Development of environmentally friendly bio-epoxy coatings for water-repellent applications

Bellido Aguilar, Daniel Angel

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SINGAPORE

**DEVELOPMENT OF ENVIRONMENTALLY FRIENDLY
BIO-EPOXY COATINGS FOR WATER-REPELLENT
APPLICATIONS**

BELLIDO AGUILAR DANIEL ANGEL

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2020

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BIO-EPOXY COATINGS FOR WATER-REPELLENT
APPLICATIONS**

BELLIDO AGUILAR DANIE ANGEL

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

4th December 2020

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I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

4th December 2020

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Date

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Professor Chen Zhong

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapter 4 is published as D. A. Bellido-Aguilar, S. L. Zheng, X. J. Zhan, Y. J. Huang, X. Zhao, X. T. Zeng, P. K. Pallathadka, Q. C. Zhang, Z. Chen. Effect of a fluoroalkyl-functional curing agent on the wettability, thermal and mechanical properties of hydrophobic biobased epoxy coatings. *Surface and Coatings Technology*. **362**, 274-281 (2019). DOI: 10.1016/j.surfcoat.2019.02.006.

The contributions of the co-authors are as follows:

- Prof. Chen, Prof. Zhang, Dr. Zeng initiated the work, and revised the draft manuscript.
- Dr. Pallathadka and Dr. Zheng helped in the revision and discussion of the manuscript.
- Dr. Zhan and Dr. Huang prepared the isosorbide epoxy resin.
- Dr. Zhao conducted the microscopy of the films.

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The contributions of the co-authors are as follows:

- Prof. Chen, Prof. Zhang, Dr. Zeng initiated the work, and participated in the discussion of manuscript drafting.
- Dr. Zheng and Dr. Huang revised the manuscript and provided insightful discussion.

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- Prof. Chen, Prof. Zhang, Dr. Zeng initiated the work, and participated in the discussion of manuscript drafting.
- Dr. Zheng and Dr. Huang revised the manuscript and provided insightful discussion.
- Dr. Huang carried out the nuclear magnetic resonance experiments.
- Sun Ye performed some of the corrosion tests.

4th December 2020

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Bellido Aguilar Daniel Angel

Abstract

Hydrophobic coatings are made of materials that have low affinity to water. Driven by their water-repellent properties, hydrophobic coatings are envisioned to be employed as anti-icing and anti-corrosion coatings. Epoxy coatings, one of the most important thermosets, are commonly hydrophilic, and, therefore, preparing hydrophobic films from hydrophilic epoxy resins is a scientific challenge. Despite of the great achievements in preparing hydrophobic epoxy films with good performance, the preparation of hydrophobic epoxy coatings still faces two serious problems. First, the epoxy resins commonly used are derived from Bisphenol A, which is an organic compound produced from petroleum sources and has been found to be an endocrine disrupting chemical. Second, the synthesis procedures involve the use organic solvents or small organic compounds that are released into the air. In other words, current hydrophobic epoxy coatings are not environmentally friendly synthesized.

Therefore, the ultimate aim of this research is to prepare hydrophobic coatings with epoxy resins obtained from biomass precursors without requiring the use of organic solvents during the film preparation. The developed bio-based coatings are examined for the anti-icing and anti-corrosion performances. Three different epoxy polymer formulations were developed based on isosorbide, cardanol and glycerol. The bio-based contents of the polymer formulations were progressively increased by incorporating bio-based curing agents and hydrophobizers. Furthermore, the hydrophobization of the bio-based epoxy polymers was achieved to different degrees by the incorporation of various hydrophobizers. In addition, the wettability, thermal and mechanical properties of the bio-based thermosets were studied. The anti-icing and anti-corrosion performances of the epoxy coatings were also evaluated in relation with the bulk and surface properties of the coatings. The overall results of this research have demonstrated that coatings with hydrophobic coatings for water-repellent applications can be prepared from bio-based compounds with tunable properties according to the selected compounds and employed synthesis method. Therefore, this research contributes to the development of green epoxy coatings for water-repellent

applications. Finally, future work is suggested for the continuation and enrichment of this research.

Lay Summary

Coatings with the ability to repel water are called hydrophobic coatings. Because of this property, hydrophobic coatings can serve as protective coatings against corrosion since water provokes the corrosion of metals. Similarly, hydrophobic coatings can also function as anti-icing coatings that prevent the formation or reduce the adhesion of ice on surfaces. Using epoxy coatings, one of the most important industrial polymer coatings, for anti-icing and anti-corrosion applications is not the best option due to their hydrophilic nature. However, considerable research has successfully been done in the preparation of new hydrophobic epoxy coatings. Although there are various reports on the preparation of epoxy films with hydrophobic properties and good performances, the elaboration of hydrophobic epoxy coatings still presents two environmental concerns. First, the raw material from which epoxy resins are commonly prepared, Bisphenol A, is a compound obtained from petroleum sources and it has been identified as a toxic chemical to human health. Second, organic solvents are generally employed in the synthesis which are naturally evaporated during the coating preparation process and, therefore, contributing to the pollution of the air. In summary, current hydrophobic epoxy coatings are based on non-renewable and toxic materials, and the process may cause environmental pollution.

The objective of this research is, therefore, to solve the above two problems of the epoxy technology by preparing new hydrophobic epoxy coatings obtained from renewable materials or biomass without the use of toxic organic solvents. Three different epoxy coatings were developed from three different bio-based precursors: isosorbide, cardanol and glycerol. The wettability, thermal and mechanical properties of the bio-based thermosets were studied as well as their anti-icing and anti-corrosion performances. The overall results of this research have proven that biomass compounds are competitive candidates for the preparation of epoxy coatings with hydrophobic coatings for water-repellent applications. Therefore, this research contributes to the progress of green hydrophobic epoxy coatings for water-repellent applications. Finally, some suggestion are given for the continuation of this research.

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Abbreviations

AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflectance
BA	Bisphenol A
CA	Contact Angle
CAH	Contact Angle Hysteresis
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
DGEBA	Diglycidyl Ether of Bisphenol A
FTIR	Fourier Transform Infrared Spectroscopy
IR	Infrared
NMR	Nuclear Magnetic Resonance
SEM	Scanning Electron Microscopy
SHE	Superhydrophobic Epoxy
SOC	Small Organic Compounds
VOC	Volatile Organic Compounds
UV-Vis	Ultraviolet-Visible
TGA	Thermogravimetric Analysis
T _g	Glass Transition Temperature

Chapter 1

Introduction

This chapter presents the overall research plan on the design of bio-based epoxy coatings for water-repellent applications. The chapter briefly introduces the current state of hydrophobic and superhydrophobic epoxy coatings followed by the hypothesis and objectives of this research. Finally, the general structure of this thesis is shown and the key findings are also summarized.

1.1 Hypothesis/Problem Statement

Epoxy-based polymers constitute an important type of thermosetting polymers because of their wide range of applications. The rich chemistry of epoxy resins has made epoxy-based polymers well-known for their good mechanical, adhesion, thermal and insulation properties [1]. Recently, a new research has emerged to prepare epoxy-based polymers as water-repellent coatings. The hydrophobic epoxy layers can prevent or delay water from reaching the substrate, and, therefore, act as anti-corrosion, anti-icing, and easy-cleaning coatings. As anti-corrosion materials, hydrophobic epoxy coatings may be used to improve the life time and safety of structures such as buildings and bridges. As anti-icing coatings, the hydrophobic coatings may be applied on aircraft as well as on wind turbine blades in which ice accretion negatively affects their performance. As easy-cleaning coatings, hydrophobic epoxy coatings are suitable for clothing, walls, floors, and windows. Thus, research on hydrophobic epoxy coatings is very significant because of their various potential applications.

Many hydrophobic and superhydrophobic epoxy coatings have been reported in the literatures [2-12]. A lot of attention has been paid in the strategies to hydrophobize epoxy resins but disregarding the sustainability of the new reported formulations. That is, despite the great effort to obtain epoxy coatings with hydrophobic properties, the epoxy coatings of the above mentioned researches were prepared from Bisphenol A (BA) compound. BA has two serious disadvantages. The first disadvantage is that BA is a non-sustainable petroleum-based chemical [13]. The second disadvantage is that, according to various studies, BA is an endocrine disrupting chemical, and, thus, harmful to human health [14, 15]. These two disadvantages are big concerns since approximately 90% of world's epoxy production is based on BA [16]. The other problem that arises in the preparation of hydrophobic epoxy coatings is the use of small organic compounds (SOC). SOC's include plasticizers, additives, surfactants and volatile organic compounds (VOC) that are used commonly as solvents. These SOC's have been recognized as harmful chemicals for both human health and environment [16-18]. Because the use of both SOC's and BA in the

preparation of hydrophobic epoxy coatings is harmful to ecosystem and human health, there is an urgent necessity to produce ‘green’ hydrophobic epoxy coatings.

Prompted by the unsustainability and harmful health effects of BA epoxy resins, an increasing number of new bio-based epoxy resins have been reported. Some of the new bio-based epoxy resins have been even regarded as potential substitutes for BA epoxy resin [19-22]. Nevertheless, studies on the hydrophobic properties of the new bio-based epoxy coatings are rare. As mentioned before, hydrophobic coatings have the potential to be used as anti-icing and anti-corrosion coatings. Therefore, a careful literature review has revealed that there is a lack of reports on the preparation of new (partially or completely) bio-based epoxy coatings with hydrophobic properties for anti-corrosion [23-26] and anti-icing [27-29] applications. In consequence, the goal of this research is to fill that scientific gap. That is, the aim of this project is to formulate new bio-based epoxy coatings and to study the anti-corrosion and icephobic properties and other bulk properties relevant to their eventual applications.

Thus, this thesis tests the general hypothesis that eco-friendly synthesized and bio-based epoxy resins can be properly formulated to prepare hydrophobic coatings for anti-corrosion and anti-icing applications.

1.2 Objective and Scope

Biomass can offer a library of organic compounds from which bio-based epoxy resin can be synthesized. Through literature review, three types of bio-based epoxy resins were employed in this research. The bio-based epoxy resins were derivatives of isosorbide, cardanol and glycerol. Although these bio-based compounds have been selected for the preparation of bio-based epoxy, it is important to highlight that their productions are not completely environmentally benign. Isosorbide can be prepared from polysaccharides such cellulose and starch [30]. However, the four chemical reactions that are involved in this process rely on the use of catalyst that are not environmentally friendly [31]. Cardanol is

extracted from the cashew nut shell liquid (CNSL) which is in turn prepared from the nut shells recovered as by-products in the cashew nut industry [32]. Although traditional techniques have employed in the preparation of CNSL such as solvent extraction, greener alternatives have been also employed such as pyrolysis and supercritical carbon dioxide extraction [33]. Solvent extraction, however, is usually employed in the isolation of cardanol from CNSL which contains various components such anacardic acid and cardol. Glycerol can be produced synthetically from propylene which is generally a petro-based derivative [34]. Nevertheless, glycerol can be also obtained as a by-product (crude glycerol) in the production of biodiesel from plant oils [35]. Crude glycerol requires further purification to obtain high quality glycerol [36].

Thus, the present research is concerned with the environmentally friendly synthesis and characterization of three different bio-based epoxy hydrophobic coatings and their application as anti-corrosion and anti-icing coatings.

The specific objectives of this research are:

- Synthesize and characterize new bio-based epoxy hydrophobic coatings with different bio-based content and with minimum or zero small organic solvents (SOC).
- Unravel the curing reaction mechanisms, thermal and mechanical properties, as well as the anti-icing and anti-corrosion performance of the bio-based coatings.

1.3 Dissertation Overview

Chapter 1 outlines the targeted problem of the research as well as its goals and findings.

Chapter 2 provides a broader context on the problem addressed and its related topics useful in this research.

Chapter 3 discusses the general characteristics of the methodology employed and the theory behind the characterization techniques used in this research.

Chapter 4 presents the results and discussion on the synthesis of isosorbide-based coatings.

Chapter 5 shows the results and discussion on the development of cardanol-based coatings.

Chapter 6 provides the results and discussion on the fabrication of glycerol-based coatings.

Chapter 7 provides an overall conclusion and outlines the future work of the research.

1.4 Findings and Outcomes/Originality

The originality of this research is that:

For the first time, novel bio-based and solvent-free epoxy coatings have been prepared from different biomass sources and with different bio-based content. Optimization was realized based on the materials characterizations and performance evaluation.

In addition, the research derived the following scientific outcome:

Hydrophobizers can be incorporated into two ways: by intermolecular forces (intermolecular entanglements) and by covalent bonds with the polymer network. In either way employed (or combination), the hydrophobizer must be incorporated into the polymer network so that it will not increase the free volume of the polymer. If the introduction of the hydrophobizer increases the free volume, water is able to penetrate into the coating, causing a degraded overall water-repellent performance. On the other hand, if the incorporation of the hydrophobizer decreases the free volume, resistance to water diffusion will be enhanced. In summary, introducing a hydrophobizer into a polymer coating may not necessarily enhance its corrosion protection if the free volume of the polymer network is considerably higher, which allows water to permeate into the coating at molecular level.

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Chapter 2

Literature Review

This chapter provides a review of the hydrophobic coatings from bio-based epoxy resins. The chapter starts with a brief discussion on the environmental problem that current polymer technology faces. Then, the main bio-based sources from which epoxy resins can be prepared are presented. Because this research focuses on epoxy thermosets, fundamental concepts about polymer science and the chemistry of epoxy resins are also explained. Basic knowledge of wettability and its main measuring techniques are discussed. Finally, a description of the strategies to prepare non-bio-based hydrophobic and superhydrophobic coatings is presented, from which lessons can be learnt when designing water-repellent coatings using bio-based epoxy resins.

2.1 Overview

2.1.1 Concerns on the sustainability of the polymer industry

Polymers constitute one of the most important materials in the development of society. Polymers have many applications in our daily lives due to the enormous advancement in their science and technology. Nevertheless, the evolution of polymer industry has not seriously taken into consideration its impact on nature. Two main problems are identified in polymer industry. First, most of the synthetic polymers are produced from fossil feedstock [1]. Second, polymers contribute to the earth contamination due to the lack of recyclability and long-term resistance to environmental degradation [2].

Petroleum resources are non-renewable and seriously contribute to the emission of greenhouse gases during the refining process[3]. Therefore, biomass has been regarded as an alternative to fossil resources in the production of polymers. However, the exploitation of biomass for the production of polymers also has its own challenges. For instance, food industry may be affected if agriculture land is used for the development of bio-based chemicals (platform chemicals). The land available for the production of crops, vegetables and fruits should not be reduced because of the need for bio-based chemicals [4].

The contamination in soil and ocean caused by the accumulation of polymers can be overcome if the polymer can be recycled and/or biodegradable [5]. In this sense, the polymer has to be designed not only with the purpose of achieving specific performance properties but also with recyclability and/or environmentally friendly degradability.

2.1.2 Recyclable polymers

Nowadays, efforts have been made to transform the polymer industry into a circular bioeconomy. In a circular bioeconomy, bio-based resources are used in the production and recycling of polymers with minimum negative effect to the environment. Three main technologies can be applied to the polymer recycling:

mechanical, chemical and microbial [6]. Mechanical recycling recovers the polymer by grinding or pulverizing it. In case of the thermoplastics, the powdery polymer can be used again to fabricate the original material by extrusion. Chemical recycling aims to recover the chemical compounds from the decomposition of the polymer. The chemical compounds obtained can be utilized for the preparation of the same polymer or for other purposes. Microbial recycling refers to the degradation of polymers by the use of microorganisms. The polymer can be completely mineralized so that it is reinserted into nature, or can be decomposed to produce chemicals that can be useful for the fabrication of other polymers.

The simplest way to degrade the polymers is by incineration. However, this methodology pollutes the environment due to the emission of toxic gases. Thus, the two most desirable methodologies are biodegradation and compostability. The biodegradation of a polymer refers to the degradation caused by the microorganisms living in a natural environment. The compostability of a polymer is also a biological degradation that occur in non-natural environments [7, 8].

The biodegradability of a polymer depends basically on two factors: polymer chemistry and environmental conditions [8]. The polymer chemistry may refer, for example, the type of chemical bonds, hydrophobicity, crystallinity and presence of additives. The environmental conditions point out to biotic factors (types and population of microorganisms) and abiotic factors (temperature, pH, humidity, light). Based on this definition, it is important to highlight that bio-based polymers are not necessarily biodegradable, and, similarly, that petro-based polymers are not necessarily non-biodegradable [9]. For instance, the bio-based polyethylene-2,5-furandicarboxylate (PEF) is not biodegradable but the petro-based polybutylene adipate terephthalate (PBAT) is biodegradable. Examples of bio-based and biodegradable polymers are polyhydroxyalkanoate (PHA) and polylactic acid (PLA).

2.1.3 Epoxy thermosets

Epoxy resins are the most important thermosetting resins as they represent 70% of the resins market. However, approximately 90% of the global epoxy resin

production is based on the petro-based compound Bisphenol A (BA). Moreover, studies have shown that BA is an endocrine disruptor that may bring serious human health issues such as cancer [10, 11]. Driven by these reasons, research has been made with the aim of synthesizing new bio-based epoxy resins with similar or better performance than that of diglycidyl ether of bisphenol A (DGEBA) [12-15]. Some reports have demonstrated that the substitution of DGEBA is possible. Moreover, as the research on new bio-based and high performance epoxy resins continues, more degradability studies must be carried out in order to achieve a more sustainable replacement for DGEBA [16, 17].

Despite the advances on the preparation of new bio-based substitutes for DGEBA, the development of other new bio-based epoxy resins should continue. Synthesis of non-high performance bio-based polymers may be used for other non-traditional applications in short usage.

2.1.4 Bio-based epoxy resins (monomers)

Bio-epoxy resins can be obtained from at least three sources: plant oils, saccharides and polyphenols and phenols [18].

2.1.4.1 Plant oils

Plant oils refer to the triglycerides that are characterized by the three fatty acids attached to glycerol. Usually, the preparation of the epoxy resin from plant oils involves the conversion of the double bonds into epoxy groups (Figure 2.1). Various sources have been used for the synthesis of bio-epoxy resins such as soybean oil [19], linseed oil [20], canola oil [21], karanja oil [22] and cottonseed oil [23].

One of the challenge of plant-oil based thermosets is that their poor mechanical properties. Because of the long and flexible carbon chains of plant-oil epoxy resins, the cured thermoset exhibits a low glass transition temperature (T_g) [24]. One common strategy to improve and adjust the mechanical properties of plant-oil epoxy polymers is by selecting an appropriate curing agent. Traditional anhydrides

are the most typical curing agents employed in the preparation of new plant-oil epoxy thermosets with improved mechanical properties [23, 25, 26]. Another strategy is to prepared new curing agents as Wang et al. [27] and Jin et al. [28] have done. They prepared a fully bio-based and carboxylic-terminated curing agent derived from the polymerization of sebacic acid and decamethylene diamine. In addition, this new hardener is characterized by its oligomeric nature with crystalline phases. The results demonstrated that the mechanical strength and toughness of the epoxidized soybean oil-derived thermosets remarkably improved in comparison with that of the thermoset cured with sebacic acid. Moreover, studies showed that the mechanical properties of the plant oil-based thermosets can be adjusted by carefully varying the molar ratio of the hardener and epoxy resin.

Figure 2.1. Typical reaction for the epoxidation of oils. Adapted from [29].

An interesting approach to prepare thermosets from plant oils with enhanced mechanical properties was reported by Wang et al. [30]. Their hypothesis was that epoxy resins with higher content of epoxy groups per molecule can produce thermosets with better mechanical properties. In this sense, soybean oil was modified thorough various reactions to prepare new epoxy resins in the forms of polymers. First, the triglycerides of the soybean oil went through a catalyzed amidation process in which they were converted to N-hydroxyalkyl fatty amides using different amino alcohols. The amidation reaction can be viewed as a decomposition reaction of the triglycerides since glycerol is a sub product. Second, these N-hydroxyalkyl fatty amide were then methacrylated and used as monomers

in a free radical polymerization, which resulted in linear polymers with pendant fatty chains. Finally, these thermoplastic polymers were epoxidized by transforming the double bonds of the fatty chains into epoxy groups. The new epoxy polymers were subsequently cured with an anhydride curing agent. The results showed that the new thermosets were much tougher than the thermoset produced from the epoxidized soybean oil and the hardener. The authors also highlighted that the mechanical properties of new epoxy thermosets can be tuned from soft to rigid polymers by adjusting the epoxy/anhydride molar ratio.

2.1.4.2 Saccharides

These are organic compounds composed only of carbon, hydrogen and oxygen. The most common bio-precursors obtained from saccharides to prepare epoxy resins are isosorbide and furan blocks.

Figure 2.2: Synthesis of isosorbide from polysaccharides. Adapted from [31].

Isosorbide (Figure 2.2) is obtained from starch through various chemical reactions and is commercially available [31]. Chrysanthos, Galy and Pascault prepared epoxy resins from isosorbide following two methodologies (Figure 2.3) [32]. Interestingly, the isosorbide epoxy obtained by route **a** was composed of a mixture of oligomers (called DGEDAS_n), while the product of route **b** is composed of just one single epoxy monomer (called DGEDAS₀). In addition, those bio-based resins were cured with IPD (isophorone diamine), and their T_g were studied in

comparison with the fossil-based network DGEBA-IPD. The results showed that the DGEBA-based polymer had the highest T_g (155°C), and the DGEDAS₀ and DGEDAS_n exhibited the lower T_g , 112°C and 96°C, respectively. Nevertheless, the thermal stability of the DGEDAS_n and DGEBA networks were very similar, while the DGEDAS₀ thermoset had the lowest thermal stability. That is, the temperatures at the maximum rate of decomposition of the DGEDAS_n, DGEBA and DGEDAS₀ thermosets were 380°C, 370°C and 350°C, respectively.

Figure 2.3: Epoxidation of isosorbide used in [32]. a) Traditional chemical route using epichlorohydrin, and, b) chemical synthesis using allyl bromide followed by epoxidation of double bonds.

Other bio-epoxy resins derived from saccharides are those characterized by their furan backbone. Jeong et al. reported the preparation of two furanic epoxy resins: one diepoxy (2,5-bis[(2-oxiranylmethoxy)methyl]-furan, BOF), and the other monoepoxy derived from 2- Furan methanol (Figure 2.4) [33]. Based on that

report, Hu et al. synthesized fully bio-based thermosets made of BOF and two furan-based amine hardeners [34]. BOF was also cured with a non-renewable curing agent, 4, 4'-methylene biscyclohexanamine (PACM), and its properties were compared with those of the furan-based thermosets. Although the T_g values of the fully bio-based thermosets was lower (56°C) than that of the BOF-PACM (72°C), they exhibited lower degradation rates than that of BOF-PACM. Based on the TGA results, it was found that at 750°C the char yield of BOF-PACM polymer was 6 wt%, while the char yield, at the same temperature, of the fully bio-based thermosets were 40 and 39 wt%. The result suggested that, during the degradation test, BOF cured with furan-based amine hardeners adopted more stable forms than that of the BOF-PACM polymer.

Itaconic acid, a bio-based and non-cyclic compound has been proposed as a potential substitute for DGEBA [35]. Itaconic acid is industrially produced from the fermentation of the carbohydrates and it is considered as an important platform chemical. The itaconic epoxy resin (TEIA) was synthesized in a two-step methodology consisting of the allylation of the itaconic acid followed by epoxidation of the carbon-carbon double bonds. When cured with methylhexahydrophthalic anhydride (MHHPA), TEIA-based thermoset showed comparable mechanical properties to those of DGEBA-based thermoset. The polymer TEIA/MHHPA showed a T_g of 133.6°C while the polymer DGEBA/MHHPA had a T_g of 144.4°C. In addition, the tensile strengths of TEIA/MHHPA and DGEBA/MHHPA were 41.97 and 42.94 MPa, respectively. However, a great advantage of the TEIA is its lower viscosity of 0.96 Pa·s over the viscosity of DGEBA as 12 Pa·s. Therefore, TEIA offers better processability than DGEBA.

Figure 2.4: Preparation of furan-derived epoxy resins. a) Preparation of a furanic diepoxy resin. b) Preparation of a furanic monoepoxy resin. Adapted from [33].

2.1.4.3 Polyphenols and Phenols

These kinds of compounds are usually obtained from bark of trees or the shells of nuts. Two of the most studied precursors of this kind are cardanol and tannins [18]. They have been epoxidized by using the general methodology as in Figure 2.3a. Good mechanical properties and heat resistance are exhibited by the thermosets derived from cardanol and tannins because of the aromatic rings.

Syringaresinol (SYR) has been proposed as a new green alternative to replace Bisphenol A in epoxy-amine thermosets [36]. Syringaresinol was synthesized from syringaldehyde, a lignin-based compound (Figure 2.5), and did not exhibit an endocrine activity. Janvier et al. prepared the epoxy resin of SYR and cured it with two bio-based curing agents (diamine and difurfurylamine) and one petro-based curing agent (isophorone diamine, IPDA). When cured with IPDA, the SYR resin presented similar thermo-mechanical properties to the DGEBA-IPDA system. The

SYR resin- IPDA system had a T_g of 126°C and lost 5% of its mass at 298°C ($T_{d5\%}$), while the thermoset based on DGEBA showed a T_g and $T_{d5\%}$ of 150°C and 319°C, respectively.

Figure 2.5: Epoxidation of syringaresinol. Adapted from [36].

Another promising bio-based epoxy is the epoxy derived from eugenol. Eugenol is an aromatic compound that can be extracted from lignin. Wan et al. prepared an epoxy resin from eugenol following a new two-step route (Figure 2.6) [37]. DEU-EP was cured with DDM (4, 4'-methylenedianiline), and its mechanical and thermal properties were compared with DGEBA-DDM thermoset. Even though the T_g of the DEU-EP-DDM polymer was lower than that of the petro-based polymer (114.4°C vs. 153.6°C), the bio-based thermoset exhibited the highest Young's modulus (4200 MPa vs. 3490 MPa) and hardness (319.2 MPa vs. 298.6 MPa). Moreover, results from microscale combustion calorimetry showed that eugenol-based polymer had a lower flammability in comparison with the DGEBA thermoset. The bio-based system exhibited a lower total heat release (16.3 kJ/g vs. 26.6 kJ/g) and also lower heat release rate at the peak (201 W/g vs. 447 W/g) than that of DGEBA-based polymer.

Figure 2.6: Synthesis of eugenol-based epoxy resin. Adapted from [37].

A new kind of bio-based epoxy resins was developed by Qi Y. et al. [38] by incorporating an N-heterocyclic motif into the resin structure. This bio-based epoxy resin was prepared in four steps. The bio-based precursors guaiacol and succinic anhydride were firstly reacted in a Friedel-Crafts acylation and then the product underwent cyclization and dehydrogenation to obtain a new compound named as GSPZ. Finally, GSPZ was epoxidized with epichlorohydrin to obtain the bio-based epoxy resin GSPZ-EP. Using 4,4'-diaminodiphenylmethane as a curing

agent, the properties of the thermoset derived from GSPZ-EP were compared with the thermoset derived from DGEBA. It was found that GSPZ-EP-based polymer had higher glass transition temperature (187°C) and higher Young's modulus (2798 MPa) than those of DGEBA-based thermoset. In addition, GSPE-EP-based polymer showed much better flame retardancy properties than those of DGEBA-based thermoset.

Another outstanding bio-based epoxy resin (DGED) was synthesized by Dai J. et al. [39] in a straightforward methodology. The synthesis only comprised the diglycidylation of daidzein that is a compound obtained from soybeans. Various properties of the cured DGED were studied in comparison with those of the traditional DGEBA-based thermoset using 4,4'-diaminodiphenylmethane as the common curing agent. The DGED-based polymers showed a remarkable T_g of 205°C, which was much higher than that of DGEBA-based thermoset (172°C). Moreover, the tensile strength (83.0 MPa) and tensile modulus (2972.6 MPa) of the bio-based polymer were much higher than those of the petro-based polymer (73.4 MPa & 2374.8 MPa, respectively). The better mechanical properties of DGED-based polymer were ascribed to their molecular rigidity and higher crosslink density that was enhanced by the additional dimerization triggered during the curing. In addition, the cured DGED showed intrinsically better flame retardancy properties than those of DGEBA-based thermoset as shown in its higher limiting oxygen index (LOI) of 31.6% and flammability ranked as V-0 in a UL94 test.

2.1.5 The chemistry of epoxy resins

2.1.5.1 Polymer science

Polymers can be classified in two types according to their molecular structure: thermoplastics and thermosets. Thermoplastics are composed of macromolecules that interact each other through intermolecular forces [40]. Thermosets, on the other hand, consists of one macromolecule that results when individual molecules covalently linked in a way to form a molecular network [41]. In this research, thermosets will be the polymers used to prepare hydrophobic coatings.

Various synthesis methodologies have been developed to prepare polymers. Among them, free radical polymerization [42] and step-growth polymerization [43] are the most basic techniques. In the former methodology, polymerization only takes place in monomers having double bonds. The double bonds are converted into radicals that subsequently react with the double bonds of other monomers. In contrast, the latter technique refers to the chemical reactions that occurs among functional groups of the monomers, and, usually small molecules (sub product) are released during the process. This research will focus on the preparation of epoxy polymers through step-growth polymerization.

When preparing polymers, it is very important to know what the chemical characteristics the monomers should have in order to synthesize either thermoplastics or thermosets. Thus, an important concept has been developed to plan the synthesis of thermoplastics or thermosets. This concept is called 'functionality'. The functionality of a molecule is the number of atomic sites that the molecule has to form bonds with other molecules under the conditions of the reaction [44]. It is important to highlight that the functionality sometimes is different from the number of functional groups. For example, ethylene contains one double bond (one functional group) but its functionality is 2 under radical polymerization because two carbon radicals (two sites) are formed that are capable of reacting with other molecules. Glycerol, which has 3 OH groups, possesses a functionality of 3 under condensation polymerization because each OH group can react with other functional groups, for example, carboxyl groups. Therefore, in order to predict what kind of polymer, thermoplastic or thermoset, will be yielded when reacting one kind of monomer or a mixture of various monomers, the functionality of each reactant and of the whole system must be studied.

The usefulness of the concept of functionality can be illustrated for an initial mixture of two components, and each component having its own functional group. The concentration of each functional groups has to be equal. Therefore, the average functionality f_{av} of the system is defined as:

$$f_{av} = \frac{\sum N_i f_i}{\sum N_i} \quad \text{Equation 2.1}$$

where f_i is the number of functional groups of the component i present in N moles [45].

Under these conditions, a thermoplastic polymer is prepared when the $f_{av} = 2$ and a thermoset is obtained when $f_{av} > 2$. For instance, consider the reaction between N moles of adipic acid and N moles of hexamethylene diamine (Figure 2.7). The average functionality of this system is calculated as follows: $f_{av} = \frac{N*2+N*2}{N+N} = 2$. Thus, the combination of those monomers in such specific concentration will lead to the formation of a thermoplastic or linear polymer. A different f_{av} value will be obtained for the systems composed of N moles of a diepoxy, such as bisphenol F diglycidyl epoxy, and N moles of a diamine like 1,4 phenylenediamine (Figure 2.7). In this case, the functionality of the diamine is 4 because for each amine hydrogen one epoxy group can be open up. Therefore, its $f_{av} = \frac{N*2+N*4}{N+N} = 3$, corresponding to the formation of cross-linked polymer or thermoset.

Figure 2.7: Functionality concept. a) Reaction giving a linear polymer. b) Reaction giving a cross-linked polymer. Author's own drawing.

As shown in the last paragraph, the concept of functionality is simple and is based on the consideration of the number of reactive sites of each monomers and on the number of possible chemical connections of the reactive sites. Therefore, the concept of functionality can be extended to complex systems such as the ones containing more than two monomers and each monomer may have different functional groups [46], [47].

2.1.5.2 Chemical reactions of epoxy resins

For step-growth polymerization, it is crucial to know what functional groups are capable of reacting with epoxy or oxirane groups. Since epoxy groups are very reactive with electrophiles and nucleophiles [48], various chemicals can be used to

synthesize epoxy polymers. These chemicals can be 1) those containing nitrogen (such as aliphatic amines, cycloaliphatic polyamines and aromatic polyamines), 2) those containing oxygen (such as carboxylic acids, anhydrides and phenols), and 3) those containing sulphur (such as polysulphides and polymercaptans) [49]. Figure 2.8 shows the reaction of an epoxy group with other chemicals.

Figure 2.8: Reaction of oxirane groups with hydroxyl, amine and carboxyl groups. Adapted from [50].

2.1.6 Wettability concepts

The affinity or repellency properties (wettability) of a liquid on a substrate can be assessed by measuring the static contact angle (CA) of a drop of that liquid over that substrate. The contact angle is defined as the angle between the liquid-solid interface and the liquid-vapor interface (Figure 2.9a). Moreover, surfaces having a water contact angle lower than 90° are classified as hydrophilic surfaces, while surfaces exhibiting a water contact angle higher than 90° are classified as hydrophobic surfaces. Superhydrophobic surfaces are those whose water contact angle is higher than 150° [51].

According to the three traditional theories, the wettability properties of a substrate depend on the two factors: the surface chemical nature (surface energy) and surface topology (roughness). Therefore, hydrophobic or hydrophilic surfaces can be

designed by adjusting their degree of roughness and surface energy. The traditional theories that predict the contact angle of a liquid on a substrate are as follows:

a) Young-Dupre Theory. This theory assumes a smooth and homogenous surface (Figure 2.9a), and therefore, the contact angle, θ , is defined as:

$$\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad \text{Equation 2.2}$$

where γ_{SV} , γ_{SL} and γ_{LV} are the surface energy of at the interface solid-vapor, solid-liquid and liquid-vapor, respectively [52].

Figure 2.9: Models of contact angle for different substrate morphologies. **a)** Young-Dupre Model; **b)** Wenzel Model; **c)** Cassie-Baxter Model [51].

b) Wenzel Theory. This theory extends the Young's theory by considering the effect of roughness on the contact angle:

$$\cos \theta^* = R \cdot \cos \theta = R \cdot \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \quad \text{Equation 2.3}$$

where θ^* is the apparent contact angle (measured experimentally), θ is the contact angle of the corresponding flat surface, and R is the ratio between the real surface area and the projected area (flat surface) [53]. A representation of the interaction of a liquid drop and surface in the Wenzel state is shown in Figure 2.9b.

c) Cassie-Baxter theory. This theory also takes into account the roughness of the surface, but unlike the Wenzel's theory, the liquid drop is not entirely in contact with the surface, as shown in Figure 2.9c. The contact angle is defined as follows:

$$\begin{aligned} \cos \theta^* &= -1 + \phi_s [\cos \theta + 1] \\ &= -1 + \phi_s \left[\frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} + 1 \right] \end{aligned} \quad \text{Equation 2.4}$$

where ϕ_s represents the surface fraction that is in contact with the liquid drop [54]. In addition, according to this theory, air is in contact with the remaining surface area.

In summary, the Young's model states that the contact angle of a droplet on a surface depends only on the chemistry of the solid, liquid and gas phase of the system. Experimentally, for the lowest surface energy material, the maximum water contact angle achievable is about 120° for a flat surface. Thus, in order to obtain superhydrophobic surfaces, a rough surface is necessary. The Wenzel and Cassie-Baxter theories explain the effect of roughness on the wettability. In the Wenzel state, when the water droplet are in total contact with surface, the water contact angle of a hydrophobic smooth surface can be increased by increasing the roughness; whereas, the water contact angle of a hydrophilic smooth surface can be decreased by increasing the roughness [55]. In the Cassie-Baxter condition, the water contact angle of a hydrophobic smooth surface can be increased by increasing the roughness and ensuring that the surface fraction ϕ_s is as low as possible.

2.1.7 Contact angle hysteresis

Even when a surface exhibits a water CA higher than 150° , water droplets do not always roll off the surface easily. Therefore, some authors have classified the surfaces that water drop does roll away as 'sticky superhydrophobic' [56]. However, these two terms, sticky and superhydrophobic, seem to contradict each other. Based on our natural intuition, a superhydrophobic film should repel water easily, and, thus, water droplets should not be attached firmly to the film surface. For this reason, it is necessary to use another measurement (apart from the static contact angle) to help us to define the wettability properties of a superhydrophobic film. This concept is called the contact angle hysteresis (CAH), and a superhydrophobic surface has been defined as a surface having a CA higher than 150° , and having a CAH lower than 10° [57].

The hysteresis on contact angles can be explained as follows. Experimentally, it is observed that the contact angle of a drop over a substrate varies depending on the selected volume of the drop [58]. This variation of the contact angle also occurs when the measurements of a single drop are carried out at different times. In this example, the contact angles varies because the drop evaporates and its volume is continuously reduced. Therefore, for most of the materials until now known, there does not exist just one single static CA that is associated with a surface, instead, a range of CAs is observed for the majority of materials. In this range of CA, the maximum CA is called the advancing contact angle (θ_A), and the minimum CA is called the receding contact angle (θ_R). The CAH is defined as the difference between the advancing receding contact angle and the receding contact angle:

$$CAH = \theta_A - \theta_R \quad \text{Equation 2.5}$$

An illustration of the advancing and receding contact angle is shown in Figure 2.10 [59].

The CAH can be measured by following the dosing/decreasing method [60]. For the calculation of θ_A , the volume of the droplet is increased by a continuous liquid injection causing the CA to increase. The maximum CA before the three-phase contact line moves outward is recorded as the θ_A . The θ_R is measured in a similar way, but in this case the volume of the droplet is reduced by continuously sucking the liquid out by the syringe. As consequence, the CA decreases, and the minimum CA before the three-phase contact line contracts is recorded as the θ_R . Another method, called the tilted plate method, has also been designed to calculate the CAH [61]. In this technique, the surface holding a droplet is tilted gradually until it starts rolling or sliding along the surface. The CAs at the lower point and highest point of the droplet before it slides are recorded and associated with the θ_A and θ_R , respectively.

Figure 2.10: Receding and advancing angle. **a)** Receding angle. The contact angle of a water drop starts decreasing because of evaporation from 1 to 2. Nevertheless, the minimum contact angle (receding angle, θ_R) is reached at 2 from which it will be kept constant in the future evaporation processes. **b)** Advancing angle. The contact angle of a water drop starts increasing due to condensation from 5 to 6, and it achieves its maximum value at 6 (advancing angle, θ_A). In the further condensation processes, the drop will advance at a constant angle (θ_A) [59].

2.1.8 New definitions on hydrophobicity/hydrophilicity

Because almost all the materials exhibit CAH, it seems that it is not correct to report the wettability properties of the surfaces by just showing one static contact angle (or the average). Instead, the CAH should be reported since it provides more realistic information on the wettability properties. In fact, this was the argument pointed out by McCarthy and his colleagues [62]. They have introduced two terminologies of hydrophobicity/hydrophilicity, and they can be characterized by the CAH.

According to McCarthy et al., the term hydrophobicity can be used to explain two different properties. In the first case, the stickiness of a horizontal surface to hold a hanging water droplet is evaluated. In the second case, it is assessed the slipperiness of a surface to make a water droplet to roll off when the surface is

Figure 2.11: Tensile and shear hydrophobicity. Tensile and shear hydrophobicity. **a)** A surface having $\theta_A/\theta_R=60^\circ/60^\circ$ is tensile hydrophilic because its work of adhesion, based on the θ_R value, is high enough that allows it to hold a drop when it is upside down. Nevertheless, the surface is shear hydrophobic since its CAH is zero. **b)** A surface having $\theta_A/\theta_R=170^\circ/120^\circ$ is tensile hydrophobic because its work of adhesion is low so that a droplet cannot be hold on the inverted surface. However, the surface is hydrophilic in a shear mode since it possess a CAH [62].

tilted. The first term is called tensile hydrophobicity and the second is called shear hydrophobicity (Figure 2.11). The tensile hydrophobicity of a surface can be evaluated by measuring the energy necessary to detach a drop from the surface, that is, the work of adhesion. Moreover, the work of adhesion is only related with the receding contact angle according to the following equation:

$$W_{adh} = \gamma_{LV}[1 + \cos \theta_R] \quad \text{Equation 2.6}$$

Thus, surfaces having higher water θ_R can repel water droplets in a tensile mode. In contrast, water droplets will not fall from an inverted horizontal surface if the surface has a lower water θ_R . On the other hand, the shear hydrophobicity is quantified by the CAH since detaching and attaching processes occur in a rolling

or sliding water droplet. The droplet starts rolling off the surface at a minimum angle of tilt (α) and it is related to the CAH as stated in following equation:

$$mg \sin \alpha / w = \gamma_{LV} [\cos \theta_R - \cos \theta_A] \quad \text{Equation 2.7}$$

where m is the mass of the droplet with a width w (the width is measured perpendicular to the direction of the water drop displacement), and g is the gravitational constant [63]. Therefore, a surface with a low CAH will exhibit a low angle of tilt.

In summary, according to McCarthy et al., CAH should be reported along with the contact angle measurements for wettability characterization because it provides vital information about the stickiness and slipperiness of a surface.

2.1.9 Non-bio based Superhydrophobic and hydrophobic epoxy films

Epoxy films having superhydrophobic and hydrophobic properties have been synthesized based on two basic methods: a) modifying the chemical composition and structure of the epoxy resins and/or the curing agent, and, b) modifying the surface and/or the bulk of the film by using additives. The first method can be referred as "intrinsic" modification, whereas the second method can be named as "extrinsic" modification. Of course, both methods can be applied simultaneously to produce superhydrophobic coatings.

2.1.9.1 Intrinsic hydrophobic epoxy films

Usually, intrinsic hydrophobic epoxy polymers are created by attaching chemically hydrophobic units to the polymeric network. These hydrophobic units, having low surface energy, are commonly fluorinated carbon chains and saturated aliphatic chains. For example, Liu Z. et al. [64] modified the phenylhydroquinone epoxy (PQE) resin by attaching a trifluoromethyl side chain. This (3-trifluoromethyl)-PQE was then cured with four different types of curing agents: poly (propylene glycol) bis (2-aminopropyl) ether (D230), 2-methylimidazole (2MI), 4, 4'-methylene-dianiline (DDM) and phthalic acid anhydride (PA) (Figure 2.12). The water contact angles were 95.9°, 96.7°, 98.0° and 105.5° for the epoxy resin cured

with 2MI, D230, DDM and PA, respectively. Therefore, the authors synthesized intrinsic hydrophobic epoxy polymers by the insertion of trifluoromethyl group.

Figure 2.12. Fluoro-based epoxy resin and curing agents (D230, 2MI, DDM & PA) employed in [64].

A similar approach to prepare hydrophobic epoxy polymers was also carried out by Yan Z. et al. [65]. In this case, the objective was to modify the structure of diglycidyl ether of bisphenol A (DGEBA) with poly(2,2,3,4,4,4-hexafluorobutyl acrylate) (CTHFA). Nevertheless, instead of attaching the CTHFA to DGEBA directly, they used a molecular spacer to expose the hydrophobic groups to the surface. The spacers used were two different poly(dimethyl siloxane) (PDMS) ($M_n = 2000$ and 4000). In this case, CTHFA-PDMS compound was first synthesized, and then, it was functionalized with isocyanate groups (NCO), yielding CTHFA-PDMS-NCO. Finally, the CTHFA-PDMS-NCO can be attached to DGEBA through the reaction between the isocyanate groups and the hydroxyl groups of DGEBA (Figure 2.13). The DGEBA was modified with CTHFA-PDMS-NCO in concentrations ranging from 0.0 to 0.5% w/w. The highest water contact angles were 110° and 120° for a low concentration (0.2% w/w).

Figure 2.13. Epoxy resin (CTHFA-PDMS graft DGEBA) prepared in [65].

2.1.9.2 Extrinsic hydrophobic epoxy films

In these kinds of systems, the epoxy network is hydrophilic but it becomes hydrophobic after the insertion of hydrophobic additives that are not chemically bonded to the epoxy network.

Si, Guo and Liu reported the fabrication of a superhydrophobic coatings from hydrophilic epoxy resins [66]. In this case, the authors did not modify the molecular structure of neither the BA epoxy resin nor the curing agent to obtain the superhydrophobic coatings. Rather, the superhydrophobicity came from the $\text{Mg}(\text{OH})_2$ micronanosheet powder that were functionalized with stearic acid. The coatings were prepared firstly by coating the epoxy resin with its curing agent on the substrate, followed by the addition of the functionalized $\text{Mg}(\text{OH})_2$ powder onto the surface. The coatings were allowed to age for 24 hours. The coatings were applied in four different substrates (cloth, typing paper, sponge and copper mesh), and in all the cases they were superhydrophobic with water contact angles higher than 150°C .

A similar approach to fabricate superhydrophobic coatings was performed by Xiu et al. [67]. In the synthesis, they mixed the BA epoxy resin with the curing agent and silica nanoparticles. Once the film was formed, the surface of the coating was

etched by O₂ plasma treatment so that the surface of the silica nanoparticles can be exposed without epoxy polymer. This was carried out to create roughness in the surface of the coating. The final step was the hydrophobization of the silica nanoparticles by a treatment with perfluorooctyl trichlorosilane. They pointed out that the superhydrophobicity was affected by the O₂ plasma treatment time, a longer treatment time would lead to a higher water contact angle and lower CAH.

2.1.10 Bio-based superhydrophobic and hydrophobic epoxy films

As shown below, few reports of bio-based hydrophobic epoxy films are found in the literature, and most of them do not focus on the surface properties.

Xiong et al. [68] used bio-epoxy resins as modifiers to transform the wettability of starch from hydrophilic to hydrophobic. The purpose of the research was to prepare composites of the hydrophobic polylactide with starch as the filler with good interfacial adhesion. Epoxies derived from itaconic acid (EIA) and cardanol (Epicard) were used as modifiers to make the surface of starch hydrophobic (Figure 2.14). They found that the neat starch was hydrophilic with water contact angle of 37°, but when it was modified with EIA and Epicard, the water contact angles increased to 110° and 95°, respectively.

Figure 2.14. Starch modified with two bio-based epoxy resins as reported in [68].

Figure 2.15: Hydrophobic bio-based thermoset. **a)** *Ortho* methylation as a strategy used to reduce hydrogen bonding of the polar groups[69]. **b)** Chemicals used for the preparation of polymers in ref.: [69] **1**: diglycidyl ether of bisphenol A (DGEBA), **2**: 4,4'-methylenedianiline (MDA), **3**: bio-epoxy resin from carvacrol, **4**: bio curing agent from *p*-cymene.

Kocaman and Ahmetli studied the influence of various hardeners on the properties of thermosets prepared from blends of Bisphenol F-type epoxy resin and acrylated epoxidized soybean oil (AESO) [70]. Water sorption and water contact angle measurements were carried out to study the hydrophobicity of the polymers. The authors found that the addition of AESO increased the water sorption of the neat Bisphenol F-based thermosets (0.172% when cured with Epamine PC 17, a cycloaliphatic polyamine). It was argued that the increment in the water sorption is caused by the polar groups of the AESO, such as its hydroxyl groups. Despite the water sorption, AESO-modified coatings exhibited hydrophobic properties. AESO-modified coatings cured with MNA (methyl nadic anhydride), SA (succinic anhydride), PhA (Phtalic anhydride), Epamine PC 17 and MXDA (m-Xylenediamine) displayed water contact angles of 133.20°, 108.50°, 101.08°, 97.80° and 91.70°, respectively. In addition, these hydrophobic films exhibited water sorption values ranging from 0.62% to 1.55%. The authors pointed out that

the water sorption properties of polymers modified with AESO depend on the polarity of the hardeners, the degree of curing and the density of the network. In relation with the last two factors, it was confirmed that the water sorption decreases when the degree of curing and the density of the network increase.

Another report is about the preparation of bio-thermosets in which a terpenoid-based epoxy resin and amine curing agent were prepared from carvacrol and *p*-cymene, respectively[69]. The strategy to prepare hydrophobic polymers was based on blocking the access of water to the polar groups of the benzene rings of the epoxy resin and amine-curing agent (Figure 2.15). In this strategy, water was blocked by methyl groups attached in the *ortho* position in relation to the polar group. The authors prepared four types of thermosets from the combination of chemicals **1** and **2**, **1** and **4**, **2** and **3**, and **3** and **4**. The hydrophobic properties of the polymers were studied only from the results of the water uptake measurements. Their results showed that the fully bio-based polymer synthesized from chemicals **3** and **4** was the most hydrophobic, and the polymer from **1** and **2** was the least hydrophobic. The enhancement in the hydrophobicity in the polymer from **3** and **4** was achieved by restricting the hydrogen bonding of the oxygen (in the epoxy resin) and the nitrogen (in the curing agent) caused by the *ortho* methyl group. In addition, the *ortho* methyl group has a major effect on improving the hydrophobicity when it is attached to the bio epoxy resin than when it is attached to the amine-curing agent. This last result indicated that the bio-epoxy resin is the component that interacts more actively with water than the curing agent.

Jiang et al. reported the preparation of a bio-based thermoset derived from a bio-based epoxy resin (BEF) and a bio-based curing agent (VBZMI) (Figure 2.16) [71]. The epoxy resin and the curing agent were synthesized from eugenol and vanillin, respectively. The hydrophobic properties of the bio-based polymers were compared with those obtained from the petro-based resin (Bisphenol F-based resin, BPF) and the commercial curing agent benzimidazol (BZMI). They found that the bio-based thermoset (BEF-VBZMI) had a higher water contact angle (94°) than that of the traditional formulation (BPF-BZMI) (75°). The better hydrophobicity of the BEF was ascribed to its allyl and methoxy groups, whereas VBZMI showed better hydrophobicity than BZMI due to its additional aromatic rings.

Figure 2.16. Epoxy resin (BFE) and curing agent (VBZMI) employed in [71].

Isosorbide-based epoxy resins have been recently applied in the preparation of hydrophobic and superhydrophobic coatings for anti-corrosion and anti-icing applications. Hydrophobic coatings from isosorbide epoxy resins were prepared by using a hydrophobic curing agent. Isosorbide-based superhydrophobic coatings were achieved by the introduction of the SiO₂ nanoparticles into the hydrophobic coatings. The anti-corrosion performance of the isosorbide-based films were assessed [72, 73]. The authors found that hydrophilic isosorbide coatings were more vulnerable to corrosion than the hydrophobic isosorbide coatings. Moreover, it was proven that superhydrophobic coatings had better corrosion inhibition performance than that of the hydrophobic films. The better anti-corrosion performance of the isosorbide-based superhydrophobic coatings was attributed to the low contact area between the corrosive solution and the coating surface caused by the entrapped air into the cavities of the rough surface. The anti-icing properties (icing temperature, icing delay time and ice adhesion strength) of isosorbide-based coatings were also investigated [74]. The bio-based coatings with hydrophilic properties exhibited higher affinity to the ice formation than that of the hydrophobic and superhydrophobic films. In addition, isosorbide-based superhydrophobic coatings exhibited better anti-icing performance than that of the hydrophobic films because of the lower contact area between the coating surface and water.

The design of isosorbide-based thermosets with low water uptake properties has also been discussed. Feng et al. [75] reported the preparation of two kinds of isosorbide-based epoxy resins: one exhibiting great affinity for water (water uptake

ratios up to 50wt %) and the other with much reduced affinity for water (water uptake ratios as low as 1.28wt %) (Figure 2.17). The authors reported that, by modifying the hydrophilic isosorbide backbone with hydrophobic aromatic groups, isosorbide-based resins with low percentages of water uptake can be achieved. In addition, when the compounds **b**) and **c**) (Figure 2.17) were cured with the curing agent methyl-5norbonene-2,3-dicarboxylic anhydride (NMA), the T_g values of the thermosets were 119 and 136.38°C, respectively. However, the T_g of the polymer based on **b**) was not stable due its high affinity to water.

Figure 2.17. Isosorbide epoxy resins prepared on [75]. Resins a) and b) absorbs great amounts of water while compound c) has the lest water uptake ratios.

Recently, a new bio-based epoxy resin was synthesized by sebacic acid and epichlorohydrin [76]. The aim of the research was to fabricate composites by using hazelnut shell waste as fillers. The neat epoxy thermoset, obtained from the reaction of the bio-based resin and m-xylenediamine, showed a water contact angle of 84°. Nevertheless, the incorporation of the different bio-based fillers in 50 % w/w enhanced the hydrophobicity of the polymer as shown in their higher water contact angles (96.8-108.5°).

Coatings for corrosion protection have also been prepared from the cashew nutshell liquid (CNSL), a byproduct of the cashew nutshell industry [77]. CNSL was directly transformed into an epoxy resin (e-CNSL) by using performic acid without solvent. The bio-based resin e-CNSL was cured with three different amines: an aliphatic (diethylenetriamine, DETA), a cycloaliphatic (isophorone diamine, IPDA) and an aromatic curing agent (p-phenylenediamine, PFDA). The

results showed that the water contact angles of the coatings were higher when e-CNSL was cured with PFDA (87.6°) and IPDA (76.9°) than with DETA (72.7°). In terms of anti-corrosion properties, e-CNSL/PFDA had the highest coating resistance ($1.0 \times 10^{12} \Omega \cdot \text{cm}^2$) in comparison with those of e-CNSL/IPDA ($4.1 \times 10^{10} \Omega \cdot \text{cm}^2$) and e-CNSL/DETA ($1.1 \times 10^{11} \Omega \cdot \text{cm}^2$). Although the coating resistances of the bio-based formulae were lower than that of the petro-based formulation DGEBA/IPDA ($6.2 \times 10^{12} \Omega \cdot \text{cm}^2$), the CNSL-based coatings still showed good anti-corrosion performances suitable for real applications.

2.2 Questions to answer based on literatures

So far, researchers know how to prepare hydrophobic and superhydrophobic films. The strategy that they have used to prepare hydrophobic coatings is to use low surface-energy materials. When superhydrophobic coatings are desired, researchers either modify an appropriate rough surface with hydrophobic compounds or make rough a flat hydrophobic surface. Nevertheless, these principles for designing superhydrophobic/hydrophobic coatings have been primarily applied on polymers derived from petroleum resources. In contrast, little research has been done on the preparation of hydrophobic and superhydrophobic coatings whose composition is based on bio-based precursors. As this research focuses on hydrophobic coatings, the outstanding questions to be answered are: can hydrophobic coatings be prepared from biomass epoxy resins that can exhibit a comparable performance as their petro-based counterparts? Moreover, can bio-based epoxy resins be used to prepare hydrophobic films for anti-corrosion and anti-icing applications?

2.3 Research in this PhD thesis in context of the literatures

Current publications on new bio-based epoxy generally have reported some traditional bulk properties of polymers but paid little or no attention to the surface properties such as hydrophobicity as discussed above. Furthermore, the study of the performance of bio-based epoxy coatings as anti-icing and anti-corrosion coatings has been rarely explored. Thus, this PhD research is proposed with the aim of filling up the scientific gaps on the preparation and understanding of bio-

based epoxy coatings with hydrophobic properties for anti-corrosion and anti-icing applications.

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Chapter 3

Experimental Methodology

This chapter provides the general methodology adopted to prepare bio-based epoxy resins with hydrophobic properties. This chapter also presents the main techniques used to study the various properties of coatings. Finally, a summary is presented of the identified strengths and limitations of the methodology chosen.

3.1 Rationale for Selection of Methods and Materials

The novelty of this PhD research relies on the development of new hydrophobic bio-based epoxy coating formulae for anticorrosion and anti-icing applications. The selection of both bio-based chemicals and hydrophobizers should be carefully considered. Since biomass offers a large number of bio-based compounds from which bio-based epoxy resins can be prepared, a judicious selection must be exercised. As such, this research has been restricted to the use of three representative bio-based epoxy resins from three different bio-based sources. Polysaccharide, cardanol and plant oil were the bio-based sources selected in this study. This selection of bio-based sources ensures that epoxy resins with distinct molecular structure can be studied and their individual advantages and disadvantages can be identified. Moreover, in the development of the epoxy formulae, the bio-based content of the polymers was gradually increased from the polysaccharide to the plant oil-based epoxy resin. Simultaneously, three different hydrophobizers were employed in the development epoxy resin formulae ranging from fluorinated compounds to bio-based chemicals.

Thermal curing has been employed for the preparation of all the bio-based epoxy coatings. The use of a conventional oven for the curing of the coatings is advantageous because it is easy to be performed and a low-cost process. In addition, all the bio-based formulae were elaborated in liquid state as it enables the use of industrial techniques (such as spin coating, dip coating and bar coating depositions) in the preparation of the polymer films.

3.2 Synthesis

The synthesis of the bio-based epoxy coatings were done by preparing a liquid mixture containing the bio-based epoxy resin, curing agent and hydrophobizer. The coatings were prepared in a metal substrate for corrosion and ice adhesion characterizations, and on glass substrates or Teflon molds for the rest of characterization techniques.

3.3 Characterization

The following sections describe the theory behind the use of the main characterization techniques employed in this research.

3.3.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a technique that permits the measurement of the mass changes that a substance undergoes when it is being heated or cooled. These mass changes may be caused by physical or chemical processes.

Figure 3.1: Typical thermobalance. a) Main components of the thermobalance. b) Arrangements of thermocouple and sample holder: (1) top-loading, (2) side-loading and (3) bottom loading [1].

The main component of the any TGA equipment is the thermobalance. The thermobalance refers to the system of the balance and furnace working together (Figure 3.1a). The balance has to be protected from the heat flow of the furnace and from the emission of chemicals originated from the sample. For this reason, the balance is enclosed in a container and it is purged by an inert gas. Depending on the design, the furnace, in which the sample is placed, can be positioned above, below or beside the balance. In addition, since the heat supply of the furnace is generated through heating coils, magnetic samples should not be used for TGA since their magnetic field can interact with the magnetic field of the heating coil, causing false mass changes [1-3].

The atmosphere of the furnace is also controlled. The atmosphere can made of an inert gas flow that is injected into the furnace to remove the evolved gases from the samples, or it may be reactive gas. It is also very important to consider the effect of the density variation of the gas inside the furnace during the mass measurements. Because the density of the gases decrease as the temperature increases, the sample can experience a buoyancy force. This phenomenon makes the sample gain weight and, therefore, the measured mass of the sample increases during heating. Therefore, buoyancy corrections must be done before testing and has to consider the following equation that relates the gas density (ρ) as function of the temperature (T), at constant pressure:

$$\rho = \rho_0 \frac{T_0}{T} \quad \text{Equation 3.1}$$

where ρ_0 and T_0 are the reference density and temperature of the gas, respectively, at 25°C. However, some instruments have included a standard buoyancy correction that is automatically included into measurements [4].

The measurement of the sample is performed by a thermocouple. As shown in Figure 3.1b, the thermocouple can be placed in different positions. It can be set below the sample holder but not touching it (1), it can be set inside the sample holder and even touching the sample (2), and it can be set below the holder and touching it (3). Thus, the configuration (2) is the most desirable since the temperature measurement is highly accurate [2, 3].

The TGA of the samples were performed in a TGA Q500 (TA Instruments). Samples weighting around 13-16g were loaded in an alumina crucible that was supported on a platinum pan. The samples were heated from room temperature to 600°C at 10°C/min under nitrogen flow (60.0 mL/min). At least three samples of each composition were measured and the data was analyzed by using the software TA Universal Analysis.

3.3.2 Differential scanning calorimetry

The differential scanning calorimetry (DSC) is a technique that measures the energy changes when a substance is being heated or cooled. Moreover, the main characteristic of this technique is that it is a differential measurement. That means that it measures the energy changes of two substances and the difference between those measurements are calculated as the final result.

Figure 3.2: Types of DSC. a) Heat flux DSC and b) Power compensation DSC [5].

Two basic types of DSC can perform this task: heat flux DSC and power compensation DSC (Figure 3.2). The heat flux DSC consists of a unique furnace in which the two substances (sample and reference) are placed. In addition, two thermocouples are set near the sample and reference position. When the oven is allowed to heat at certain rate, the temperatures of the sample and reference are measured. If during the heating (or cooling), the sample and reference do not experience any physical or chemical change, the temperature of both is the same and the thermocouple voltage is zero. However, if a change occurs during the heating, the temperature of the sample will be different from the reference, and, therefore, the thermocouple voltage is no more zero [3, 6].

The power compensation DSC, on the other hand, is designed in a way that the sample and reference are placed in different microfurnaces. In this configuration, the sample and the reference are maintained at the same temperature as that of the preset heating rate. In

addition, when any change in the sample arises, causing a temperature difference, the microfurnace provides (or withdraw) heating power if a loss energy (or gain energy) has happened [3, 6].

Figure 3.3. Heat flux DSC. a) Simplified heat flux DSC, and its b) equivalent electric circuit [6].

As shown, the temperatures of the sample and the reference are the only data that are measured by the DSC equipment during the test. Therefore, it is necessary to develop a model to relate that heat flow of the sample (the data that users seek) with the temperature of the sample and the reference. In Figure 3.3b, a simplified equivalent electric circuit of a heat flux DSC is shown [6]. This electric is converted into a thermal circuit by changing the current and voltage for the heat flow and temperature, respectively. A mathematical model has been deduced from that thermal circuit by considering the following assumptions:

- Constant heat flow rates with the exception of the heat flow from the sample (caused by a reaction, melting, etc.).
- The heat capacities of the sample (C_S) and reference (C_R) are considered only.
- The thermal resistance between the furnace and sample (R_{FS}) is equal to the thermal resistance between the furnace and reference (R_{FR}). No resistance exists between the sample and reference.

The circuit on Figure 3.3b shows that there are a heat flow from the furnace to the sample (ϕ_{FS}) and a heat flow from the furnace to the reference (ϕ_{FR}), and those heat flows are due when the furnace is heating initially. If, during the furnace heating the sample experiences an exothermic reaction, a new heat flow will come out of the sample (ϕ_r). So, the equation that shows the balance of the heat flow through the sample is:

$$C_S \frac{dT_S}{dt} = \phi_{FS} - \phi_r$$

By using the definition that $\Delta T = T_S - T_R$, a new equation results:

$$C_S \frac{dT_R}{dt} + C_S \frac{d\Delta T}{dt} = \phi_{FS} - \phi_r$$

On the reference, the heat flow balance is:

$$C_R \frac{dT_R}{dt} = \phi_{FR},$$

since no reaction (or other process) is happening.

When ϕ_{FR} is subtracted from ϕ_{FS} , the following expression results:

$$\phi_{FS} - \phi_{FR} = (C_S - C_R) \frac{dT_R}{dt} + C_S \frac{d\Delta T}{dt} + \phi_r$$

In addition, the heat flows of the sample and reference from the furnace are:

$$\phi_{FS} = \frac{T_F - T_S}{R_{FS}} \text{ and } \phi_{FR} = \frac{T_F - T_R}{R_{FR}}$$

But, as stated before, $R_{FS} = R_{FR} = R$, and, therefore,

$$\phi_r = -\frac{\Delta T}{R} - (C_S - C_R) \frac{dT_R}{dt} - C_S \frac{d\Delta T}{dt} \quad \text{Equation 3.2}$$

The DSC of the thermosets was carried out in (heat flux) DSC Q10 (TA Instruments). The measurements were carried out in standard aluminum pans in which the samples weighted around 13-17g. Under nitrogen flow (50 mL/min), the pans were heated from -50°C to 200°C at 10°C/min. This heating process was done three times and the data of the third process was used for analysis by using the software TA Universal Analysis. For statistical considerations, at least three samples of each composition were measured.

3.3.3 Fourier-Transform Infrared Spectroscopy

Spectroscopy is a technique for the identification of compounds based on their interaction with electromagnetic radiation. In spectroscopy, it is necessary to take into account the different energy contributions to the total energy of any molecule:

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translational} \quad \text{Equation 3.3}$$

The electronic energy refers to the energy of the electrons around nuclei, while the vibrational energy corresponds to the atoms vibrations. The electronic and vibrational energies can be perturbed when ultraviolet-visible (UV-VIS) and infrared (IR) energy interact with the molecule, respectively. Rotational energy is related to the rotation of the molecule around a specific axis and this energy falls into the microwave region. The translational energy of a molecule is associated with its displacement and is dependent on its temperature [7].

Therefore, IR spectroscopy is the technique that aims for the identification of functional groups by studying their absorbance in the IR region. This IR absorbance can only be possible if the molecular groups experience a net change in their dipole moment when they vibrate. The vibration, for example, of a diatomic molecule can be described as a quantum harmonic oscillator, and, thus, its energy associated is:

$$E_i = \left(v_i + \frac{1}{2} \right) h\nu ; v_i = 0, 1, 2 \dots \quad \text{Equation 3.4}$$

where ν is the vibrational frequency of the bond, and v_i is the quantum number that can take only integer numbers [8, 9].

Figure 3.4: Schematic of FTIR in ATR mode. In this illustration, the refractive index (n) of the specimen has been assigned as 1.46 [10].

Apart from the traditional transmission mode of Fourier-transform infrared spectroscopy (FTIR), FTIR can be used in a different mode: attenuated total reflectance (ATR) mode (Figure 3.4). Under this configuration, the IR beam is internally reflected in a crystal that does not absorb a great portion of the IR region. This condition of the IR beam creates evanescent waves going out the ATR crystal perpendicular to the interface. Approximately, the penetration depth of the evanescent waves can be less than one micron up to 10 microns. The IR evanescent waves can be used to interact with a sample if the sample is placed on the top of the ATR crystal. Therefore, if the sample being studied absorbs IR energy, the intensity of the IR beam under total reflectance will be attenuated [11].

The samples were studied in a FTIR MIR/NIR Frontier (Perkin Elmer) in the ATR mode. The analyses were carried out within a wavelength range from 4000-600 cm^{-1} , with 32 scan accumulations and 4 cm^{-1} resolution.

3.3.4 Contact angle and surface energy measurements

Two basic techniques exist to measure the contact angles of films: the sessile drop method and the Wilhelmy plate [12]. The sessile drop method, in which a goniometer is used to calculate the CA, has been employed in this research (Figure 3.5). In this methodology, a

Figure 3.5: Basic elements in a goniometer for measuring CA [10].

droplet is placed on the sample that is horizontally aligned in front of a camera. The drop shape is recorded by the camera and then it is processed by a software that measures the contact angle. When taking the photo of droplet, illumination on the droplet is important since the software recognizes the drop shape based on the grey scale of the photo.

Apart from the contact angle measurements, the surface energy of solids is another parameter that helps in the characterization of solid surfaces. One of the methodologies to

calculate the surface energy of solids is the OWRK method developed by Owens, Wendt, Rabel and Kaelble [13-15]. What follows is a description of that method.

Thermodynamically speaking, the surface free energy change, ΔG_{ab} , when two surfaces of different composition (a and b) are brought into contact, is calculated as:

$$\Delta G_{ab} = \gamma_{ab} - \gamma_a - \gamma_b$$

where γ_a and γ_b are the surface energy of the material a and b , respectively, and γ_{ab} is the interfacial energy between a and b . The opposite energy to separate the two materials, called work of adhesion (W_{ab}), is therefore, defined as:

$$W_{ab} = \gamma_a + \gamma_b - \gamma_{ab}$$

When dealing with solids and liquids in air (as in the wettability of solids), the above equation becomes:

$$W_{SL} = \gamma_S + \gamma_L - \gamma_{SL} \quad \textbf{Equation 3.5}$$

where the subscripts S and L stand for solid and liquid, respectively. In order to find a relationship between the work of adhesion and the measurable contact angles, Equation 3.5 has been combined with the Young-Drupe equation, $\cos\theta = \frac{\gamma_{SV}-\gamma_{SL}}{\gamma_{LV}} = \frac{\gamma_S-\gamma_{SL}}{\gamma_L}$ (Equation 2.2), to obtain the following equation:

$$W_{SL} = \gamma_L(\cos\theta + 1) \quad \textbf{Equation 3.6}$$

In the OWRK method, two assumptions are made [10, 16]. The first assumption is that the work of adhesion of the solid and the liquid is equals to the geometric mean of the surface energy of the liquid and solid:

$$W_{SL} = 2(\gamma_S\gamma_L)^{1/2} \quad \textbf{Equation 3.7}$$

Thus, combining Equation 3.7 and Equation 3.5, the following relation is obtained:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2(\gamma_S \gamma_L)^{1/2}$$

The above equation is further developed with the second assumption, which states that the surface energy comes from the contribution of polar (p) and dispersion (d) interactions of the surface, that is, $\gamma_i = \gamma_i^p + \gamma_i^d$. The dispersion interactions refer to the London forces, whereas the polar interactions include hydrogen-bonding, acid-basic interactions, among others. Therefore, a new equation can be written as:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2 \left((\gamma_S^d \gamma_L^d)^{1/2} + (\gamma_S^p \gamma_L^p)^{1/2} \right) \quad \text{Equation 3.8}$$

When Equation 3.8 is combined with the Young-Drupe equation (Equation 2.2), it is obtained:

$$\gamma_L (\cos \theta + 1) = 2 \left((\gamma_S^d \gamma_L^d)^{1/2} + (\gamma_S^p \gamma_L^p)^{1/2} \right)$$

Rearranging this equation in a linear form $y = ax + b$, it becomes:

$$\frac{\gamma_L (\cos \theta + 1)}{2(\gamma_L^d)^{1/2}} = (\gamma_S^p)^{1/2} \left(\frac{\gamma_L^p}{\gamma_L^d} \right)^{1/2} + (\gamma_S^d)^{1/2} \quad \text{Equation 3.9}$$

Equation 3.9 can be solved for γ_S (γ_S^p , γ_S^d) if at least two liquids with known polar and dispersion surface energies are used when measuring the contact angles. Nevertheless, Equation 3.9 can be solved with more accuracy by a linear regression if at least three different liquids are used.

The wettability properties of the polymers were studied by measuring their static contact angles in OCA 20 goniometer (Dataphysics). The CAH of the samples was not measured since it was found that the surfaces of the samples were sticky (high CAH). For the surface energy determination, at least three measurements for each sample were done by using 5 μ L of DI water, ethylene glycol and n-hexane. The surface energy analysis was done following

the OWRK method [13-15]. All the measurements were performed at 25°C and the data was analyzed by using the software SCA 20 (Dataphysics).

3.3.5 Dynamic Mechanical Analysis

Ideal elastic materials are characterized by their ability to deform instantaneously to the application of a stress. When the applied stress is released, the material recovers its original condition. The behavior of elastic materials is expressed mathematically by the Hooke's law:

$$\tau = G * \gamma \quad \text{Equation 3.10}$$

where τ , G and γ are the shear stress, shear modulus and shear strain, respectively.

On the other hand, ideal viscous materials are also deformable during the application of a stress. However, the material does not recovery its original condition once the stress has been released. These materials behave according to the Newton's law:

$$\tau = \eta \frac{d\gamma}{dt} \quad \text{Equation 3.11}$$

where η and $d\gamma/dt$ are the viscosity and strain rate [17].

Viscoelastic materials are the ones that have both viscous (liquid-like) and elastic (solid-like) characteristics. In order to quantify the viscous and elastic nature of materials, dynamic mechanical analyses (DMA) are performed. In a typical DMA test, the material is subjected to a sinusoidal stress and the resulting strain is measured. The sinusoidal stress applied must be within the range of stresses that permits only the elastic behavior of the material. If this condition is met, the resulting strain is also a sinusoidal wave with phase angle (Figure 3.6). Therefore, DMA tests are performed within linear viscoelastic region of the material[18].

Figure 3.6: Sinusoidal waves of the applied stress and material response [18].

A sinusoidal tensile stress $\sigma(t)$ applied to a material can be expressed as:

$$\sigma(t) = \sigma_0 \sin \omega t$$

where ω and σ_0 are the frequency and the maximum stress, respectively. Similarly, the resulted sinusoidal strain $\varepsilon(t)$ has the expression:

$$\varepsilon(t) = \varepsilon_0 \sin(\omega t + \delta)$$

where ε_0 and δ are the maximum strain and phase angle, respectively. For a pure elastic material $\delta = 0^\circ$ and $\varepsilon(t)$ is in phase with $\sigma(t)$. For a pure viscous material $\delta = 90^\circ$ and $\varepsilon(t)$ is out of phase with $\sigma(t)$ by 90° . A viscoelastic material exhibits a phase angle between those values ($0^\circ < \delta < 90^\circ$), showing that it has an elastic component and a viscous component [19].

Based on trigonometry, the strain function can also be written as sum of two periodical functions as:

$$\varepsilon(t) = \varepsilon_0 [\sin(\omega t) \cos \delta + \cos(\omega t) \sin \delta]$$

where one function ($\varepsilon_0 \cos(\omega t) \sin \delta$) is in phase with $\sigma(t)$ and the other one ($\varepsilon_0 \sin(\omega t) \cos \delta$) is out of phase with $\sigma(t)$ by 90° . Since $\varepsilon(t)$ can be expressed in terms of the sum of a cosine and a sine function, it can also adopt a complex notation as:

$$\varepsilon^* = \varepsilon' + i\varepsilon''$$

where

$$\varepsilon' = \varepsilon_0 \cos \delta$$

$$\varepsilon'' = \varepsilon_0 \sin \delta$$

Under a similar treatment, the Young's modulus ($E^* = \sigma^*/\varepsilon^*$) can be expressed in a complex number notation as:

$$E^* = E' + iE'' \quad \text{Equation 3.12}$$

where

$$E' = (\sigma_0/\varepsilon_0)\cos \delta \quad \text{Equation 3.13}$$

$$E'' = (\sigma_0/\varepsilon_0)\sin \delta \quad \text{Equation 3.14}$$

Here, E' is called the elastic or storage modulus and E'' is called the viscous or loss modulus. E' and E'' provide information on the ability of the material to store energy and dissipate energy, respectively [18]. Moreover, the damping properties of the material can be quantified by:

$$\tan \delta = \frac{E''}{E'} \quad \text{Equation 3.15}$$

3.4 Strengths and Limitations of Methodological Approach

There are several advantages of the chosen liquid-based coating formulations. First, this is a liquid-based dispersion that is suitable for a variety of coatings deposition techniques such as spin, dip and spray-coating. Liquid-based coating technology has a clear advantage in comparison with other formulations like those in which the precursors need to be melted before they are coated. Second, the process to produce the ultimate bio-based coatings is much environmentally friendlier than the conventional procedures to prepare hydrophobic coatings because in this research organic solvents are not used in the final coating formulations. Third, this is a facile route from the preparation of the epoxy resin until the preparation of the coating. That is, making the hydrophobic bio-based coatings requires only mixing the respective liquid components and curing them on a regular oven.

However, some limitations of the methodology used have been identified. One limitation is the use of thermal curing at temperatures higher than 100°C. This characteristic is not desired in the market where most regular coatings are characterized by their ability to cure at room temperature once the components are mixed. As the focus of this research is on the utilization of bio-based epoxies and their applications, this research does not involve the development of catalysts for room temperature curing. Another limitation is that the developed coatings in this research do not include the use of functional additives. That is, the development of these new epoxy coatings has been restricted to the use of three main components: epoxy resins, curing agents and hydrophobizers. Regular coatings usually include various additives to improve their properties such as additives for better adhesion, thermal stability or light stability. Investigation on the development of new bio-based additives is beyond the time frame of this PhD research.

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Chapter 4

Isosorbide-based coatings^{*}

This chapter shows the results on the preparation and characterization of hydrophobic and bio-based films from isosorbide. A detailed discussion on the wettability, thermal and mechanical properties of the new water-repellent and bio-based samples is presented. The anti-corrosion properties of the isosorbide-based coatings were also assessed.

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4.1 Introduction

As discussed in previous chapters, 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. As highlighted in previous chapters, 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 bio-based 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. As discussed before, superhydrophobic coatings have $WCA > 150^\circ$ and $CAH < 10^\circ$, 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. As discussed in Chapter 2, 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 bio-based 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 preparation of 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.

4.2 Experimental Methods

4.2.1 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.

4.2.2 Synthesis of isosorbide-based resin

Isosorbide epoxy resin was prepared in a similar way as reported elsewhere (Figure 4.1) [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.

Figure 4.1. Synthesis of isosorbide resin. Adapted from [28].

4.2.3 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).

4.2.4 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.

Corrosion tests were performed in a three-electrode electrochemical cell connected with a regular potentiostat. The working, counter and reference electrodes were the coating, platinum and Ag/AgCl, respectively. The corrosion protection of coatings with thicknesses around 200 μm was evaluated in a $\text{NaCl}_{(\text{aq})}$ 3.5% w/w.

4.3 Results

4.3.1 Characterization of the precursors

The successful preparation of an epoxy resin from isosorbide was confirmed by FTIR (Figure 4.2). 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 4.3) and ^{13}C NMR (Figure 4.4).

Figure 4.2. FTIR spectra of isosorbide and its derivatives.

Figure 4.3. ^1H -NMR spectrum of isosorbide resin. . The assignation of the peaks was done based on the previous analysis performed elsewhere[28]. In addition, the peak of DMSO may have overlapped with the peaks of H1.

Figure 4.4. ^{13}C -NMR spectrum of isosorbide resin. The spectrum showed the same characteristics peaks as those found in the report of Chrysanthos et al.[28] Moreover, the confirmation of the

oligomer nature of isosorbide resin was proven by the Cr peak that corresponded to the hydroxyl carbon of the 2-propanol segment that links two isosorbide units

On the other hand, isosorbide resin was able to cure without the participation of any curing agent. Figure 4.2 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 4.5) [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.

Figure 4.5. Homo-polymerization of the isosorbide resin. **a)** Two linear isosorbide oligomers linked together thorough the reaction of a free hydroxyl group and epoxy group. **b)** The new polymer can continue growing by reacting with other epoxy oligomers.

The hydrophobic curing agent, F8815, was also examined by FTIR (Figure 4.6). The results confirm that F8815 possesses three functional groups (fluoroalkyl, aminoalkyl and silanol groups, illustrated in Figure 4.7). The presence of the fluoroalkyl groups was proven 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 proven 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 4.6). 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.

Figure 4.6. FTIR spectra of the hydrophobic curing agent uncured (F8815) and cured (F8815c).

Figure 4.7. Estimated molecular structure of the hydrophobic agent F8815 based on available information from the supplier. As being a commercial product, the exact molecular structure of F8815 has not been revealed. Nonetheless, the chemical is an oligosiloxane with three functional groups: fluoroalkyl, aminoalkyl and silanol groups. Although possessing a polar group (aminoalkyl), it seems that F8815 is able to act as a hydrophobic agent due to the high concentration (n value) and long chains of the fluoroalkyl in comparison with those of the aminoalkyl groups.

4.3.2 Characterization of bio-based 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 4.1). 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. In addition, the similarity of the WCAs of the samples S0.25-S2 can be attributed to the saturation of the hydrophobizer within each polymer. That is, all the samples contained more than the minimum concentration of the hydrophobizer to reach the highest water contact angle.

Table 4.1. Wettability properties of bio-based films and F8815 film.

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

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 bio-based samples were studied by TGA (Figure 4.8). The results show that there was a weight loss in the beginning of the heating process for all the bio-based 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 ambient. The water sorption was also confirmed by DSC results as shown in Figure 4.9. 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 forces. 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 bio-based 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.

Figure 4.8. TGA thermographs of isosorbide-based polymers and F8815_c.

Figure 4.9. DSC thermographs (first test) of the bio-based polymers and F8815. The samples exhibited a low T_g value and a endothermic peak. For the isosorbide-based polymers, the low T_g was associated to the plasticization effect of water on the polymer network; the endothermic peak was associated to the water desorption. In the case of F8815_c, its T_g was originally difficult to find, and therefore, the test was done from -70°C. F8815_c also showed a small and smooth endothermic peak that can be attributed to water desorption. The violent endothermic peaks of F8815_c at the end of the measurement was ascribed to the reaction (curing) of F8815.

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 4.10. F8815_c has the lowest T_d while all the bio-based 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.

Figure 4.10. Decomposition temperature at 5% weight loss (T_d) of the bio-based and F8815c samples.

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 4.11. 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 4.10). 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 proven in S0.25, S0.5 (maximum value achieved) and S1 samples.

Figure 4.11. T_g of the dried samples.

On the other hand, the addition of F8815 also affects the thermomechanical properties of the bio-based samples as shown in the DMA results. The DMA results shown in Figure 4.12 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 S2¹.

¹ Significant difference at the 0.05 level (ANOVA).

Figure 4.12. Storage modulus (E') at the rubbery state of the samples. The temperature selected was $T_{\tan\delta} + 30\text{K}$ [28].

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 4.13 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.

Figure 4.13. Enthalpy of polymerization as function of F8815 concentration. Samples with new concentration (S0.1, S0.3, and S4) were prepared for this measurement.

FTIR spectroscopy was carried out to investigate the crosslink reactions between the isosorbide resin and F8815 (Figure 4.14). Similar to the FTIR spectrum of iso_{net} (Figure 4.2), the spectra of the hydrophobic bio-based 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 CF_2 scissoring (696 cm^{-1}) and the amino bands (NH_2 bending, 808 and 780 cm^{-1}).

Figure 4.14. FTIR spectra of the isosorbide-based samples and F8815c.

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

$$A = \epsilon cl \quad \text{Equation 4.1}$$

where ϵ , c and l stand for absorption coefficient ($l \text{ mol}^{-1} \text{ cm}^{-1}$, 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 4.15a). These bands were selected for this analysis since they facilitate the identification of primary and secondary bands. As proven 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 4.15b). 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.

Figure 4.15. FTIR spectra showing a) amino groups with the reference bands and b) carbonyl groups for the deconvolution.

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 4.16. 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.

Figure 4.16. Integrated absorbance of a) NH₂ and b) C=O 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 NH₂ 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 4.16b), it is clear that the C=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 NH₂ concentration left after curing). In addition, the C=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 NH₂ 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 forces since FTIR results showed high content of NH_2 groups after curing. Nevertheless, the S0.5 seemed to have better a molecular rigidity due to its high concentration of carbonyl groups (Figure 4.16b). Therefore, the best properties found in S0.5 can be attributed to the best balance between the rigidity of isosorbide resin and $\text{C}=\text{O}$, 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.

Figure 4.17. FESEM images of a) isonet, b) S0.25, c) S0.5, d) S1, e) S2 and f) F8815c.

In order to prove the entanglement hypothesis mentioned above, FESEM images of the thin films were obtained (Figure 4.17). The surface of iso_{net} was smooth and compact

(Figure 4.17a), while the surface of F8815_c possessed a rough surface (Figure 4.17f). 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 4.17c and Figure 4.18). 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.

Figure 4.18. FESEM images of S0.5 at a) low and b) high magnification.

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 4.16). 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 4.1). 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.

Finally, the anti-corrosion property of a hydrophilic coating was compared with that of a hydrophobic coating (Figure 4.19, Table 4.2). The unprotected metal substrate showed the highest corrosion current (I_{corr}) and the lowest corrosion potential (E_{corr}), indicating its natural tendency to corrode. Nevertheless, the incorporation of the bio-based coating provided a better corrosion protection as shown in their lower I_{corr} and higher E_{corr} values. However, the anti-corrosion performances of the iso_{net} and S0.5 were different. The sample S0.5 demonstrated to better protect the metal substrate than iso_{net} as proven by its lowest I_{corr} and highest E_{corr} . The better corrosion protection of S0.5 was attributed to its better barrier properties and hydrophobic nature.

Figure 4.19. Tafel curves of the hydrophilic and a hydrophobic coating.

Table 4.2. Corrosion current and potential density of isosorbide-based coatings in 3.5% w/w NaCl.

Sample	I_{corr} ($\mu\text{A}/\text{cm}^2$)	E_{corr} (V vs Ag/AgCl)
Bare Fe	101.3	-1.013
Isonet	7.780	-0.527
S0.5	1.021	-0.503

4.4 Conclusions

Bio-based 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 bio-based 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. In terms of corrosion protection, the hydrophobic coating S0.5 showed better anti-corrosion properties than those of the hydrophilic coating. Finally, the coating enjoys the advantage of using water as the only solvent in preparation, opening possibility for environmentally-friendly coating applications in the future.

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Chapter 5

Cardanol-based coatings^{*}

This chapter presents the preparation and characterization of new bio-based hydrophobic coatings from cardanol. In comparison with the isosorbide-based coatings, these new polymers are characterized by their higher bio-based content as bio-based curing agents were employed. A fluorine-free hydrophobizer was also used and its effect on the chemical, anticorrosion and anti-icing properties of the polymers was studied.

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5.1 Introduction

Despite its relevance in the market due to its various applications [1, 2], epoxy resin industry is still greatly lacking of sustainability since it continues relying on the non-renewable BA. In fact, the most important and widely used epoxy resin is diglycidyl ether of Bisphenol A (DGEBA), which represents approximately 75% of the commercial epoxy resins [3, 4]. Therefore, great efforts are currently being made to overcome the dependency on DGEBA by preparing new epoxy resins from biomass compounds.

As previously discussed, epoxy resins can be prepared from different kinds of bio-based sources such as vegetable oils [5, 6], saccharides [7, 8] and natural phenolic compounds [9, 10]. One of these bio-based phenolic compounds is cardanol, which is extracted from the liquid of the cashew nutshell [11]. For instance, Jaillet et al.[12] studied the mechanical and thermal properties of bulk thermosets based on cardanol. Kanehashi et al. prepared and characterized the properties of cardanol-based epoxy coatings but no specific applications of the coatings were studied [13]. Moreover, cardanol resins have been used in the synthesis of thermosets from epoxy blends [14, 15] and as tougheners in epoxy polymers [16-18].

The preparation of hydrophobic cardanol epoxy polymers using ionic liquids has been reported recently. However, there were no evaluations of their anti-icing and anti-corrosion performances [19]. On the other hand, studies on the corrosion protection of cardanol epoxy coatings have been carried out [20, 21] using non-bio-based curing agents. As part of the objectives of this research to increase the bio content of the coatings, this research focuses on the study of anti-corrosion and anti-icing properties of hydrophobic cardanol epoxy coatings using bio-based curing agents. In the past years, there is an increasing research activity in preparing hydrophobic coatings using bio-based epoxies [22-25], however, the bio content of these coatings is limited by the non-bio-based curing agent. To the best of our knowledge, there have been very few reports on the hydrophobic thermosets using bio-based epoxy resins and bio-based curing agents [26-28].

In this work, two types of bio-based curing agents were studied, *viz.*, furfurylamine (FA) and 1,8-Diamino-p-menthane (DAPM). FA is a derivative of furfural, obtained from lignocellulosic biomass [29]. Despite the studies of FA as a curing agent since 1992 [30], attention has been only paid to its use for the preparation of polybenzoxazines [31-34]. There has been no report on the use of FA solely as a curing agent for the preparation of epoxy coatings. On the other hand, DAPM is a derivative from the monoterpene limonene [35], and its use as a curing agent for the synthesis of epoxy thermosets is rare [36]. Thus, in the current study, we will investigate the influence of the bio-based curing agents FA and DAPM on the anti-corrosion and anti-icing performances of cardanol-epoxy coatings. Effect of a hydrophobic additive, poly(dimethylsiloxane), on the coating performances has also been evaluated.

5.2 Experimental methods

5.2.1 Materials

Cardanol epoxy resins NC-547 and NC-514S (abbreviated as NC-514) were obtained from Cardolite. FA, DAPM (85%, mixture of *cis* & *trans* isomers) and poly(dimethylsiloxane), bis(3-aminopropyl) terminated (abbreviate as PDMS; average M_n ~2500) were obtained from Sigma Aldrich. All chemicals were used as received without any further purification. Figure 5.1 shows the molecular structure of the bio-based compounds and PDMS. Among many available hydrophobic additives, we choose PDMS because it is cheaper and non-toxic in comparison with the fluorinated hydrophobic additives.

Figure 5.1. Molecular structures of the bio-based epoxies (NC547, N514), bio-based curing agents (FA, DAPM) and hydrophobizer (PDMS).

5.2.2 Synthesis

Two sets of samples were prepared. This first set of samples was prepared from the combination of an epoxy resin and a curing agent: NC547-FA, NC547-DAPM and NC514-DAPM. The second set of samples was prepared by adding in 10% (w/w) PDMS as hydrophobic additive into the first set of samples. The samples with PDMS were denoted as NC547-FA-PDMS, NC547-DAPM-PDMS and NC514-DAPM-PDMS, respectively.

To avoid the release of volatile organic compounds during coating processing, this study did not use of any solvent. The epoxy resin and the curing agent were mixed with a spatula in a stoichiometry ratio based on the epoxy equivalent weight (EEW) and amine hydrogen

equivalent weight (AHEW). The EEWs of the resins were obtained by titration and AHEWs of the curing agents were calculated theoretically. For the preparation of the second set of samples, PDMS was mixed with the mixture of the epoxy resin and curing agent. The mixture was then degassed with the aid of an ultrasonicator. Thick coatings and thin coatings were prepared by drop-casting method on Fe substrates. Curing was carried out at 180°C for 5.5 hours in a conventional oven. Thin coatings with thickness around 3-9 μm were used exclusively in electrochemical analysis, while thick coatings (thickness higher than 30 μm) were employed for the rest characterizations and performance evaluations.

5.2.3 Characterization

The EEWs of the NC-547 and NC-514 were measured by titration following a standard method (ASTM D1652).

Thermogravimetric Analysis (TGA) of the samples were carried out in a TGA Q500 (TA Instruments). The samples with weights of approximately 10 mg were placed in alumina crucibles and heated from room temperature to 600°C at 10°C/min under nitrogen flow (60 mL/min). Three measurements were performed for each sample and the data was analyzed by the software TA Universal Analysis.

A DSC Discovery (TA Instruments) was used for studying the curing kinetics of the epoxy resins. The samples were analyzed immediately after the preparation of the mixture. The samples with weight around 1-4 mg were encapsulated in hermetic pans and heated from 25°C to 300°C under nitrogen flow (50 mL/min). Four different heating rates (5, 10, 15 and 20 °C/min) were used for the analyses and at least two measurements were carried out for each heating rate.

The measurement of the viscosity of the all formulations was carried on a rheometer Discovery HR-3 (TA Instruments) using a parallel-plate geometry with a gap of 500 μm at 25°C.

The identification of the functional groups of the coatings were performed by Fourier-transform infrared (FTIR) spectroscopy. Coatings were tested in a FTIR MIR/NIR Frontier (Perkin Elmer) in an attenuated total reflectance (ATR) mode. The analyses were conducted in a wavelength range of 4000-600 cm^{-1} , with 32 scan accumulations and with a resolution of 4 cm^{-1} . The baselines of the spectra were corrected by the software Spectrum (PerkinElmer).

Static contact angles of 5 μL droplets of DI water, ethylene glycol and glycerol deposited on the coatings were measured in an OCA 20 goniometer (Dataphysics). The surface energy was calculated using the Neumann's equation of state [37] as provided in the software SCA 20 (Dataphysics). The water contact angle hysteresis was measured by the sessile drop method in which the droplet volume was increased and reduced by 5 μL at a rate of 1 $\mu\text{L/s}$.

Dynamic mechanical analysis (DMA) was carried out in a DMA Q800 (TA Instruments) with a deformation amplitude of 4 μm at 1 Hz. Due to the different stiffness, NC547-based coatings were tested in compression mode while NC514-based coatings were evaluated in tension mode. The pairs of polymers, NC547-FA and NC547-FA-PDMS, NC514-DAPM and NC514-DAPM-PDMS, and NC547-DAPM and NC547-DAPM-PDMS, were heated from -30°C to 150°C, -30°C to 100°C, and -20°C to 150°C, respectively. Three samples were tested for each composition.

A surface profiler (KLA Tencor) was used to determine the thickness of the coatings. The stylus of the profilometer runs across uncoated region to the coated region, and the difference in height is the coating thickness.

Atomic force microscopy (AFM) was carried out in an AFM Cypher S (Asylum Research) in tapping mode using a soft cantilever. Area of 20 $\times$ 20 μm^2 was scanned in three different locations of each coating.

The ice adhesion of the samples was evaluated by measuring the shear strength to remove an ice block formed on the surface of coating. The set up used for these measurements was the same as that described before[38] . The ice block was formed by placing a cap filled with water on the surface the coatings at -20°C for 24 hours in an ice chamber (Cincinnati Sub-Zero environmental chambers, USA). An adhesion tester placed inside the ice chamber was used to measure the shear force necessary to remove the ice. The force was normalized by the area of the ice block and reported in Pa. The reported ice adhesion for each sample was the average of at least 3 measurements.

Electrochemical analysis was carried out in three-electrode cell in an electrochemical workstation (CHI 660d, Shanghai Chenhua Instrument Corporation). The tests were conducted in a 3.5% NaCl solution using Ag/AgCl and Pt as the reference and counter electrodes, respectively. The coatings with area of 1 cm² were immersed in the electrolyte for 1 hour before the experiment.

5.3 Results

The EEWs of NC547 and NC514 found by the titration methodology (ASTM D1652) were 786 g/eq and 450 g/eq, respectively. These values were within the range of the EEWs of NC547 (550-850) and NC514 (425-575) provided by the supplier.

The main functional groups of the precursors were identified by FTIR (Figure 5.2a). The presence of the amino groups of the bio-based curing agents, FA and DAPM, was confirmed by the appearance of the absorption band at ~1600 cm⁻¹. The ether group of FA was also identified and assigned to the absorption band at 1148 cm⁻¹. The epoxy rings of NC547 and NC514 were distinguished and associated to the stretching absorption band at 910 cm⁻¹ [13] In the hydrophobic additive, PDMS, two kinds of vibration (stretching and bending) of the bond C-H were identified and associated to the bands at 2963 and 1258 cm⁻¹, respectively [39]. The absorption bands of Si-O and Si-C were also found at 1011 and 789 cm⁻¹, respectively.

ATR-FTIR analysis was also carried out on the surface of the bio-based coatings (Figure 5.2 b-d). Two main aspects can be highlighted from the FTIR spectra. First, all the coatings are characterized by the presence of carbonyl groups after curing. The origin of the carbonyl groups can be attributed to the thermal oxidation due to the presence of oxygen [13, 40]. Second, the conversion of the epoxy groups is different for each sample and depends on the kind of epoxy resin. It is evident that the epoxy groups still remained after the heat treatment in the samples NC547-FA, NC547-FA-PDMS, NC547-DAPM and NC547-DAPM-PDMS (Figure 5.2 b and c, inset). However, epoxy groups were totally consumed during the curing reaction in the preparation of the samples NC514-DAPM and NC514-DAPM-PDMS (Figure 5.2d, inset). A possible explanation for the different degree of curing in the NC514-based coatings and NC547-based coatings is the viscosity of the epoxy resins. Based on the product information from the supplier, the viscosity of NC547 ranges from 20 to 50 Pa·s, while the viscosity of NC514 varies from 1 to 3 Pa·s. The differences in viscosity between the NC547-based and NC514-based formulations are shown in Figure 5.3. The results showed that in the Newtonian region the viscosity of NC547-based formulations varied from 58 to 225 Pa·s, while the viscosity of NC514-based formulations changed from 2.4 to 3.5 Pa·s. Since no solvent was used in the preparation of the coatings, the high viscosity of NC547 might have prevented the full reaction between epoxy and amino groups during the thermal treatment.

Figure 5.2. FTIR spectra of a) precursors, b) coatings NC547-FA and NC547-FA-PDMS, c) coatings NC547-DAPM and NC547-DAPM-PDMS, and d) coatings NC514-DAPM and NC514-DAPM-PDMS.

Figure 5.3. Viscosity measurements of NC514, NC547 and the bio-based formulations before curing.

The degree of epoxy conversion of the coatings (α_{coat}) is given in equation 1 [41]:

$$\alpha_{coat} = \frac{I_{er} - I_{coat}}{I_{er}} \quad \text{Equation 5.1}$$

where I_{er} and I_{coat} are the normalized intensity of the epoxy absorption peak (910 cm^{-1}) in the epoxy resin and the coating, respectively. For comparison, two reference bands at 1581 and 1503 cm^{-1} were used for the normalization. These two peaks can be assigned to the stretching vibrations of aromatic carbon-carbon bonds that remain stable and unreacted during the curing process[42]. The 1503 cm^{-1} reference band works well with NC547-DAPM samples since there is no interference with other bands from DAPM or PDMS. Similarly, the 1581 cm^{-1} reference band works well with NC547-FA samples because of the non-interference with other bands of FA or PDMS. As shown in Table 5.1, when comparing samples without the hydrophobic additive PDMS, the degrees of epoxy conversion of the samples NC547-FA and NC547-DAPM were similar regardless of the chosen reference band. A similar effect in the epoxy conversion was also found in the samples with PDMS. Moreover, the epoxy conversion was higher in the coatings containing PDMS than the ones without. Due to its low viscosity ($1.96 \text{ Pa}\cdot\text{s}$), PDMS may

have acted as a plasticizer and, thus, promoting the reaction between the amino and epoxy groups. Another possibility is that PDMS reacted with the epoxy groups, therefore, increasing the epoxy conversion rate. More insights into the roles by PDMS will be discussed later based on DSC results.

Table 5.1. Various properties of the bio-based coatings.

Sample	Epoxy conversion (%)		E_a (kJ/mol Epoxy)	WCA (°)	Surface energy (J/m ²)
	Reference band 1581 cm ⁻¹	Reference band 1503 cm ⁻¹			
NC547-FA	65	51	30.57 (±2.95)	83.51 (±1.44)	31.54 (±1.46)
NC547-DAPM	69	54	45.41 (±4.78)	75.68 (±3.53)	32.35 (±3.29)
NC514-DAPM	~100%	~100%	46.43 (±1.93)	95.43 (±1.04)	26.14 (±0.49)
NC547-FA- PDMS	80	73	28.47 (±2.73)	97.22 (±1.38)	21.20 (±2.06)
NC547-DAPM- PDMS	83	76	60.93 (±3.65)	100.19 (±1.74)	20.34 (±1.40)
NC514-DAPM- PDMS	~100%	~100%	43.14 (±0.93)	114.00 (±0.63)	13.25 (±1.01)

Further analyses of the curing reactions were carried out through the calculation of the activation energies by using the Kissinger equation [43-45]:

$$\frac{d \ln(q/T_p^2)}{d(1/T_p^2)} = -\frac{E_a}{R} \quad \text{Equation 5.2}$$

where q , T_p , E_a and R are, respectively, the heating rate, peak temperature, energy of activation and the universal gas constant. It was found that some of the DSC curves of reactions showed two exothermic peaks (Figure 5.4). The two peaks can be attributed to two different reactions: the reaction between a primary amino group and the epoxy group, and the reaction between a secondary amino group and the epoxy group [36]. Therefore, reaction curves with two peaks were deconvoluted (inset, Figure 5.4) and the first peak was used for the calculation of activation energies. Figure 5.5a shows the Kissinger plots and Table 5.1 lists the E_a values. When comparing samples without PDMS, the E_a values of samples cured with FA and DAPM were ~30 kJ/mol and ~45 kJ/mol, respectively. It is noticeable that the E_a values of samples containing PDMS were the same as those without PDMS for each kind of curing agent. One exception was the E_a of NC547-DAPM-PDMS

that showed an increased activation energy (57.75 kJ/mol) in comparison with that of NC547-DAPM (45.41 kJ/mol).

Figure 5.4. Typical exothermic curve of the reaction between amino and epoxy groups. The inset shows the deconvolution of the curve. Green curves are the resulted Gaussian curves; dash read curve (largely overlaps with the black solid line) is the sum of the green.

Figure 5.5. Kissinger plots for the calculation of the activation energies of a) the all the coatings and b) the mixture of NC547 and PDMS.

The lower E_a values of samples cured with FA in relation with those cured with DAPM can be explained in terms of steric hindrance. FA has an amino group that is not sterically hindered (which enables it to react freely). In contrast, DAPM has two amino groups in

which both are two carbon-carbon bonds apart from the methyl groups. Thus, DAPM is highly hindered by the presence of the methyl groups. This difference in steric hindrance is the reason that FA showed a lower E_a in comparison with that of DAPM.

Moreover, the incorporation of PDMS did not change the E_a values of the samples with the same kind of curing agent. This suggests that the curing agent was the main component that participated in the reaction with the epoxy groups. In addition, this result showed that PDMS acted as plasticizer that promoted the reaction between the epoxy and amino groups as seen in the increment of the epoxy conversion.

However, the E_a value increased in the sample NC547-DAPM-PDMS, which indicates that PDMS has participated in the reaction with epoxy groups in this exceptional case. This reaction may have happened through the available amino groups at the end of the siloxane chain. In order to prove this hypothesis, NC547 was mixed with PDMS in a stoichiometry molar ratio and the energy activation was calculated from the Kissinger plot (Figure 5.5b). The E_a of NC547-PDMS was 100.77 kJ/mol, which is much higher than that of NC547-DAPM (45.41 kJ/mol). The higher E_a of the reaction of PDMS and NC547 was attributed to the obstruction of the long siloxane chains that have prevented the encounter of the amino and epoxy groups. Therefore, since the reaction between PDMS and NC547 was energetically costly, the increment in the energy of activation of NC547-DAPM caused by the addition of PDMS was because that PDMS also links with the epoxy resin. As a consequence, PDMS not only acts as plasticizer in NC547-DAPM-PDMS but also as a curing agent. Finally, despite the different activation energies of the six samples, the results suggest that viscosity was the main factor that govern the degree of the epoxy conversion. The 5.5 hours curing time was long enough to suppress the differences in the activation energies, and the final epoxy conversion was the result of the viscosity of the mixture.

Wettability

The wettability properties of the coatings were assessed by measuring the water contact angles (WCA) and surface energy (Table 5.1). In the absence of PDMS, all the samples were hydrophilic ($WCA < 90^\circ$) with the exception of NC514-DAPM ($WCA = 95.43^\circ$). This

result can be explained by the percentage of epoxy conversion. The hydrophilicity of NC547-FA and NC547-DAPM is due to the moderate concentration of the remaining epoxy groups which can form hydrogen bonds with water. In contrast, NC514-DAPM was slightly hydrophobic due to adequate exposure of the long carbon chains without the chemical interference of unreacted epoxy groups. The same argument can be used for the explanation of the surface energy of the PDMS-free coatings, where NC514-DAPM has the lowest surface energy among the three coatings. On the other hand, the incorporation of PDMS has caused the coatings to become hydrophobic ($\text{WCA} > 90^\circ$) for all the NC547-based coatings. Although epoxy groups still remained in the cured samples, the concentration of PDMS was high enough to overcome the hydrophilic properties of the unreacted epoxy groups. In case of the NC514-based samples, the addition of PDMS into NC514-DAPM caused the coating to show a higher WCA (from 95.43° to 114.00°). This is a consequence of the increment of the methyl groups of PDMS on the surface of the coating. The high concentration of PDMS on the surface of NC514-DAPM-PDMS can be proven by its FTIR spectrum that resembled that of PDMS (Figure 5.2d). This result suggests that certain amount of PDMS was present on the coating surface. In all the cases, addition of PDMS was accompanied by the decrease of the surface energy of the coatings (Table 5.1).

Thermal and mechanical properties

The thermal properties of the bio-based coatings were studied by TGA (Figure 5.6). The onset temperature of decomposition (T_d) and amount of residue of the samples are shown in Table 5.2. The T_d and the residue percentages of the coatings without PDMS decreased in the following order: NC547-FA > NC547-DAPM > NC514-DAPM. In case of samples based on NC547, the result suggested that FA provided better thermal resistance than that of DAPM. This can be supported by the fact that aromatic compounds like FA are well known by their high thermal resistance in comparison with non-aromatic compounds such as DAPM [46]. However, despite the better thermal resistance showed by FA in comparison with DAPM in the beginning of the pyrolysis, the residue percentages of NC547-FA (11.19%) and NC547-DAPM (10.74%) were quite similar. This is because the

curing agents (FA and DAPM) were mostly decomposed in the form of gases and the epoxy resin (NC547) remained as the major component of the char. On the other hand, the effect of epoxy resin can be studied from the T_d of NC547-DAPM and NC514-DAPM. The slight difference in the T_d of NC547-DAPM (254.76°C) and NC514-DAPM (247.57°C) demonstrates that NC514 was slightly less resistant than NC547. Nevertheless, a considerable difference in the residues between NC547-DAPM (10.74 %) and NC514-DAPM (5.39 %) was noticed. This indicates that most of the mass of NC514 was decomposed in the form of gases, which can be attributed to the lower concentration of benzene rings of N514 (two benzene rings per molecule) in comparison with that of N547 (five benzene rings per molecule).

Figure 5.6. TGA thermographs of the epoxy cardanol-based coatings.

With the incorporation of PDMS, the T_d values of the samples followed the same order as the ones without PDMS (NC547-FA-PDMS > NC547-DAPM-PDMS > NC514-DAPM-PDMS), and all of them were lower than their PDMS-free counterparts. Therefore, the reduction of the T_d values can be attributed to the early decomposition of PDMS. In addition, the T_d results also demonstrate that FA imparted a better thermal resistance than DAPM in the beginning of the pyrolysis. Moreover, the lower T_d value of NC514-DAPM-

PDMS (224.38°C) in relation to that of NC547-DAPM-PDMS (243.21°C) clearly shows that NC514 was less thermally resistant than NC547.

Although PDMS started to decompose early, much of the mass of PDMS in its decomposed form remained after burning, and has increased the residue percentages. The residues of NC547-FA-PDMS (20.93%) and NC547-DAPM-PDMS (20.07%) were quite similar and supported the mechanism in which FA and DAPM decomposed firstly and the residues mainly originated from the NC547 and PDMS. Moreover, the lower residue percentage of NC514-DAPM-PDMS (15.63 %) in comparison with NC547-DAPM-PDMS (20.07%) proves once again that NC514 degraded mainly in the form of volatile gases.

Table 5.2. Thermal and mechanical properties of the bio-based samples.

Sample	T _d (°C)	Residue (%)	T _g (°C)	v_e (mol/m ³)
NC547-FA	288 (±1)	11 (±0)	31 (±2)	25 (±3)
NC547-DAPM	255 (±3)	11 (±1)	46 (±4)	24 (±4)
NC514-DAPM	248 (±3)	5 (±0)	46 (±0)	45 (±1)
NC547-FA-PDMS	275 (±2)	21 (±1)	30 (±1)	30 (±3)
NC547-DAPM-PDMS	243 (±3)	20 (±2)	41 (±2)	28 (±4)
NC514-DAPM-PDMS	224 (±2)	16 (±2)	44 (±1)	36 (±2)

DMA was carried out to measure the glass transition and crosslink density of the bio-based thermosets (Table 5.2). The glass transition (T_g) of the coatings was measured as the temperature corresponding to the peak of the Tanδ (T_{Tanδ}). The crosslink densities (v_e) of the thermosets were measured according to the following equation derived from the rubbery elasticity theory:

$$v_e = \frac{E}{3RT} \quad \text{Equation 5.3}$$

where E is the storage modulus at the temperature T (T = 30°K + T_{Tanδ}) and R is the universal gas constant [47]. The T_g values of the samples without PDMS showed a dependency on the type of bio-based curing agent rather than on the type of epoxy resin. That is, the samples cured with DAPM (NC547-DAPM and NC514-DAPM) had very similar T_g values (~46°C), while the sample cured with FA had a lower T_g (31.28°C). The

difference in the T_g was ascribed to the size and branched nature of the curing agents. Apart from being a molecule bigger than FA, DAPM is a dynamic molecule that undergoes conformations and has bulkier CH_3 - groups that can prevent the movement of the polymer network more effectively than FA, and thus, the increase in the T_g . On the other hand, it seemed that the incorporation of PDMS did not change the T_g values.

The crosslink density values (v_e) of bio-based coatings were also analyzed. Among the samples without PDMS, the v_e values of NC547-FA and NC547-DAPM were similar ($\sim 24 \text{ mol/m}^3$), and lower than that of NC514-DAPM (44.60 mol/m^3). The low and similar v_e values of NC547-FA and NC547-DAPM can be explained by the low and similar degree of epoxy conversion (Table 5.1). Similarly, the NC514-DAPM exhibited a higher v_e as the result of the complete conversion of epoxy groups. After the incorporation of PDMS, v_e of the NC514-based samples decreased. This decrease in v_e can be attributed to the hindrance caused by the diffusion of PDMS to the surface during curing. That is, although PDMS did not affect the degree of curing, its migration to the surface might have reduced the closeness of the crosslink points, and therefore, decreased the crosslink density. On the other hand, the effect of PDMS on the v_e values of NC547-based coatings was not clear due to their similar v_e values.

In addition of their higher v_e values, NC514-based samples also showed higher $\text{Tan}\delta$ peaks than NC547-based samples (Figure 5.7). The high $\text{Tan}\delta$ peaks of the NC514-based polymers means that the coatings have a higher degree of viscous behavior than those of the NC547-based polymers. This result can be explained in terms of the rigidity of the molecular structure of the bio-epoxies. NC514 is more flexible due to the presence of two separated benzene rings per molecule while NC547 is more rigid due to its five consecutive benzene groups per molecule.

Figure 5.7. Tan δ plots of the bio-based coatings.

Anti-icing performance

The potential use of the coatings as protection against the formation of ice on the surface was evaluated by measuring the ice adhesion strengths (Figure 5.8, Table 5.3). The results show that all the coatings had a low affinity to the ice in comparison with the bare iron substrate. Moreover, the coatings with PDMS showed a further lower ice adhesion strength than the coatings without PDMS². Most researchers in the community have accepted the suggestion that coatings with ice adhesion strength lower than 100 kPa can be considered as icephobic [48]. Based on this definition, the bio-based coatings are icephobic since the average ice adhesion strength of all the coatings was about 50 kPa. However, there are other suggestions that icephobic coatings for real applications should have ice adhesion strengths lower than 10 kPa[49]. As discussed recently, it is not possible to have a fair comparison among the ice adhesion test results reported in the literature due to the lack of a standard protocol[49, 50]. Different testing methods have been used under different sample and facility conditions. Thus, the ice adhesion strengths of the bio-based coatings obtained in this study can be best compared with coatings reported using the same ice-adhesion set up and conditions. The ice adhesion strengths of the new bio-based films were

² Significant differences at the 0.05 level (ANOVA).

better than the superhydrophobic isosorbide-based coatings that exhibited ice adhesion strengths around 100 kPa [22], and comparable to the hydrophobic bio-epoxy coatings with ice adhesion strengths around 50 kPa [26].

According to literature, various factors affect the ice adhesion of the coatings such as surface topology, roughness, surface energy and wettability [51-53]. Therefore, the anti-icing performances of the coatings were evaluated by comparing the surface properties (Table 5.3).

Figure 5.8. Comparison of ice adhesion strength of the bio-based coatings.

The roughness of the coatings was assessed as the root mean square (RMS) of the heights of the surfaces. The results show that all coatings are very smooth with RMS largely below 30 nm. With such a small roughness, the actual surface area is close to the nominal area. As reported in the literature, properly designed surface topology with a high roughness in the range of hundreds of nanometers might be suitable for anti-icing application as it can trap much air on the surface structure [38, 54]. However, this mechanism is not operative in the ultra-smooth coatings in the current work.

The lower ice adhesion strengths in the current work come from the lower surface energy in comparison with the bare substrate. The WCAs of the coatings were higher than that of

the iron substrate ($\text{WCA}=59.31 \pm 0.77^\circ$). Similarly, the better anti-icing performances of the PDMS-containing coatings in relation with PDMS-free samples were ascribed to their higher WCAs and lower surface energies (Table 5.1) [55]. It is worth mentioning that although NC514-DAPM was hydrophobic ($\text{WCA}=95.43^\circ$) before the incorporation of PDMS, its surface energy was not low enough to exhibit an ice adhesion strength value similar to those of the PDMS-containing samples.

Contact angle hysteresis may have an influence on the anti-icing performances of the coatings [56, 57]. Therefore, the water contact angle hysteresis data of the coatings were also assessed (Table 5.3). The contact angle hysteresis ($\theta_A - \theta_R$) of samples without PDMS were higher than the samples with PDMS. This reveals that water affinity was higher on the surfaces of coatings without PDMS. Moreover, the contact angle hysteresis in each series of samples (coatings with/without PDMS) did not vary as significantly as in the surface energy measurements (Table 5.1). Thus, apart from the surface energy properties, the contact angle hysteresis may serve as an indicator of the ice adhesion strengths. Surfaces with low WCA hysteresis has a better ability to repel water, therefore low ice adhesion strengths are expected on this type of smooth surface.

The reduction of the contact angle hysteresis caused by PDMS can be attributed to its liquid-like and smooth surface at the molecular level [58]. A liquid-like surface is unable to hold a liquid firmly and, therefore, causing the liquid to slide. The liquid-like surface of PDMS can be attributed to the arrangement of methyl groups along the siloxane chain. The methyl groups in PDMS are separated from each other by an oxygen bridge that can be considered as a molecular spacer[59]. This molecular space allows the methyl groups to have a free movement that causes the formation of an unstable surface (liquid-like surface). Contrarily, in the hypothetical case of the absence of the oxygen bridges, methyl groups would pack better and, as a consequence, a more rigid molecular surface would form. In addition of its liquid-like surface, PDMS also has a smooth molecular surface that relies on the uniformity of the branches in the siloxane chain. The methyl groups constitute the main branches of the siloxane chain and therefore, it creates a smooth surface that reduces the hysteresis. In case of PDMS having different kinds of branches such as alternating

methyl and octyl groups, the surface would be rough at the molecular level and probably exhibiting a higher hysteresis. The positive effect PDMS on anti-icing properties resembles that of the slippery liquid-infused porous surfaces (SLIPS) [60], which consists of porous surfaces impregnated with an immiscible liquid. The low hysteresis of SLIPS comes from the thin hydrophobic liquid layer that offers a defect-free and smooth surface at the molecular level [61, 62].

Table 5.3. Ice adhesion values, RMS and θ_A and θ_R of water droplets.

Sample	Ice adhesion strength (kPa)	RMS (nm)	θ_A (°)	θ_R (°)	$\theta_A - \theta_R$ (°)
Fe substrate	140.7 ($\pm$ 36.4)	-	-	-	-
NC547-FA	68.5 ($\pm$ 8.8)	8.61 ($\pm$ 1.33)	83.16 ($\pm$ 0.97)	46.33 ($\pm$ 0.93)	36.83
NC547-DAPM	55.6 ($\pm$ 2.9)	19.62 ($\pm$ 1.95)	86.56 ($\pm$ 0.67)	51.54 ($\pm$ 1.18)	35.02
NC514-DAPM	55.0 ($\pm$ 5.2)	8.51 ($\pm$ 2.58)	107.59 ($\pm$ 0.31)	72.39 ($\pm$ 0.59)	35.2
NC547-FA-PDMS	42.6 ($\pm$ 4.0)	27.91 ($\pm$ 10.02)	104.92 ($\pm$ 0.81)	77.46 ($\pm$ 1.34)	27.46
NC547-DAPM-PDMS	36.9 ($\pm$ 2.6)	31.50 ($\pm$ 6.62)	102.95 ($\pm$ 0.91)	71.48 ($\pm$ 1.03)	31.47
NC514-DAPM-PDMS	37.6 ($\pm$ 0.9)	*	117.21 ($\pm$ 0.45)	85.85 ($\pm$ 0.33)	31.36

* It was not possible to measure the roughness of NC514-DAPM-PDMS due to its soft surface that prevented the AFM scanning.

Anti-corrosion performance

The anti-corrosion performance of the thin samples was assessed by calculating the corrosion potential (E_{corr}) and corrosion current (I_{corr}) from the Tafel curves (Figure 5.9). The Tafel curves of the coatings shifted to higher potentials (E_{corr}) and lower current densities (I_{corr}) in comparison with the unprotected Fe substrate (Table 5.4). It is clear that all coatings (with or without PDMS) are able to improve the corrosion resistance of the Fe substrate, as evidenced by the much positive corrosion potentials and the ~ 2 orders of magnitude reduction in the corrosion current densities. However, due to the varying viscosity, it was difficult to prepare coatings with the same thickness for a better comparison, since the E_{corr} and I_{corr} values can be affected by the coating thicknesses.

The anti-corrosion performance of the coatings can be analyzed from the point of view of crosslink density and hydrophobicity. A high crosslink-density coating is generally characterized by a reduced free volume of the polymer network that can block the diffusion

of the electrolyte better than a low crosslink-density coating [63]. Similarly, hydrophobic surfaces are expected to have a better corrosion protection than hydrophilic surfaces because of their low affinity with water [64]. The E_{corr} and I_{corr} values of the samples without PDMS showed that NC514-DAPM and N547-DAPM had better anti-corrosion properties than NC547-FA. The higher E_{corr} value and low I_{corr} value of NC514-DAPM, despite its thinner thickness, can be ascribed to its high crosslink density as well as its inherent hydrophobicity.

Figure 5.9. Typical Tafel curves of the bio-based coatings.

Nonetheless, the explanation of the high E_{corr} value and lowest I_{corr} value of NC547-FA was not clear since the coating exhibited a low crosslink density and hydrophilicity. Therefore, it is possible that the good anti-corrosion properties of NC547-FA were caused by its higher thickness. In case of NC547-DAPM, its low anti-corrosion performance could be attributed to its low crosslink density and hydrophilicity. Thus, corrosion data of the samples without PDMS suggest that high E_{corr} and low I_{corr} values were obtained when the coatings had higher crosslink density and hydrophobicity.

There is a difficulty in thoroughly analyzing the influence of PDMS addition on the anti-corrosion performance because of different thicknesses obtained in this study. Nevertheless, two pairs of coatings with similar thickness were compared. The first pair was between NC514-DAPM (2.98 μm) and NC547-DAPM-PDMS (2.72 μm), and both were hydrophobic. The hydrophobicity of NC514-DAPM came from the surface exposure of the long carbon chains while their hydrophobicity of NC547-DAPM-PDMS was caused by siloxane chains of PDMS. Despite the fact that both of them are hydrophobic, the anti-corrosion performance of the coatings was different. NC514-DAPM had a higher E_{corr} and lower I_{corr} than those of NC547-DAPM-PDMS. The difference in performance can be ascribed to the different crosslink densities. As analyzed above, NC547-DAPM-PDMS did not cure completely while NC514-DAPM did. Therefore, when hydrophobicity condition is achieved in the coatings, crosslink density becomes an important factor on the anti-corrosion properties of the coatings. The second pair for comparison was NC547-FA-PDMS (7.28 μm) and NC514-DAPM-PDMS (7.57 μm). Both were hydrophobic due to the presence of PDMS but they showed different anti-corrosion performance. NC514-DAPM-PDMS demonstrated a better protection against corrosion than NC547-FA-PDMS. Since both of them were hydrophobic, the crosslink density difference seemed to be the most reasonable explanation for the different anti-corrosion performances. As shown in Table 2, NC514-DAPM-PDMS had higher v_e value (35.95 mol/cm^3) than that of NC547-FA-PDMS (29.89 mol/cm^3). This suggests again the anti-corrosion properties of the hydrophobic coatings are affected by the crosslink density. These results are similar to other recent results in which the importance of balancing the hydrophobicity and crosslink density (barrier properties) of coatings was highlighted [65-68].

Table 5.4. Corrosion data together with thickness values.

Sample	Thickness (μm)	E_{corr} (V vs Ag/AgCl)	$\log(I_{\text{corr}})$ (A/cm^2)	I_{corr} (A/cm^2) $\times$ 10^{-7}
Fe substrate	-	- 1.00 (± 0.01)	-4.10 (± 0.11)	820 (± 231)
NC547-FA	9.13 (± 3.89)	-0.49 (± 0.05)	-7.88 (± 1.64)	3.4 (± 5.58)
NC547-DAPM	4.54 (± 0.65)	-0.54 (± 0.04)	-6.28 (± 0.29)	11.13 (± 14.11)
NC514-DAPM	2.98 (± 1.17)	-0.49 (± 0.09)	-6.72 (± 1.48)	5.85 (± 3.05)
NC547-FA-PDMS	7.28 (± 2.90)	-0.53 (± 0.05)	-6.25 (± 0.20)	6.08 (± 3.03)
NC547-DAPM-PDMS	2.72 (± 0.73)	-0.57 (± 0.02)	-5.76 (± 0.20)	18.80 (± 9.77)
NC514-DAPM-PDMS	7.57 (± 4.60)	-0.48 (± 0.05)	-6.95 (± 0.03)	1.12 (± 0.07)

5.4 Conclusions

The use of FA and DAPM as curing agents was explored in the preparation of new thermosets coatings from bio-based cardanol-derived epoxy resins NC547 and NC514. The coatings were also hydrophobized by incorporating PDMS, and their anti-icing and anti-corrosion properties were evaluated. Due to its low viscosity, NC514-based coatings exhibited a complete consumption of the epoxy groups while the NC547-based coatings could not achieve a full consumption. Samples became more hydrophobic with the addition of PDMS. Both series of coatings (with and without addition of PDMS) displayed sufficiently low ice adhesion strength (< 100 kPa), which makes them good candidates for icephobic applications. The addition of PDMS has resulted in a further reduction of the ice adhesion. The incorporation of PDMS might have mixed effects on the anti-corrosion performance. On the one hand, the increased hydrophobicity favors the enhanced anti-corrosion performance. On the other hand, this enhancement may be compromised if the crosslink density of the coating remains low. Future clarification should be carried out with a better-controlled thickness in the coatings. Finally, due to its inherent hydrophobicity and fully bio-based content, NC514-DAPM is a promising solvent-free coating formulation for anti-corrosion and anti-icing applications. NC514-DAPM demonstrated a low ice-adhesion strength at 55.0 ± 5.2 kPa, and when coated on a Fe substrate with a thickness of $3\text{ }\mu\text{m}$, the corrosion potential was shifted positively by 0.51 V , and the corrosion current density was reduced by 2 orders of magnitude.

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Chapter 6

Glycerol-based coatings^{*}

This chapter reports the preparation of new bio-based epoxy coatings with the highest bio-based content developed in this research. The bio-content of these new polymers is higher than that of the cardanol-based polymers because bio-based additives were included as potential hydrophobizers. This study focuses on the effect of three bio-based additives on the mechanical, thermal, wettability and anticorrosion properties of a glycerol-based polymer.

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6.1 Introduction

The development of full bio-based epoxy polymers still remains a great challenge despite the great effort done to synthesize bio-based epoxy resins from sources such as lignin [1], vegetable oils [2], cellulose [3] and terpenoid [4]. Ideally, not only the epoxy resin should come from bio-sources, but also the other reagents in the overall formulation. Moreover, applications for anticorrosion, easy cleaning and anti-icing would require the materials to possess certain degree of hydrophobicity [5, 6].

In this research, new polymers were prepared in which the epoxy resin, curing agent and the hydrophobic additives were all derived from biomass. The bio-based thermoset used in this study was prepared from the epoxy resin diglycidyl ether of glycerol (GDE) and the curing agent was citric acid (CA). To the best of our knowledge, this bio-based epoxy formula has not been reported in literature [7-11]. GDE and CA have been used separately in different epoxy formulae. GDE is a bifunctional epoxy resin that can be obtained from glycerol, which is a byproduct of the biodiesel industry [12-14]. However, the bio-based content of GDE can be negatively affected by type of epichlorohydrin used. Although epichlorohydrin can be obtained from bio-based glycerol, it is still mostly produced from non-renewable sources. Nevertheless, GDE is still an attractive bio-based chemical used in the synthesis of thermosets [15-22]. CA is a tricarboxylic acid that can be industrially prepared from sugar or from food and agricultural waste [23]. Although CA, as a curing agent, suffers from the inconvenience of being a solid at normal conditions, it has been used as a bio-based curing agent in the synthesis of epoxy coatings [24-26]. Due to their molecular structures, thermosets prepared by GDE and CA are hydrophilic. Therefore, hydrophobic additives have to be added to improve the hydrophobicity when water repellency is required.

Hydrophobic materials are well known for their ability to repel water that makes them potential candidates for a series of applications such as easy cleaning, anti-icing, and anticorrosion [5, 6]. To improve the anticorrosion performance of polymers derived from GDE and CA, bio-based hydrophobic additives have to be incorporated. Potential candidates for bio-based hydrophobizers include hexanoic acid (HA), trans-resveratrol

(RV), and a bio-based resin NC-514S. HA or caproic acid is an aliphatic carboxylic acid that can be obtained from certain oils and from the fats of animals [27, 28]. Although HA has been used as pendent chains in the preparation of the branched polymers [29], no reports have been found for its use as an additive in the synthesis of epoxy thermoset. HA is expected to impart some degree of hydrophobicity due to its aliphatic chain. RV is a polyphenol that can be extracted from grapes and peanuts [30-32]. The use of RV in the preparation of thermosets is scarce [33-36]. Due to its low water solubility (0.05 mg/mL) [37], RV may confer better hydrophobicity on GDE-CA polymers. Finally, NC-514S is epoxy resin derived from cardanol which is obtained from the cashew nutshell. NC-514S has been used in the preparation of bio-based thermosets [38-40] or composites [41, 42]. NC-514S was selected as a potential bio-based hydrophobizer in the current study since a thermoset derived from NC-514S was proven to be hydrophobic [43].

6.2 Experimental methods

6.2.1 Materials

Glycerol diglycidyl ether (technical grade) (GDE), citric acid (CA) and hexanoic acid (HA) ($\geq 98\%$) were purchased from Sigma Aldrich. The epoxy resin NC-514S (abbreviated as NC) was obtained from Cardolite. Trans-resveratrol (98%) (RV) was purchased from S1-Lab (Singapore). The molecular structures of the chemical used are shown in Figure 6.1.

6.2.2 Synthesis

This research focuses on studying the accumulative effect of potential bio-based hydrophobizers (HA, RV and NC) on a basic epoxy formulation made of GDE and CA. Therefore, five different formulae were developed: two unmodified formulae (GDE-CA-0.90, GDE-CA-0.73) and three modified formulae (GDE-CA-HA, GDE-CA-HA-RV, and GDE-CA-HA-RV-NC) (Table 6.1). The three modified formulae were developed in order to understand how the accumulative incorporation of bio-based additives influenced on the hydrophobicity of the polymers. The amount of bio-based additives, HA, RV, and NC used

in relation with GDE was 15%, 9% and 1% w/w, respectively. The concentrations of these bio-based additives were carefully selected after investigating formulae with different concentrations of the bio-based additives. At these specific concentrations, hydrophobic effect was achieved on the basic formula of GDE and CA.

The molar ratio of epoxy groups of GDE to the carboxylic groups of CA was 1:0.9 for GDE-CA-0.90 and 1:0.73 for the other four formulae. Samples with molar ratios of GDE and CA higher than 1:0.9 were not included in this research as the coatings were produced with various surface defects. In addition, only the bio-based polymers with molar ratio 1:0.73 (GDE : CA) were modified because at this ratio the bio-based additives could be mixed homogeneously without any physical segregation.

Table 6.1. Composition of the five epoxy resin formulae.

Sample	Molar ratio of epoxy groups (GDE) to carboxylic groups (CA)	Bio-based additives (% w/w) with respect to GDE		
		HA	RV	NC
GDE-CA-0.90	1: 0.9	-	-	-
GDE-CA-0.73	1: 0.73	-	-	-
GDE-CA-HA	1: 0.73	15	-	-
GDE-CA-HA-RV	1: 0.73	15	9	-
GDE-CA-HA-RV-NC	1: 0.73	15	9	1

The preparation of the unmodified formulae (GDE-CA-0.9 and GDE-CA-0.73) was done as follows. First, CA was dissolved in water in a mass ratio of 1:1. The CA solution was then heated at 120°C in an oil bath under agitation for 10 minutes to remove around half of its water content to enable a good quality coating in the subsequent process. Afterwards, the hot CA solution was taken out of the oil bath and GDE was added and mixed for about 10 minutes.

For the preparation of the modified formulae (GDE-CA-HA, GDE-CA-HA-RV and GDE-CA-HA-RV-NC), the procedure to prepare the CA solution was the same as described above. In preparing GDE-CA-HA, HA and GDE were mixed first before being mixed with the CA. However, in the preparation of GDE-CA-HA-RV and GDE-CA-HA-RV-NC, GDE was initially mixed with RV (or RV and NC) and heated to 120°C for about 10 minutes under constant stirring. Thereafter, the mixture was cooled down at ambient

condition and mixed with HA. The reason for such processing procedure will be further explained later.

The final mixture was then poured on PTFE molds and stainless steel substrates (0.25 mm thick). The coatings were cured at 150 °C for 2 hours with a heating and cooling rate of 0.5°C/min, comprising around 10 hours for the curing cycle. The slow heating and cooling rate was chosen in order to prevent the formation of surface defects on the coatings. The films prepared on the stainless steel substrates were used for the measurements of the wettability and corrosion tests. The samples prepared in PTFE molds were used for the rest of the characterizations. All the samples were analyzed immediately after their preparation.

Figure 6.1. Molecular structure of the bio-based compounds used in this research: GDE (glycerol diglycidyl ether), CA (citric acid), HA (hexanoic acid), RV (resveratrol) and NC (a cardanol-based resin).

6.2.3 Characterization

The epoxy equivalent weight (EEW) of the resins was obtained according to the standard titration method described in ASTM D1652. Two to four measurements were performed for each sample conditions.

Thermogravimetric analysis (TGA) was performed in a TGA Q500 (TA Instruments). Samples of about 8-12 mg were heated from room temperature to 600°C at 10°C/min under nitrogen flow (60 mL/min). Three measurements were conducted for each sample.

Differential scanning calorimetry (DSC) was carried out in a DSC Discovery (TA Instruments). The solid samples with the weight of around 7-11 mg were prepared in aluminum pans and heated three times sequentially from -70 to 200°C at 10°C/min under nitrogen flow (50 mL/min). In order to remove the thermal history of the samples, the data of the last heating was used for the analysis. Three to five measurements were carried out for each formulation. For the reactivity tests, liquid samples with the weight around of 1-4 mg were prepared in hermetic aluminum pans and heated from 25 to 250°C at four different heating rates (5, 10, 15 and 20°C/min). In this experiment, the reported temperature is an average of two measurements.

The viscosity of the preheated samples was measured on a rheometer Discovery HR-3 (TA Instruments) configured in a parallel-plate geometry with a 500- μ m gap at 25°C.

Fourier-transform infrared (FTIR) spectroscopy was performed in a FTIR MIR/NIR Frontier (Perkin Elmer) in an attenuated total reflectance (ATR) mode for all the samples except for HA which was done in transmission mode using KBr pellets. The wavelength range of the analyses was 4000-600 cm^{-1} with a resolution of 4 cm^{-1} and 32 scan accumulations. A baseline correction was done in all the spectra using the software Spectrum (PerkinElmer).

The wettability of coatings was assessed in an OCA 20 goniometer (Dataphysics) by measuring the static contact angles of 5 μ L droplets of three different liquids (DI water, glycerol and ethylene glycol). The surface energy was calculated using the OWRK methodology [44-46] using the software SCA 20 (Dataphysics).

Dynamic mechanical analysis (DMA) was carried out in a DMA Q800 (TA Instruments) in a single cantilever mode with a deformation amplitude of 15 μ m at 1 Hz. The samples, prepared in rectangular shapes (35 mm in length, 14.3 mm in width, and 2.6-3.6 mm in

thickness), were heated from -20 to 110°C at a rate of 3°C/min. At least three measurements were performed for each sample.

Hydrogen nuclear magnetic resonance (¹H-NMR) spectroscopy was carried out on a Bruker Advance 300 NMR spectrometer with tetramethylsilane as the internal reference and chloroform-d (CDCl₃) and dimethyl sulfoxide-D6 (DMSO-D6) as solvents under ambient temperature. CDCl₃ was used only for the sample NC while DMSO-D6 was employed for the rest of the samples. NMR data were collected via chemical shift (ppm, CDCl₃ and DMSO-D6 resonance as the internal standard), multiplicity and integration.

Fresh samples with rectangular shapes, similar to those prepared for DMA, were soaked in DI water for water uptake measurements. The weights of the samples were measured using an analytical balance before being soaked and daily during the water immersion test until a water uptake equilibrium was achieved. The water uptake was reported as the percentage increase with respect to the dry sample.

The anti-corrosion performance of the coatings was analyzed in an electrochemical workstation (CHI 660d, Shanghai Chenhua Instrument Corporation). The measurements were carried out in a 3.5% w/w NaCl solution with Ag/AgCl and Pt as the reference and counter electrodes, respectively. Coatings with an exposed area of 1 cm² were soaked in the electrolyte for 7 days before the electrochemical analysis. At least three samples of each formulation were analyzed together with measurements of their thicknesses by using a conventional digital micrometer.

6.3 Results

Curing of coatings

The EEW of GDE was 146 g/eq and the presence of the epoxy groups was confirmed by the absorbance bands at 1254 cm⁻¹ and 907 cm⁻¹ that are related to epoxy ring vibrations[19, 47] (Figure 6.2). These epoxy bands were not present in the spectrum of the bio-based coatings, which would suggest a complete curing. However, a detailed inspection of the spectrum showed that the epoxy bands could be overlapped by other absorbance bands at the same wavenumber of the curing agent and precursors. Therefore, it was not possible to

measure the degree of curing because of this overlapping. As it will be shown later, DSC was employed to determine whether the curing reaction was complete or not. In relation with the spectrum of the bio-based coatings, all the samples had a characteristic band at around 1727 cm^{-1} that was attributed to the carbonyl group originated mainly from the presence of the curing agent CA [25]. In addition, samples containing RV showed a small absorbance band at around 1515 cm^{-1} , which was ascribed to the aromatic C=C bond of RV [48].

Figure 6.2. FTIR spectra of the bio-based precursors (GDE, CA, HA and RV) and the bio-based coatings.

To determine whether there was an unreacted compound within the GDE coatings, DSC was performed as shown in Figure 6.3. The DSC curves only exhibited a glass transition point without trace of unreacted GDE. Therefore, we consider all the bio-based coatings were cured completely. Finally, it is worth mentioning that samples tend to plasticize when stored in humid conditions. A typical DSC curve of a plasticized polymer usually displays a lower glass transition and an endothermic process related to water desorption [49].

Figure 6.3. DSC curves of the solid bio-based samples.

The reactivity of the curing reactions was analyzed by heating the samples at different heating rates. Figure 6.4 shows typical DSC curves of the bio-based formulae. The curve displayed two characteristic peaks, one exothermic at the beginning of the heating and one endothermic at the end. In addition, some small endothermic peaks also occurred before the broad endothermic process. The exothermic process always occurred in the beginning of the heating while the intensity, width and position of the endothermic processes varied randomly. Therefore, due to its consistent presence, we believe that the exothermic peak is associated with the reaction between the epoxy groups of GDE and the carboxyl groups of the bio-based acid CA and HA. The small endothermic peaks may be the result of the secondary reactions whereas the broader endothermic peak is related to the water desorption prior to the polymer decomposition.

Figure 6.4. Typical DSC profiles of the liquid bio-based formulae: a) GDE-CA-0.90, b) GDE-CA-0.73, c) GDE-CA-HA, d) GDE-CA-HA-RV and e) GDE-CA-HA-RV-NC.

The reactivity of the main exothermic peak was studied by calculating the temperature at the maximum heat flow ($T_{\max}$) for different heating rates (Table 6.2). The results clearly

showed a common trend in the $T_{\max}$ for all the heating rates. The lowest $T_{\max}$ was found in GDE-CA-0.90, followed by GDE-CA-0.73. The $T_{\max}$ continued to increase when HA was included. The $T_{\max}$ was similar among formulae containing HA (GDE-CA-HA, GDE-CA-HA-RV, and GDE-CA-HA-RV-NC).

Table 6.2. Temperatures ($^{\circ}\text{C}$) at the maximum heat flow ($T_{\max}$) of the exothermic peak at different heating rates (Values in parentheses represent the standard deviation).

Sample	$T_{\max}$ @5 $^{\circ}\text{C}/\text{min}$	$T_{\max}$ @10 $^{\circ}\text{C}/\text{min}$	$T_{\max}$ @15 $^{\circ}\text{C}/\text{min}$	$T_{\max}$ @20 $^{\circ}\text{C}/\text{min}$
GDE-CA-0.90	83.3 (± 0.6)	93.6 (± 0.8)	99.8 (± 0.9)	104.1 (± 0.9)
GDE-CA-0.73	88.1 (± 0.9)	99.1 (± 1.1)	105.0 (± 0.8)	109.4 (± 1.1)
GDE-CA-HA	94.0 (± 0.2)	105.0 (± 1.6)	111.4 (± 1.1)	116.6 (± 1.8)
GDE-CA-HA-RV	92.2 (± 1.2)	104.0 (± 2.1)	112.5 (± 0.5)	116.3 (± 2.2)
GDE-CA-HA-RV-NC	94.1 (± 1.9)	106.1 (± 1.0)	113.6 (± 1.0)	118.5 (± 1.8)

The reaction of GDE and CA was more favorable when the concentration of the curing agent CA was higher. This suggests that CA is not only acting as a curing agent but also as a catalyst. That is, an autocatalytic reaction seemed to have occurred in the reaction of epoxy-carboxyl reaction caused by CA. However, the sole inclusion of HA (GDE-CA-HA) decreased the overall reactivity of the epoxy-carboxyl reaction as shown by the higher $T_{\max}$. A possible explanation for this result is that certain concentration of HA may have reacted with GDE which has caused an increase in the $T_{\max}$. HA is expected to be less reactive towards GDE than CA because of its lower acidity. The acidity of the first two deprotonations of CA ($\text{p}K_{\text{a}1} = 3.14$, $\text{p}K_{\text{a}2} = 4.76$, $\text{p}K_{\text{a}3} = 6.39$)[50] are higher than that of HA ($\text{p}K_{\text{a}} = 4.83$)[51]. Therefore, due to its lower acidity, HA was expected to react with GDE at a higher temperature than CA. Thus, the higher $T_{\max}$ observed in GDE-CA-HA can be ascribed to the effect caused by the reaction of HA with GDE. In summary, these results suggest that in GDE-CA-HA both CA and HA are simultaneously reacting with GDE.

The subsequent incorporation of RV and NC did not change the $T_{\max}$, which suggests that neither RV nor NC has taken part in any epoxy group reaction in the DSC experiment. Therefore, the exothermic processes of GDE-CA-HA-RV and GDE-CA-HA-RV-NC were

still attributed to the main reaction of GDE with CA and HA with no participation of RV and NC under these experimental conditions. Further discussion will be made next on how RV is incorporated into the polymer network.

Characterization of GDE-RV and GDE-RV-NC

In order to understand how RV and RV/NC were incorporated into the polymer network, it is important to recall the methodology to prepare GDE-CA-HA-RV and GDE-CA-HA-RV-NC. As described in the experimental section, GDE was first mixed and heated with RV or RV/NC before being mixed with CA and HA. The purpose of this experimental step was to allow the solid RV to be dissolved in GDE first so that a liquid mixture is formed that will allow the further addition of the other liquid compounds. The mixture GDE-RV and GDE-RV-NC was analyzed by NMR as shown in Figure 6.5 a, b and compared with the spectra of GDE, RV and NC in Figure 6.6. It can clearly be seen that the spectrum of GDE+RV is just a simple overlay by those of GDE and RV. In the spectrum of GDE-RV, the peaks from 6.0 ppm to 10.0 ppm are from RV, while those lower than 6.0 ppm correspond to GDE. Similarly, the spectrum of GDE-RV-NC is almost the same as that of GDE-RV (Figure 6.5 c). In addition, no characteristic peaks of NC were found in the spectrum of GDE-RV-NC. This can be explained by the low concentration of NC (1 % w/w), which has made it hardly detectable.

Figure 6.5. ^1H -NMR spectra of a) GDE-RV and b) GDE-RV-NC and c) GDE-RV and GDE-RV-NC together.

Figure 6.6. ^1H -NMR spectra of a) GDE, b) RV and c) NC.

Other characterizations were also performed for GDE-RV and GDE-RV-NC. The titration results showed that EEWs of GDE-RV and GDE-RV-NC were 181 and 191 g/eq, respectively. Therefore, the EEWs of GDE-RV and GDE-RV-NC were similar to each other but higher than that of GDE (146 g/eq). The higher EEWs of GDE-RV and GDE-RV-NC were attributed to the dilution effect caused by the incorporation of RV and RV/NC. Moreover, the viscosities of GDE, GDE-RV and GDE-RV-NC were 1.33 P, 4.17 P and 4.33 P, respectively. Thus, the higher viscosities of GDE-RV and GDE-RV-NC (than GDE) were also ascribed to the presence of the bio-based additives RV and NC. To further assist the analysis, DSC profiles of GDE, GDE-RV and GDE-RV-NC were also obtained from -90°C to 300 °C, as shown in Figure 6.7a. The DSC profile of GDE showed a characteristic glass transition at -67°C and exothermic process around 150°C. The glass transition exhibited by GDE demonstrates that GDE is not a single molecule; rather it has an oligomeric structure. A possible cause of the oligomeric nature of GDE could be related to the synthetic methodology employed in the epoxidation of glycerol. A typical epoxidation of an alcohol with epichlorohydrin usually produces oligomers rather than an epoxy monomer. This observation is also corroborated with higher EEW (146 g/eq) of GDE in comparison with its theoretical EEW (102 g/eq). On the other hand, the exothermic process can be attributed to the presence of impurities as GDE is of technical grade. In contrast, GDE-RV and GDE-RV-NC displayed a shift in the glass transition (-59 °C) and some small endothermic peaks from 140 °C to 170°C. The slightly higher glass transition temperature may be a result of the higher entanglement of GDE with RV and NC. The small endothermic peaks were assigned to the presence of impurities or some unknown reactions. However, it is worth mentioning that these small endothermic peaks are not related to the melting of RV as it happens at around 270 °C (Figure 6.7b).

In summary, based on the NMR results (Figure 6.5 & Figure 6.6), RV has not chemically reacted with GDE during the pre-curing step (120°C, 10 minutes). In addition, since the analysis of the DSC thermographs (Table 6.2, Figure 6.4) suggests that the RV did not chemically reacted with GDE during the heating ramp, some of the RV may have remained and not covalently bonded to the polymer network in GDE-CA-HA-RV and GDE-CA-HA-RV-NC. The lower reactivity of RV in comparison with CA and HA can be seen in its

lower acidity ($pK_{a1} = 9.16$, $pK_{a2} = 9.77$, $pK_{a3} = 10.55$) [52]. The low acidity of RV does not favor the reaction between its hydroxyl groups and the epoxy groups of GDE as it is expected in a polyphenol compound and epoxy resin [53, 54]. Furthermore, in terms of stoichiometry, the total amount of CA and HA employed in the formulation can react with 93% of the epoxy groups of GDE, and half of the RV is in excess in relation with GDE. Therefore, considering the above results and the fact that all the epoxy groups were consumed (Figure 6.3), it is reasonable to assume that some remaining RV has not covalently bonded to the polymer network. Regarding NC, it is difficult to prove if NC has cross-linked with CA due to its low concentration.

Figure 6.7. DSC curves of a) the precursors GDE-RV and GDE-RV-NC compared with that of GDE and b) RV.

Thermal and mechanical properties

Glass transition temperatures (T_g) of the bio-based coatings were measured by DSC (Table 6.3). In addition, the T_g from DMA was calculated as the temperature at which $\tan\delta$ was the maximum and considered as the T_g values obtained from the DMA experiments (Figure 6.8 & Table 6.3). Both DSC and DMA results showed a characteristic trend of the T_g as the bio-based additives were successively incorporated into the polymer. GDE-CA-0.90 had the highest T_g while GDE-CA-0.73 possessed a slightly lower T_g . The sole incorporation of HA (GDE-CA-HA) caused a further drop in the T_g . However, the

subsequent inclusion of RV (GDE-CA-HA-RV) and the further addition of NC (GDE-CA-HA-RV-NC) did not significantly change the T_g ³. The trend of the T_g values was also corroborated with the storage modulus (E') at 25°C of the polymers, which showed that the unmodified samples were stiffer than the modified samples (Table 6.3).

Figure 6.8. a) Storage modulus and b) $\text{Tan}\delta$ plots of the bio-based polymers.

In addition, we have also assessed the crosslink densities (v_e) of the bio-based polymers. The v_e value is calculated from the following equation:

$$v_e = \frac{E'}{3RT} \quad \text{Equation 6.1}$$

where E' is the storage modulus at a specific temperature T in the rubbery state, and R is the universal gas constant [55]. For the calculations, $T = 30K + T_g$. Samples GDE-CA-0.90 and GDE-CA-0.73 displayed similar and highest v_e values. The introduction of HA decreased the v_e , and the combined incorporation of HA and RV reduced the v_e even more⁴. Further incorporation of NC did not cause a significant change in the v_e .

³ No significant differences at the 0.05 level (ANOVA).

⁴ Significant differences at the 0.05 level (ANOVA).

Table 6.3. Glass transition temperature (T_g) and DMA data (storage modulus (E'), crosslink density (v_e) and T_α) of the bio-based polymers (Values in parentheses represent the standard deviation).

Sample	T_g (°C) (DSC)	T_α (°C) (DMA)	E' @ 298.15 K (MPa)	E' @ $T_\alpha + 30K$ (MPa)	v_e (mol/m ³)
GDE-CA-0.90	37.3 (± 2.7)	51.1 (± 0.8)	1998 (± 266)	9.2 (± 0.7)	1046 (± 78)
GDE-CA-0.73	30.6 (± 0.9)	45.5 (± 1.2)	2272 (± 172)	10.2 (± 0.4)	1178 (± 39)
GDE-CA-HA	22.6 (± 5.4)	30.8 (± 4.5)	745 (± 482)	6.9 (± 1.3)	824 (± 153)
GDE-CA-HA-RV	26.2 (± 3.1)	34.8 (± 2.0)	606 (± 238)	4.6 (± 0.8)	538 (± 90)
GDE-CA-HA-RV-NC	30.4 (± 1.7)	37.2 (± 2.9)	858 (± 378)	4.2 (± 0.6)	489 (± 70)

GDE-CA-0.90 had a higher T_g than that of GDE-CA-0.73 but its v_e was similar to that of GDE-CA-0.73. This result is unusual since GDE-CA-0.90 was expected to have a higher v_e than that of GDE-CA-0.73 due to the higher concentration of CA in GDE-CA-0.90 that can crosslink with GDE [56]. However, a similar phenomenon was reported in which the T_g of an epoxy polymer increased but its v_e decreased while increasing the concentration of the curing agent [25]. According to the authors, this effect was caused by the intramolecular reactions of the epoxy resin alone. However, the results of Table 6.3 suggest a possible situation that not all the carboxylic groups of CA in GDE-CA-0.90 have been cross-linked during the polymer reaction. Thus, the incomplete reaction of carboxylic groups may have led to the creation of pendant groups in the polymer network. Although the formation of pendant groups can decrease the T_g [57], it can also have the opposite effect. The presence of pendant groups could also have favored the formation of more entanglements in the polymer and caused an increase in the T_g [58, 59]. Therefore, in comparison with GDE-CA-0.73, an increase in the concentration of CA in GDE-CA-0.90 did not favor an increase in v_e despite that it did favor the formation of pendant groups.

On the other hand, the lower T_g observed in GDE-CA-HA was a result of its low crosslink density. The DSC results (Table 6.2, Figure 6.4) suggest that there was a simultaneous reaction between the bio-based acids (CA and HA) and GDE. Due to the different acidity between CA and HA, it was expected that CA would react with most of the epoxy groups of GDE rather than HA. Therefore, HA was expected to react with the secondary OH groups formed out of the reaction between CA and GDE in the later stage of the curing.

However, the DSC results suggest a simultaneous reaction of CA and HA with the resin that may have caused the formation of a branched polymer structure. Thus, the normal reaction between CA and GDE to form a polymer network was hampered by the concurrent reaction between the monofunctional carboxyl acid HA and GDE. In consequence, GDE-CA-HA possessed not only a branched structure but also a low crosslink density (the lower ν_e of GDE-CA-HA was proven by DMA results in Table 6.3). Therefore, the lower T_g of GDE-CA-HA was ascribed to its low ν_e that had a major effect over its branched structure.

Nevertheless, the subsequent incorporation of RV and RV/NC did not significantly change the T_g of the polymer. The T_g values of the modified samples (GDE-CA-HA, GDE-CA-HA-RV and GDE-CA-HA-RV-NC) were quite similar. When comparing GDE-CA-HA and GDE-CA-HA-RV alone, it was expected that GDE-CA-HA-RV would have higher T_g than that of GDE-CA-HA because of the presence of a rigid additive such as RV. However, this effect was not found because the incorporation of RV decreased the ν_e of the polymer (Table 6.3). Nevertheless, the decrease of the ν_e of GDE-CA-HA-RV did not cause a drop in its T_g . Therefore, the results indicate that the lower ν_e of GDE-CA-HA-RV might be compensated by the rigidity of RV which has caused its T_g to be similar to that of GDE-CA-HA. On the other hand, GDE-CA-HA-RV and GDE-CA-HA-RV-NC had similar T_g and ν_e values, which suggests that NC did not cause any change on these properties. Although NC could have increased the T_g by creating more entanglements through its aliphatic chains, its low concentration (1%) may have prevented this effect from being perceptible.

The decomposition temperatures of the samples were investigated by TGA. The temperature at 5% mass loss, at 10 % mass loss and at the maximum rate of decomposition were calculated and denoted as $T_{d5\%}$, $T_{d10\%}$ and T_{dmax} ($^{\circ}\text{C}$), respectively (Figure 6.9, Table 6.4). The results show that all the samples possessed very similar $T_{d5\%}$, $T_{d10\%}$ and T_{dmax} . Thus, the bio-based additives did not affect the thermal decomposition properties of the polymers. However, there was an effect on the amount of residue caused by the additives. The percent residues of the unmodified samples (GDE-CA-0.90 and GDE-CA-0.73) and GDE-CA-HA were the lowest among all samples, while GDE-CA-HA-RV and GDE-CA-

HA-RV-NC had the highest residue percentages (almost double those of the former group of samples). The highest residue values of the aforementioned samples were ascribed to the presence of RV. This is in agreement with recent reports that polymers containing RV showed higher char yield [34, 48]. Therefore, due to its unique molecular structure, RV releases a low concentration of gases when burned and, therefore, conferring a higher char yield.

Figure 6.9. TGA thermographs of the epoxy cardanol-based coatings.

Table 6.4. Decomposition temperatures and percent residue. (values in parentheses represent the standard deviation).

Sample	T _{d5%} (°C)	T _{d10%} (°C)	T _{dmax} (°C)	Residue (%)
GDE-CA-0.90	262.7 (±7.4)	301.6 (±3.4)	362.1 (±1.8)	7.50 (±0.12)
GDE-CA-0.73	268.0 (±4.0)	306.8 (±2.1)	362.2 (±0.3)	7.30 (±0.36)
GDE-CA-HA	258.5 (±1.6)	301.5 (±0.8)	364.2 (±0.7)	6.04 (±0.30)
GDE-CA-HA-RV	263.0 (±5.3)	305.3 (±3.2)	365.5 (±1.0)	13.28 (±0.12)
GDE-CA-HA-RV-NC	261.6 (6.2)	304.1 (3.1)	365.5 (0.7)	12.82 (0.14)

Wettability

The water affinity of the samples was assessed by contact angle measurement on coating surfaces and bulk water uptake (Table 6.5). Based on the wettability properties, the unmodified samples (GDE-CA-0.90 and GDE-CA-0.73) had similar water angles and

surface energy. The incorporation of HA and RV did not improve the hydrophobicity. GDE-CA-0.90/0.73 and the modified coatings GDE-CA-HA and GDE-CA-HA-RV displayed similar water contact angles (WCAs) and surface energies. On the other hand, the incorporation of NC caused an increase in the WCA by around 12° and a decrease in the surface energy by 7 mJ/m^2 when compared with the other coatings. The displayed intrinsic hydrophobic properties of NC were in accordance with a previous report [43]. Our results confirm that NC has a better hydrophobic effect over the other bio-based additives (HA and RV). The concentration of the additives did not seem to play a major role in their ability to hydrophobize the coating, as the amount of added NC was the least (1% w/w) as compared with HA (15% w/w) and RV (9% w/w). A possible explanation of the better hydrophobic properties of NC may rely on its molecular structure. As shown in Figure 6.1, NC is more flexible, longer and more branched than the other bio-based additives. Thus, it is reasonable to suggest that the molecular structure (length and ramification) of the additive has a great influence on its hydrophobization ability.

Table 6.5. Wettability and water uptake data of various formulae (values in parentheses represent the standard deviation).

Sample	WCA ($^\circ$)	Surface energy (mJ/m^2)	Water uptake (%)
GDE-CA-0.90	72.19 (± 2.40)	30.89	33.62 (± 0.91)
GDE-CA-0.73	72.25 (± 3.96)	31.86	32.60 (± 0.91)
GDE-CA-HA	74.96 (± 3.95)	29.87	22.18 (± 0.57)
GDE-CA-HA-RV	75.40 (± 1.90)	28.17	24.15 (± 0.73)
GDE-CA-HA-RV-NC	87.22 (± 1.42)	22.40	23.73 (± 1.08)

The water uptake results were analyzed in terms of the degree of hydrophobicity and crosslink density. It is worth mentioning that water uptake data might be affected by the possible leaching of unreacted soluble components in the formulation. This is an intrinsic issue of this type of experiment. One has to be cautious when comparing the uptake values between formulae that contain precursors with very different solubility.

The unmodified coatings (GDE-CA-0.90 and GDE-CA-0.73) exhibited similar and the highest percent water uptake regardless of the amount of curing agent used. However, the samples modified with the bio-based additives showed similar and lower water uptake

values. The unmodified samples had the highest water uptake due to their high degree of hydrophilicity despite of their high degree of crosslink density. Although higher cross-linked polymers are expected to have lower water uptake, the higher hydrophilicity of the GDE and CA drives the diffusion of water into the polymer network. In contrast, the lower water uptake of the samples modified with the bio-based compounds was ascribed to the higher degree of hydrophobicity although they possessed a lower crosslink density. Due to their aliphatic chains and/or benzene groups, the bio-based additives HA, RV and NC are able to improve the hydrophobicity of the polymers. However, the introduction of the additives caused a decrease in the crosslink density that may favor the diffusion of water molecules. Nevertheless, the hydrophobicity imparted by the bio-based additives played a more dominant role in the water uptake over the crosslink density.

The similar water uptake of the three modified samples can be explained by the similar overall degree of hydrophobicity and crosslink density. For example, GDE-CA-HA had a higher v_e than that of GDE-CA-HA-RV, but both of them had very similar water uptake. This suggests that the hydrophobicity action of RV and HA was more effective than that of HA alone. GDE-CA-HA-RV compensated its lower v_e with a better bulk hydrophobicity granted by RV, which has led to a very similar water uptake as that of GDE-CA-HA. RV seemed to be a better hydrophobizer than HA due to its bigger and more rigid structure. In case of GDE-CA-HA-RV and GDE-CA-HA-RV-NC, their similar water uptake values were the result of their similar v_e values and bulk hydrophobicity. That is, the low concentration of NC did not affect the ultimate bulk hydrophobicity of the polymer network but only the surface hydrophobicity as shown in the WCA and surface energy results. Therefore, the hydrophobic surface effect of NC did not prevent water from coming into the bulk polymer. In summary, the three modified samples had very similar combined effect of crosslink density and hydrophobicity as far as water uptake is concerned.

Anticorrosion performance

The anticorrosion properties of GDE-CA-0.90, GDE-CA-0.73 and GDE-CA-HA-RV-NC were studied by Tafel analyses (Figure 6.10). Table 6.6 shows the start of corrosion signal,

the thicknesses of the samples, the corrosion potential (E_{corr}) and corrosion current (I_{corr}). Materials with high resistance to corrosion are expected to have higher E_{corr} values and lower I_{corr} values. However, after reaching the equilibrium in the seventh day, some samples displayed inconsistent trend for E_{corr} and I_{corr} values, which makes the comparison difficult among them in terms of corrosion resistance (e.g., GDE-CA-0.73 showed a better I_{corr} , but a worse E_{corr} than SS). Nevertheless, the anti-corrosion performance can still be evaluated from the perspective of corrosion delay. The results show that SS without coating started to corrode immediately after being immersed in the electrolyte. In contrast, the corrosion started after several days' immersion in the electrolyte for SS coated with the bio-based polymers. Among the bio-based polymers, GDE-CA-HA-RV-NC delayed the corrosion reaction by 2 more days than GDE-CA-0.90 and GDE-CA-0.73. Since the thicknesses of the bio-based coatings were quite similar, this result indicates that GDE-CA-HA-RV-NC protected SS against corrosion better than GDE-CA-0.90 and GDE-CA-0.73 in terms of the corrosion delay. This is in good agreement with the water uptake results (Table 6.5) in which GDE-CA-HA-RV-NC absorbed less water than GDE-CA-0.90 and GDE-CA-0.73. Overall, the modified coating showed a better corrosion protection than that of the unmodified coating because of its delay effect.

Figure 6.10. Typical Tafel curves of the bio-based coatings.

Table 6.6. Corrosion parameters of the bio-based coatings and SS after 7 days of soaking (values in parentheses represent the standard deviation).

Sample	Coating thickness (mm)	Start of Corrosion Signal	E_{corr} (V vs Ag/AgCl)	I_{corr} (A/cm ²) x 10 ⁻⁸
Stainless Steel (SS)	-	Immediately	-0.288 (±0.05)	109 (±49.7)
GDE-CA-0.90	2.52 (±0.078)	~ 5 th day	-0.388 (±0.01)	34.9 (±23.4)
GDE-CA-0.73	2.54 (±0.045)	~ 5 th day	-0.236 (±0.03)	55.1 (±33.9)
GDE-CA-HA-RV-NC	2.66 (±0.002)	~ 7 th day	-0.368 (±0.00)	3.39 (±0.23)

6.4 Conclusions

New fully bio-based epoxy polymers were prepared using only water as the solvent. The influence of the curing agent concentration and three bio-based additives (HA, RV, NC) on the mechanical and thermal properties, as well as the hydrophobicity and corrosion resistance of the epoxy thermosets were studied. The results show that bio-based additives have been chemically incorporated into the polymer network. Incorporation of the bio-base additives has caused a decrease in the crosslink density, which would eventually affect the mechanical properties of cured polymers. Two main factors were ascribed to this effect. First, HA obstructed the reaction of CA and GDE by reacting with GDE simultaneously. Second, the incorporation of RV and NC has caused a steric impediment on the curing reaction of the small and flexible molecules (GDE, CA and HA) because of their bigger molecular sizes. Nevertheless, the samples modified with the additives were able to absorb a lower amount of water despite of their low crosslink density. The lower water uptake of GDE-CA-HA-RV-NC allowed it to have better anticorrosion performance than GDE-CA-0.90 and GDE-CA-0.73 as shown in its better corrosion delay. Moreover, RV-containing samples were characterized by having higher percentages of chars while NC-containing samples were characterized by their lower surface energy. Finally, it is suggested that the hydrophobic properties of the samples can be improved if the crosslink density is improved. Higher degree of curing can be achieved by various methods such as increasing the curing

time/temperature or using catalysts to accelerate specific reactions. We wish that the current work opens an avenue towards fully bio-based environmentally-friendly epoxy coatings for hydrophobic applications.

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Chapter 7

Conclusions and Recommendations

This chapter summarizes key findings of the thesis work. Based on the lessons learnt, general plan for preparing superhydrophobic bio-based epoxy coatings is discussed. The extent to which this research plan aims to achieve is compared with the available resources to conduct this research, as well as its inherent challenges. Recommendation for future research in this area is given in the end of the chapter.

7.1 Conclusions

New hydrophobic bio-based epoxy coatings have been prepared and their anti-corrosion and anti-icing properties evaluated in the current thesis. Three different bio-based epoxy resins were selected and employed from three different bio-based sources: isosorbide, cardanol and glycerol. Isosorbide is a derivative of polysaccharides, while cardanol and glycerol can be obtained from the cashew nutshell liquid and natural oils, respectively. This selection was based on the nature of the molecular structure, and the three bio-based epoxy resins show different molecular structures. Isosorbide is characterized by its fused furan rings, whereas cardanol possess phenolic rings with aliphatic chains as substitutes, and glycerol is a short aliphatic polyol. The hydrophobization of the bio-based epoxy resins were carried out using different compounds. The hydrophobization of isosorbide-based coatings were done by using a fluoroalkyl compound whereas cardanol and glycerol-based coatings were hydrophobized using fluorine-free compounds. Cardanol-based coatings were hydrophobized by a polysiloxane and glycerol-based coatings were hydrophobized by various bio-based additives. The bio-based content increased gradually as the research work progressed. In the isosorbide-based coatings, the bio-based content relied on the isosorbide resin since the hydrophobic additive, which also played the role of curing agent, was not a bio-based compound. In the case of the cardanol-based coatings, the bio-based content was increased by including bio-based curing agents but the hydrophobizer (an amino-terminated PDMS) remained non bio-based. In the glycerol-based coatings, both the curing agent and the hydrophobizers are derived from biomass (100% bio-content).

The overall results demonstrated that initial hypothesis, that eco-friendly synthesized and bio-based epoxy resins can be properly used to prepare hydrophobic coatings that can applied as anti-corrosion and anti-icing coatings, was proven to be true to some degree. The proposed hypothesis can be analyzed in two different aspects: a) composition and preparation, and b) performance.

In relation with the composition and preparation, the research has proven that hydrophobic epoxy coatings can be prepared by using bio-based epoxy resins and without the use of

organic solvents. In the synthesis of isosorbide-based coatings, coatings were prepared by mixing water soluble precursors (hydrophilic) but became hydrophobic with the addition of the hydrophobizer (F8815). In addition, due to the fact that F8815 was soluble in water, water was the only solvent used in the preparation of the polymer coatings. In the fabrication of the cardanol-based coatings, most of the unmodified coatings were hydrophilic but were hydrophobized with the addition of an amino-terminated PDMS. In this systems, no solvent was used as all the employed compounds were liquid at room temperature. In case of the preparation of the glycerol-based coatings, water was used as solvent to dissolve citric acid. However, in this system, the hydrophobization was not enough to attain coatings with $WCA > 90^\circ$. It was shown that the unmodified sample and some other modified samples were hydrophilic ($WCA \sim 75^\circ$). However, the incorporation of NC514 bestowed the coatings with better hydrophobicity with $WCA=87^\circ$.

In terms of performance, the results proved that hydrophobic coatings can exhibit better anti-corrosion and anti-icing properties than those of hydrophilic coatings. In the isosorbide-based coatings, the hydrophobic coating (S0.5) showed better anti-corrosion performance than that hydrophilic coating (iso_{net}). In case of the cardanol-based coatings, the evaluation of the anti-corrosion performance was difficult because of the different thicknesses of the coatings. Nonetheless, the analysis done on the samples with similar thicknesses provided an interesting insight into the relationship between crosslink density and hydrophobicity. It was found that transforming a coating from hydrophilic to hydrophobic may not necessarily cause an improvement in its anti-corrosion properties if the crosslink density is still low. Furthermore, the anti-icing properties of the bio-based coatings were improved by the incorporation of the hydrophobizer. The investigation on the glycerol-based coatings showed that hydrophobic coatings had a better corrosion protection than those of the hydrophilic coatings. Hydrophobic coatings excelled at their longer retardation on the corrosion processes over the hydrophilic coatings.

7.2 Future work

This research has demonstrated that polymer coatings with hydrophobic properties can be prepared from bio-based epoxy resins. In addition, it was shown that a well-designed hydrophobic coatings exhibited better anti-corrosion and anti-icing properties than those of hydrophilic coatings. Therefore, bio-based epoxy resins have the potential to replace petro-based epoxy resins for the preparation of anti-corrosion and anti-icing coatings. However, the market insertion of the bio-based epoxy resins must be done by considering two important aspects: cost and recyclability. The production of bio-based epoxy resins must be economical so that they can compete with the non-renewable epoxy resins. Furthermore, bio-based epoxy resins must be designed with the ability to be recyclable. These two topics are suggested as the future work in line with this PhD thesis.

The new bio-based epoxy resins must be produced from bio-based chemicals that have a potential to develop in the market. For example, the US. Department of Energy has proposed 12 types of bio-based chemicals with great potential to be well established in the market. This group of strategic bio-based chemicals is characterized by its simple production that requires one single step from sugar as a precursor [1]. Moreover, these bio-based chemicals are also considered building blocks because other relevant compounds can be synthesized from them. Figure 7.1 shows this group of bio-based chemicals together with other platform chemicals added by Stadler et al. [2]. These platform chemicals can also be used for the preparation of bio-based curing agents and hydrophobizers. Therefore, it is proposed that new bio-based epoxy coatings must be developed from platform bio-based chemicals so that their incorporation into the market is favored.

Figure 7.1. Platform chemicals suggested by the U.S. Department of Energy (in black). Other platform chemicals are shown in red [2] .

Another aspect to be considered in the continuation of this research is on the biodegradability and toxicity of the epoxy thermosets. As discussed in Chapter 2, the use of bio-based chemicals do not necessarily ensure the creation of biodegradable polymers. Therefore, the biodegradability of the bio-based epoxy thermosets must be intentionally considered since the selection of the bio-based precursors. For example, it is known that ester linkages are prone to undergo hydrolysis which can be done in naturally humid environments. Thus, epoxy thermosets designed with ester linkages can be biodegraded by the action of water and bacteria [3]. Another indirect approach to study the biodegradability of epoxy thermosets is by searching the types of bacteria and conditions in which the epoxy polymer can be biodegraded [4]. In this sense, it is proposed that epoxy polymers must be

designed with chemical bonds that are sensitive to break under certain environmental conditions. Another aspect to consider is the toxicity of the polymer coating during its performance. Although bio-based polymers with biodegradability properties could be designed, the biodegradability of a polymer does not make it a completely non-toxic material. That is, biodegradable and bio-based polymers may still have the potential to be toxic to the environment by the leaching of additives or uncrosslinked reagents which may negatively affect the ecosystem [5]. Therefore, designing epoxy thermosets with specific biodegradability, minimum toxicity and without significant negative effects on their performances are still challenges in the field of polymer science.

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