is, the high concentration of F8815 gradually overcame the rigidity effect of the isosorbide resin and the strong covalent interaction of F8815 and isosorbide resin. Therefore, this effect **has resulted** in reduced thermal and mechanical properties.

In order to prove the entanglement hypothesis mentioned above, FESEM images of the thin films were obtained (Figure 11). The surface of iso_{net} was smooth and compact (Figure 11a), while the surface of F8815_c possessed a rough surface (Figure 11f). These surface characteristics of the iso_{net} and F8815_c agreed very well with their thermal and mechanical properties, in which iso_{net} **has** better thermal and mechanical properties **than F8815_c**. As the concentration of F8815 increased, the surface of the hydrophobic samples gradually became similar to that of F8815_c. **This implies improved** miscibility between the isosorbide resin and F8815, supporting the hypothesis of oligomer entanglements that occur at molecular level. However, the surface of S0.5 was different from others. The S0.5 surface was similar to that of iso_{net} but with small nanoparticles rested on the **surface** (Figure 11c and Figure 12). These nanoparticles were labeled as the F8815_c **as they were excess F8815 that have not reacted with isosorbide resin. They were segregated in the isosorbide polymer network and self-cured.** Therefore, the hypothesis of polymer entanglements that explains the better properties of S0.5 remained invalid. Consequently, the thermal and mechanical properties of S0.5 can be explained by a composite effect caused by the F8815_c nanoparticles. Under specific conditions, fillers can improve the mechanical and thermal properties of epoxy polymers [42-44] by supporting the mechanical tension and hindering the polymer mobility. Usually a remarkable

improvement in the properties of the polymer composite is achieved at a low concentration of the filler. Nonetheless, in the case of S0.5, the improvement caused by the F8815_c nanoparticles was not high. The inherently weak mechanical properties of F8815_c seems to be the main factor.

The segregation of F8815_c in S0.5 could be caused by the miscibility of isosorbide resin and F8815 at the specific mass ratio (1:0.5). It seems that isosorbide resin was able to function very well as a dispersion phase for F8815 at a mass ratio of 1:0.25 (S0.25). However, when the concentration of F8815 increased (mass ratio 1:0.5, S0.5), isosorbide resin was not able to cope with the higher amount of F8815. For even higher concentrations of F8815 (S1 and S2), it seems that F8815 functions as the dispersing phase and was capable to disperse isosorbide resin. The FESEM results of S0.5 are consistent with the FTIR results (Figure 10). The higher content of C=O groups and amino groups in S0.5 suggests that isosorbide and F8815 do not mix very well. Furthermore, the segregation of F8815 in S0.5 can also be validated by the small difference in the apparent surface energy of S0.5 (Table 1). While the apparent surface energy of the hydrophobic coatings was below 11 mJ/m², the apparent surface energy of S0.5 was 13.61 mJ/m². This small increase is likely to be caused by the partial exposure of the hydrophilic isosorbide network at micro and nanoscale.

4. Conclusion

Biobased hydrophobic epoxy coatings derived from isosorbide resin have been successfully prepared through a simple aqueous method. Isosorbide epoxy resin was cured with different concentrations of the curing agent F8815. The wettability, thermal and mechanical properties of polymers were examined. Due to the presence of fluoroalkyl chains, F8815 is able to hydrophobize the hydrophilic isosorbide thermoset. Moreover, F8815 is also capable of improving the mechanical and thermal properties of the biobased

polymers (S0.25 and S0.5). The effect of F8815 on the properties of isosorbide-based polymers **are** explained based on polymer entanglement and segregation effect. S0.25 possessed better properties than the pure sample iso_{net} because of the reinforcement of isosorbide oligomer chains with the oligosiloxanes of F8815. In the case of S0.5, its better properties were ascribed predominantly to the composite effect caused by the segregation of F8815 that has led to the formation nanoparticles. The evidence of the segregation of F8815 in S0.5 was supported by SEM images and the FTIR analysis that showed the high content of amino groups left after curing. The coating enjoys the advantage of using water as the only solvent in preparation, opening possibility for environmentally-friendly coating applications in the future. **Evaluation of the performance of hydrophobic isosorbide-based coatings for anti-icing, anti-corrosion and self-cleaning applications is suggested for future work.**

5. Acknowledgments

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List of Tables.

Table 1. Wettability properties of **biobased** films and F8815 film.

Sample	Static CA (5 μ L)	Apparent Surface Energy (mJ/m ²)
iso _{net}	52.60 ° ($\pm$ 1.62)	45.27
S0.25	110.64 ° ($\pm$ 0.75)	10.83
S0.5	104.16 ° ($\pm$ 2.24)	13.61
S1	108.75 ° ($\pm$ 2.54)	10.27
S2	112.07 ° ($\pm$ 4.65)	10.37
F8815 _c	110.63 ° ($\pm$ 0.71)	10.88

List of figure captions.

Figure 1. FTIR spectra of isosorbide and its derivatives.

Figure 2. FTIR spectra of the hydrophobic curing agent uncured (F8815) and cured (F8815c).

Figure 3. TGA thermographs of isosorbide-based polymers and F8815c.

Figure 4. Decomposition temperature at 5% weight loss (T_d) of the **biobased** and F8815c samples.

Figure 5. T_g of the dried samples.

Figure 6. Storage modulus (E') at the rubbery state of the samples. The temperature selected was $T_{\tan\delta} + 30K$ [28].

Figure 7. Enthalpy of polymerization as function of F8815 concentration. Samples with new concentration (S0.1, S0.3, and S4) were prepared for this measurement.

Figure 8. FTIR spectra of the isosorbide-based samples and F8815c.

Figure 9. FTIR spectra showing a) amino groups with the reference bands and b) carbonyl groups for the deconvolution.

Figure 10. Integrated absorbance of a) NH_2 and b) $C=O$ groups.

Figure 11. FESEM images of a) iso_{net} , b) S0.25, c) S0.5, d) S1, e) S2 and f) F8815c.

Figure 12. FESEM images of S0.5 at a) low and b) high magnification.

Figure 1.

Figure 2.

Figure 3.

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