Scientific Research Publishing

Journal of Materials Science and Chemical Engineering, 2024, 12, 94-106
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

Phlorotannins from Brown Algae as a Sustainable Aquatic Feedstock for Epoxy Resins

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How to cite this paper: Winkel, A., Kahlmeyer, M., Böhm, S., Fuhrmann-Lieker, T. and Burk, M.H. (2024) Phlorotannins from Brown Algae as a Sustainable Aquatic Feedstock for Epoxy Resins. *Journal of Materials Science and Chemical Engineering*, **12**, 94-106.
https://doi.org/10.4236/msce.2024.1211006

Received: October 7, 2024
Accepted: November 26, 2024
Published: November 29, 2024

Abstract

Bisphenol A (BPA) is the primary chemical used in the production of epoxy resins but as of today is not widely available in a bio-based form. BPA is also classified as a substance of very high concern due to its reproductive toxicity and endocrine-disrupting effects. Phlorotannins, a type of polyphenols, offer a promising structural alternative to bisphenol A as a more sustainable option. They are found in high quantities in brown algae, which are already harvested for alginate production. As a result, phlorotannins present an under-researched yet promising marine resource for the chemical industry, particularly in the area of epoxy resin formulation. In this study, a model epoxy resin compound based on phloroglucinol, the simplest phlorotannin, was chosen to explore its reactivity and the thermo-mechanical properties of epoxy resins based thereof. As hardeners well-established systems like isophorone diamine for ambient temperature cure as well as heat-curing anhydrides and dicyandiamide were used. Across all cases, thermosets with glass transition temperatures above 100˚C were achieved under cross-linking conditions similar to those used today. One phthalic anhydride derivative yielded a glass transition temperature of 198˚C, highlighting the significant potential of these algae-based epoxy resins for industrial uses, such as impregnating resins for fiber-reinforced plastics.

Keywords

Epoxy Resins, Algae, Phlorotannins

1. Introduction

1.1. General Discussion

The replacement of petroleum-based chemicals with sustainable alternatives derived from biological raw materials has become increasingly crucial as the global community seeks to achieve CO_2 reduction targets and mitigate global warming. Consequently, fundamental research has broadened in recent years to include polymeric materials that possess similar properties to established systems but with a lower carbon footprint. This often coincides with the growing demand for high recyclability and biodegradability [1]. This trend is especially evident in the thermoplastic sector, where products made from starch [2], cellulose [3], proteins [4], and other materials have been developed. In the case of polylactic acid (PLA), such products are already widely available [5].

While thermoplastics make up the majority of all polymer types, largely driven by the high demand from the packaging industry, thermosets, particularly epoxy resins, play a critical role in manufacturing. Epoxy resins are highly valued for applications such as coatings, potting agents, matrices for fiber-reinforced plastics, and adhesives. Due to their exceptional technical properties, including high mechanical strength, chemical resistance, and strong adhesion, epoxy resins remain irreplaceable in many applications where alternatives like acrylics or polyurethanes fall short. As a result, the bio-based synthesis of epoxy resin precursors or components is essential for enhancing the sustainability of these thermoset systems.

However, bisphenol A (BPA), the key chemical used in epoxy resin production, is still not widely sourced from biological origins [6], though initial efforts have been made, such as facilities producing BPA from biomass naphtha [7]. In recent years, potential alternatives to BPA, such as epoxidized vegetable oils (EVOs), have emerged. These are derived by epoxidizing the aliphatic unsaturated fatty acid backbone using peracids, peroxides, or molecular oxygen. Currently, EVOs are used as plasticizers, stabilizers, or reactive additives in epoxy resin formulations. However, their reactivity is lower compared to bisphenol- or novolak-based resins, which means thermosets made entirely from EVOs often require longer curing times and higher curing temperatures, such as when cured with anhydrides. Additionally, these resins typically have relatively low glass transition temperatures, limiting their application in high-temperature environments [8]. Furthermore, ambient curing with amines can result in undesirable side reactions, such as the conversion of ester groups into amides. These limitations restrict the use of EVOs as thermosetting resins for demanding industrial applications, highlighting the increasing need for additional biological feedstock that can be easily converted into reactive resin components through established methods for sustainable manufacturing.

1.2. Phlorotannin-Based Epoxy Resins from Brown Algae

1.2.1. Phlorotannins

Phlorotannins are a class of polyphenols primarily found in brown algae [9]. They are essentially oligomers derived from phloroglucinol (1,3,5-trihydroxybenzene). The classification of phlorotannins depends on the type of linkage between subunits – such as direct phenyl-phenyl linkage, ether linkage, a combination of ether and C-C bonds, or dibenzo-p-dioxin linkage - and the nature of the subunits themselves, which can include simple phloroglucinol units or aromatic rings bearing additional hydroxyl groups. Based on these variations, six categories of phlorotannins can be identified: fucols, phlorethols, fuhalos, fuco-phlorethols, eckols, and carmalols, whose general structures are illustrated in **Figure 1**.

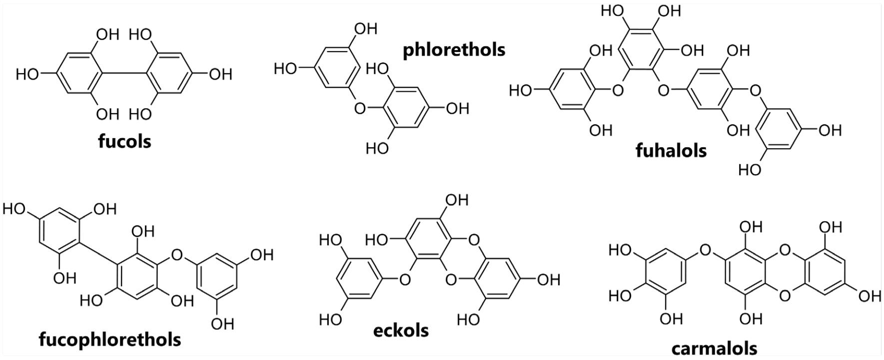

Figure 1. Classification of phlorotannins.

Phlorotannins are found within algal cells in organelles known as physodes and in the cell walls, where they are crosslinked to alginates. Consequently, phlorotannin extraction in the long term could theoretically largely rely on the same harvesting methods already established for alginate production. Estimates suggest that approximately 30,000 to 40,000 tons of alginate are extracted globally each year [10] [11], with a maximum content exceeding 40% of the dry algae mass [12]. Considering these figures and the potential contribution of phlorotannins, which can account for up to 20% by weight of the dry matter [13], this could ideally yield an annual production of 15,000 to 20,000 tons of algae-based phlorotannins without the need for dedicated algae farming specifically built up for phlorotannin extraction. However, the composition of the phlorotannin mixture varies significantly among different algal species and is also heavily influenced by growth conditions. The compounds that constitute the largest share of phlorotannins in brown algae are illustrated in **Figure 2**.

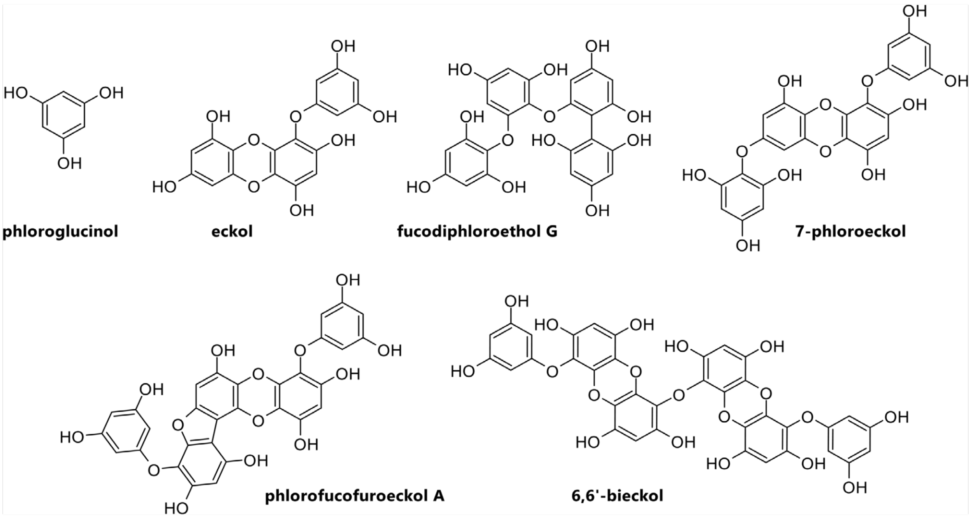

Figure 2. Phlorotannins derivates with the largest share in brown algae.

Phlorotannin extraction is typically performed using water with a certain amount of alcohol or acetone, often assisted by ultrasound. The crude fractions obtained can be further purified by extraction with organic solvents. Although various procedures, mainly based on solid-liquid extraction, have been documented in the literature [14], efficient extraction methods tailored to specific algal species for industrial applications have yet to be developed. In addition, it remains unclear whether the theoretically promising utilization of alginate extraction by-products can be efficiently achieved.

Several colorimetric methods exist to determine the phenolic content in crude or purified phlorotannin extracts, such as the Folin-Ciocalteau method [15] and the DMBA assay [16]. The DMBA assay uses 2,4-dimethoxybenzaldehyde, which reacts specifically with 1,3- and 1,3,5-substituted phenols. The total hydroxyl content can be measured by reacting the phlorotannin with acetic anhydride and titrating the resulting acetic acid with sodium hydroxide [17]. Understanding the hydroxyl number of the phlorotannin mixture is crucial for the subsequent introduction of epoxy groups, as described in the following section.

1.2.2. Epoxy Resins of Phlorotannins

The standard approach for introducing epoxy groups into phenolic compounds involves reacting them with epichlorohydrin (EPI) [18], either with or without a phase transfer catalyst, followed by a basic workup. In this process, the compound typically serves both as a reactant and a solvent and is thus applied in excess amounts. EPI itself can be produced from bio-glycerol, making it a potentially sustainable chemical. However, due to its carcinogenic nature, alternative reaction pathways are being explored. A prominent one is the reaction with allyl chloride, followed by a Prilezhaev reaction, which can be carried out enzymatically [19]. Both reaction pathways, using phloroglucinol as a representative for the phlorotannin compound class, are illustrated in **Figure 3**.

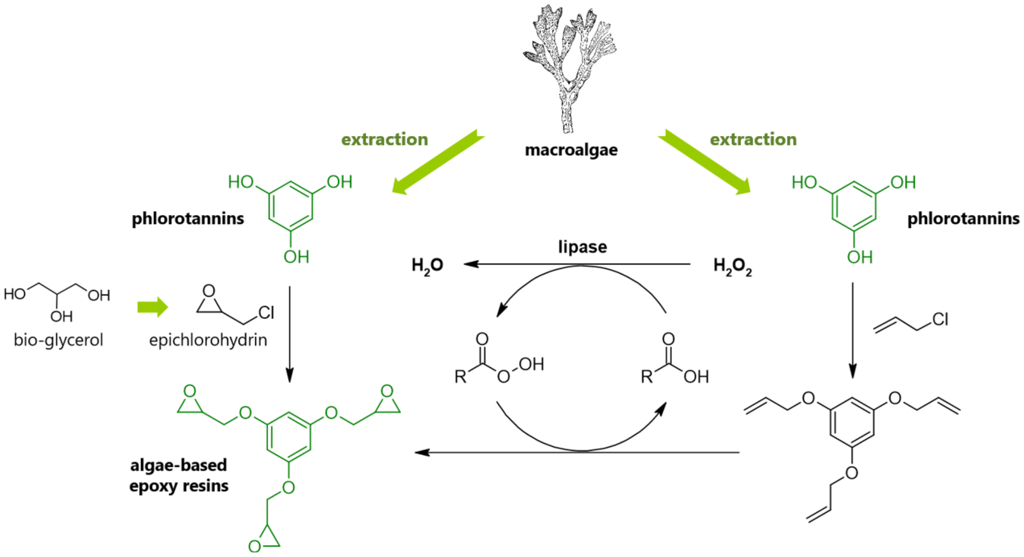

Figure 3. Most prominent reaction pathways leading to the introduction of epoxy groups into phenolics.

1.3. Requisite Factors for Industrially Applicable Epoxy Resins

Thermosets can be tailored for a wide range of applications due to the numerous combinations of resins, curing agents, catalysts, additives, and curing methods available. As a result, it is challenging to make broad generalizations about the characteristic properties of epoxy resins. Nevertheless, some observations can be made regarding the curing of BPA-based systems with well-established curing agents like amines and anhydrides, as cited in the literature [20]:

1) Curing with aliphatic amines typically occurs readily at room temperature but can be accelerated at elevated temperatures.

2) Anhydride-curing is a slow process that requires heat for efficient cross-linking, sometimes demanding temperatures of up to 200˚C.

3) The curing process with anhydrides can be accelerated by adding catalysts such as tertiary amines or imidazoles.

4) Anhydride curing tends to exhibit low curing enthalpies.

Among the various properties that provide information about the performance of epoxy resins, curing kinetic-related factors are particularly important for assessing their suitability for industrial purposes. For instance, the gelation time during ambient temperature curing and the gelation temperature during heat curing indicate the transition point in the hardening process when the system changes from a gel to a solid state, thus gaining a certain degree of internal strength. Additionally, the heat released during curing, the curing enthalpy ΔH, should remain low to prevent self-combustion of the mixture due to the exothermic nature of the curing reaction. Moreover, it is advantageous for cross-linking to occur efficiently at lower temperatures, even in heat-curing systems, as this significantly reduces energy consumption during manufacturing and helps to keep the product carbon footprint low. From a thermo-mechanical perspective, the glass transition temperature is also vital since it constrains the thermoset's use in higher-temperature applications, where the polymer may behave in a rubber-like manner.

For an initial assessment of the potential of algae-based epoxy resins for demanding applications, in this study, these characteristics mentioned above were evaluated for a glycidyl ether derived from phloroglucinol, the simplest phlorotannin, in combination with well-established hardeners.

2. Experimentals

2.1. Materials and Methods

The phloroglucinol glycidyl ether (PGE, (**1**)) with an epoxy content of 8.3 meq/g, which equals an average value of 3.57 epoxy groups per oligomer molecule, was purchased from Specific Polymers. As curing agents, amines for ambient-temperature cure have been tested: Diethylene triamine (**2**) (Sigma-Aldrich), isophorone diamine (**3**) (TCI Chemicals), and Jeffamine D230 (**4**) (Sigma-Aldrich). Admerginic acid (**6**), kindly provided by HOBUM Oleochemicals GmbH, Hamburg, Germany, and 4-methyl cyclohexane dicarboxylic acid anhydride (**5**) (TCI

Chemicals) were used as hardeners for heat-cure. These systems were also catalyzed by 2-ethyl imidazole (**9**) and DMP-30 (**10**), both were supplied by TCI Chemicals. Dicyandiamide (**7**) and the uron catalyst UrAcc57 (**8**) were obtained from AlzChem. All chemicals were used as received. **Figure 4** shows an overview of the chemicals used in this study, **Table 1** lists the different resin mixtures.

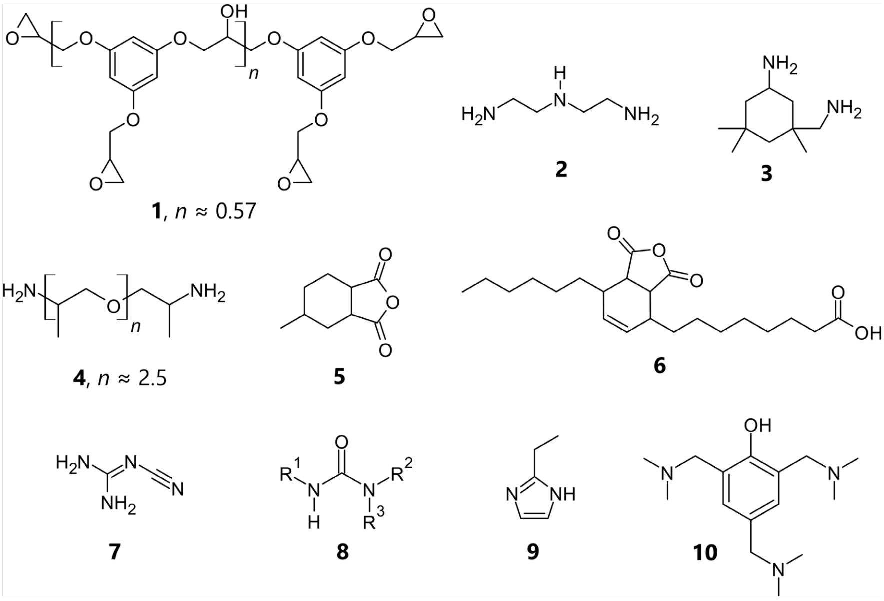

Figure 4. Overview of chemicals used in this study.

Table 1. Overview of resin compositions investigated in this study.

Resin	Curing agent	Curing agent type	Catalyst	Catalyst type
R1	**2**	amine	---	---
R2	**3**	amine	---	---
R3	**4**	amine	---	---
R4	**5**	anhydride	---	---
R5	**5**	anhydride	**9**	imidazole
R6	**5**	anhydride	**10**	tertiary amine
R7	**6**	anhydride	---	---
R8	**6**	anhydride	**9**	imidazole
R9	**6**	anhydride	**10**	tertiary amine
R10	**7**	dicyandiamide	---	---
R11	**7**	dicyandiamide	**8**	uron

2.2. Preparing the Epoxy Resin Formulations

Approximately 2 g of reactive resin was prepared by combining epoxy resin **1** with the appropriate amount of curing agent, based on a stoichiometric reaction of the functional groups involved. In this context, the functionality of dicyandiamide (**7**) was considered to be 6. Catalysts **8**, **9**, and **10** were included at a total concentration of 5 weight% of the combined mass of the resin and hardener. All mixtures were thoroughly homogenized using a centrifugal mixer (SpeedMixer DAC 150 SP, Hauschild, Germany) before further use.

2.3. Gel Point Determination

An Anton-Paar MCR 502 rheometer was employed to determine the gel point. All experiments used disposable aluminum plates with a top plate diameter of 15 mm and a gap of 0.15 mm. The deformation was set at 5% with a frequency of 1 Hz. Gel points were identified by the intersection of the storage modulus and loss modulus. Resins containing amines **2**, **3**, and **4** were analyzed at 20˚C, while systems incorporating anhydrides **5** and **6**, as well as dicyandiamide **7**, were heated from 20˚C to 200˚C at a rate of 5 K/min. Consequently, the gelation point for the first group of resins is reported as a time value, whereas for the latter group, it is reported as a temperature value.

2.4. Determination of Curing Enthalpy and Curing Kinetics

In a typical curing experiment, 5 to 10 mg of resin were heated in a 40 μL aluminium crucible from −25˚C to 300˚C in a Mettler Toledo DSC 1 differential scanning calorimeter. For each system, four different heating rates were applied (2.5, 5, 10, and 20 K/min.). The activation energy E_A of each cross-linking reaction was calculated according to Kissinger [21] from the best-fit line's negative slope multiplied by the gas constant R when $\ln[\beta/T_P^2]$ is plotted against $1000/T_P$ (where β and T_P are the heating rate and the temperature associated with the corresponding curing peak, respectively). The exothermic curing peaks of the 5 K/min. experiments are the basis for the associated peak temperature T_P and the individual curing enthalpies ΔH which themselves represent the basis for determining the conversion-temperature dependency as shown in **Figures 5-7**.

2.5. Determination of the Glass Transition Temperature

Each cured sample from the 5 K/min. DSC experiment was first heated from 25 to 250˚C, then cooled, and reheated within the same temperature range. The heating and cooling rates were ±20 K/min. The glass transition temperature T_g was identified at the midpoint of the step height for each cycle.

3. Results and Discussion

The value-based results of the different experiments are summed up in **Table 2**.

3.1. Amine-Curing Epoxy Resins

Of the amines used, especially diethylene triamine (**2**) proved to be highly reactive, up to the point, where the exothermic curing reaction was so violent that the mixture underwent self-combustion when working with bigger amounts, even without additional heating. In addition, **R1** possesses the highest curing enthalpy

Table 2. Determined data for the epoxy resins investigated.

Resin	Gel point	ΔH [J/g]	T_P [˚C]	E_A [kJ/mol]	T_g [˚C]
R1	65.4 min.[a]	483.10	68.37	57.6	152.7
R2	128.4 min.[a]	428.91	78.29	56.7	115.6
R3	404.6 min.[a]	446.26	91.91	53.1	102.6
R4	135.6˚C	400.82	166.24	75.6	198.0
R5	98.9˚C	317.11	108.79	74.4	152.0
R6	90.6˚C	198.10	103.82	74.6	168.5
R7	169.8˚C	327.06	170.70	67.1	103.5
R8	105.6˚C	301.60	112.88	80.6	107.2
R9	110.0˚C	278.04	114.18	72.6	141.9
R10	147,4˚C	677.08	151.26	75.6	136.7
R11	126.2˚C	556.59	116.71	74.4	128.8

a. Time-related gel point since curing already takes place at room temperature.

of all mixtures examined, and the gel point of **R1** could be determined to be 65.4 min., the lowest value of the amine-cured systems. In comparison, **R2** and **R3** have gel points of 128.4 and 404.6 min. at 20˚C, respectively. These differences in reactivity are also mirrored by the various glass transition temperatures, that of **R3**, containing the biggest and thus the most slow-reacting amine, being the lowest (102.6˚C), whereas the highest T_g was obtained for **R1** (152.7˚C).

Although the amine-curing resins already convert at room temperature into hardened thermosets, curing can be enhanced by additional heating. The increase of conversion as a function of temperature is shown in **Figure 5** for a 5 K/min. heating rate. Under these conditions, the reaction partners' noticeable conversion already occurs at moderate temperatures of around 60 to 80˚C. In addition, a high conversion is first reached for amine **2**, followed by isophorone diamine (**3**) and Jeffamine D230 (**4**) which again illustrates the order of amine reactivity. However, in terms of the activation energy E_A, resins **R1** to **R3** only differ marginally but exhibit lower values than the systems using anhydrides as curing agents, even when applying catalysts **9** and **10**.

3.2. Anhydride-Curing Epoxy Resins

The anhydride curing agents **5** and **6** only make a marginal difference in terms of conversion-time dependency, as can be seen for resins **R4** and **R7** in **Figure 6**. Since these systems are un-catalyzed, they require higher temperatures for the curing reaction to proceed.

Although the bespoke resins behave similarly in this regard, the smaller and thus more reactive anhydride **5** delivers a cured thermoset that reaches the gel point 35˚C earlier than the mixture using admerginic acid (**6**) (135.6˚C compared

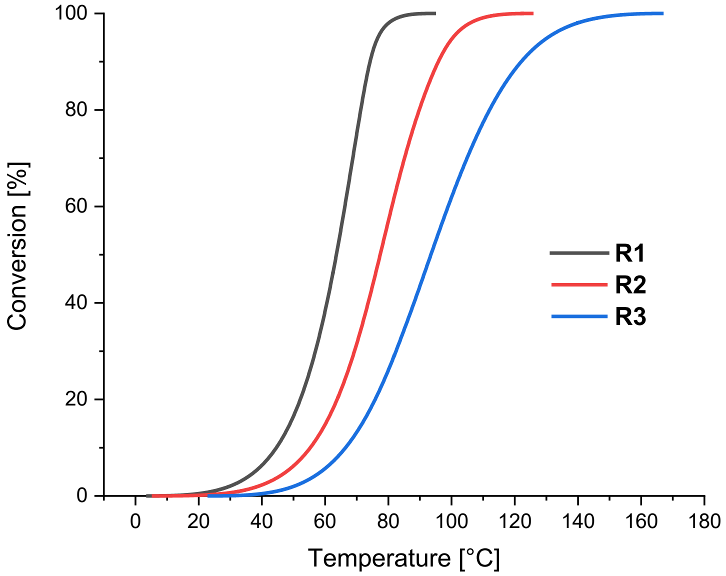

Figure 5. Conversion-temperature plots for the amine-cured resins **R1**, **R2** and **R3**.

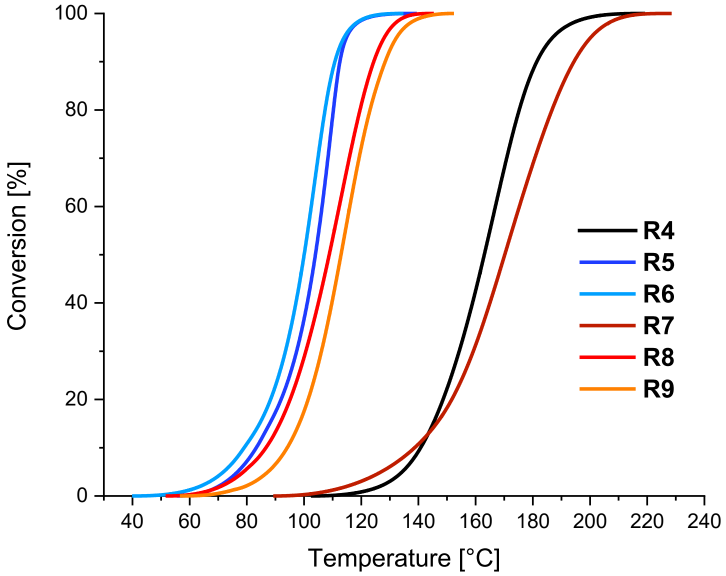

Figure 6. Conversion-temperature plots for the anhydride-cured resins **R4** to **R9**.

to 169.8˚C). In addition, the T_g of **R4** (198˚C) is nearly twice that of resin **R5** (103.5˚C).

Adding catalysts **9** and **10**, respectively, can drastically alter the curing behavior. E.g., the gel points of **R5** and **R6** are reasonably lower than compared to **R4**. Furthermore, the time for reaching 50% and 99% conversion at 160˚C, as deduced from the kinetic experiments, is only but a fraction of the value for **R4**, illustrating the ability of **9** and **10** to improve the curing rates drastically. However, the activation energies E_A for the hardening of **R4** to **R6** do not differ to that a high extent as one could conclude the catalysts' activity. In addition, the T_g values for the resins containing a catalyst are lower in comparison to resin **R4** where no catalyst is applied.

This behavior is not found for the admerginic acid-containing resins **R7** to **R9**. With the addition of a catalyst, the T_g increases distinctly, with **10** being the most potent one in this regard (T_g of **R9** is 141.9˚C, compared to **R7** with a T_g of 103.5˚C). However, in terms of the gel point, the imidazole catalyst **9** proved to be more beneficial as compared to DMP30 (**10**), although the difference is not markedly pronounced.

Furthermore, the activation energies of **R7** to **R9** differ significantly without any obvious trend, thus it is not possible to derive any tendency about the reaction rate from this.

3.3. Dicyandiamide-Curing Epoxy Resins

Dicyandiamide is a curing agent that is virtually inactive at room temperature but dissolves at higher temperatures, usually perceptibly at around 150˚C to 160˚C, in the surrounding resin, which initiates the curing (as can be seen from **Figure 7**). It is a prominent hardener for latent-reacting one-component epoxy resins. The activation energy of **R10** is in the mid-range, compared to all other resins examined, and does not change drastically when adding the catalyst **8**. However, the gelation point is lowered by approximately 20˚C which becomes apparent from **Figure 7**. In addition, **R10** by far shows the highest curing enthalpy ΔH (677.08 J/g) of all resin mixtures investigated, and self-combustion is evident when trying to cure bigger amounts of the resin in the oven. Nevertheless, despite their high reactivity, dicyandiamide-cured phloroglucinol-based epoxy resins **R10** and **R11** show high glass transition values (~130˚C) which also makes these resins suitable for high-demanding industrial applications, e.g. as adhesives in the body-in-white construction.

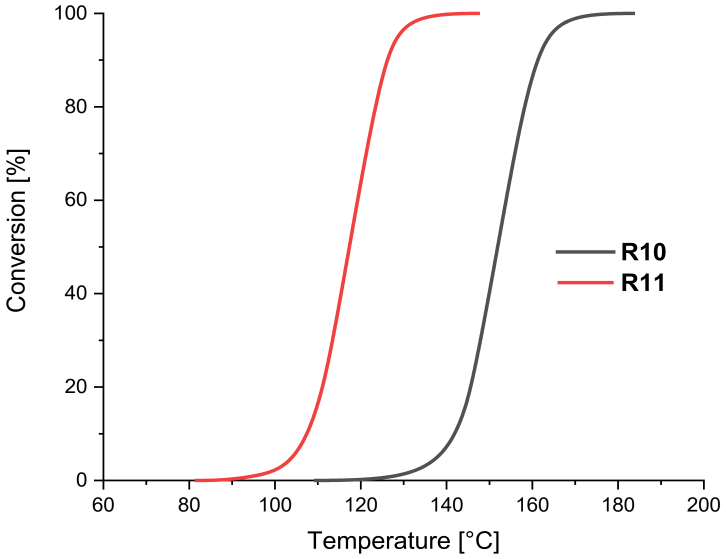

Figure 7. Conversion-temperature plots for the dicyandiamide-cured resins **R10** and **R11**.

4. Conclusion

The phloroglucinol-based epoxy resin **1** demonstrated the ability to produce duromers with glass transition temperatures exceeding 100˚C when reacted with established curing agents. In certain systems, these temperatures reached over 140˚C and in some instances approached even 200˚C. In all cases, cross-linking occurred within temperature ranges and time frames similar to those reported in the literature for conventional bisphenol A resins. In particular, the catalyzed blends using admerginic acid as a curing agent proved to be particularly promising, as this curing agent is derived from sustainable sources, *i.e.* fatty acids. In conclusion, the authors believe that algae-derived phlorotannins and the epoxy resins derived from them represent a viable alternative not only to petrochemical-based reactive resins but also to those based on epoxidized vegetable oils.

5. Outlook

The authors presented findings on a phloroglucinol-based epoxy resin that serves as a model for algae-based phlorotannin systems. The observed curing behavior and high glass transition temperatures indicate its general suitability for industrial applications, especially with catalytically enhanced anhydride-curing mixtures. However, several issues need to be addressed before large-scale production of epoxy resins from brown algae can be realized in the long term:

- Optimization of phlorotannin content based on macroalgal species, age, size, tissue type, and abiotic factors.
- Development of efficient and sustainable extraction methods.
- Chemical characterization of phlorotannin mixtures.
- Separation of structurally promising phlorotannins and their conversion into epoxy-bearing components for matrix resin production, ideally using sustainable chemistry.
- Investigation of the crosslinking behavior of algae-based epoxy resins (including kinetics and rheology) in relation to established industrial hardeners or newly developed sustainable alternatives.
- Mechanical characterization of the produced thermosets, including evaluation after material aging.
- Evaluation of adhesion to various substrates for applications such as adhesives and potting materials with a focus on joint aging.
- Introduction of advanced material functionalities, including self-healing properties or incorporation of the vitrimer concept.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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