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A preliminary evaluation of bio-based epoxy resin hardeners for maritime application

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Abstract

A screening of different hardeners derived from cashew nut shell liquid (CNSL) was performed; they were compared to a conventional hardener in an epoxy resin system for composite production by infusion process. All samples were submitted to different post-curing processes before tensile strength and moisture uptake were evaluated. It was observed that the use of CNSL hardeners produced cured epoxies similar in Young's Modulus (YM) to the conventional hardener with a lower moisture uptake however, the hardeners resulting in a low YM had a marked reduction in moisture uptake. Studies of the post-curing process showed that the moisture uptake of the conventional system can be improved but, depending on the temperature applied, the process can be detrimental to the CNSL hardeners, provided that moisture uptake was increased after post-curing. The results indicate that biobased content can be introduced to a conventional epoxy resin system by replacing the conventional hardener commonly used by a sustainable one derived from cashew nut shell liquid with an additional moisture uptake reduction.

1. Introduction

The most used and economical end-of-life methods for disposing composite materials are still incineration and landfill deposition. Still these methods can cause great impact to the environment, mainly incineration for the toxic by-products that can be generated [1]. In this context, phenalkamines and phenalkamides feature a series of benefits that make themselves interesting as sustainable hardeners applied in the epoxy resin suitable for infusion process,

highly used in boat production. They are obtained from cardanol, shown in Fig. 1, a component present in the cashew nut shell, which is treated as a by-product in the industry [2–4]. These CNSL hardeners can bring a set of good properties to the resins where they are applied, such as chemical resistance, adhesiveness, water resistance and low temperature curing [5].

In a phenalkamine structure, there is an aromatic ring present, responsible for chemical and fire resistance, a long aliphatic chain, capable of bringing a hydrophobic character to the resin and increase the water resistance. Further, a phenolic hydroxyl, which increases the reactivity at low temperatures and consequently facilitates curing, and finally a chain with amines, which brings high mechanical properties to the resin by improving the crosslinking density [5–7].
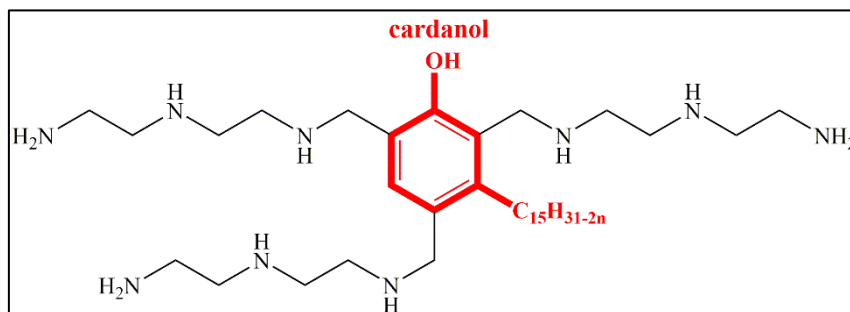

Fig. 1. Phenalkamine molecule.

Nomenclature

CNSL	Cashew Nut Shell Liquid
YM	Young's Modulus

Dai *et al.* studied the temperature sensitivity in the curing of a conventional epoxidic coating system cured by commercial phenalkamines, whose production is described by Sato *et al.* [8]. The synthesis consists on the reaction of cardanol, diethylenetriamine (DETA) and formaldehyde. It was found that the degree of curing at given temperatures was different due to their different compositions, but the pattern was the same. Further, the moisture uptake of the systems were compared to systems cured with conventional curing agents in salty water, at 25ºC and 65ºC for three weeks. The systems containing phanelkamines absorbed at least 50% less water than the system with polyamide and around 35% less than systems containing cycloaliphatic and Mannich bases curing agents [7]. Cheng *et al.* also described the synthesis procedure of another phenalkamine containing more aromatic rings, it was used 1,3-bis(aminomethyl)cyclohexane [9].

Kathalewar and Sabnis studied the synthesis of high molecular weight phenalkamine hardeners. The degree of crosslinking was determined by dynamic thermo-mechanical analysis, the phenalkamine synthesized with a higher ratio of formaldehyde and amine exhibited the highest crosslinking density. The resistance to water, acid (HCl 5%) and alkali (NaOH 5%) was tested, none of the samples showed any delamination, loss of gloss, or blistering effect [4].

Tambe *et al.* compared phenalkamines and phenalkamides with conventional curing agents with varied curing temperatures and relative humidity (RH). The curing temperature altered the properties of the cured material however RH did not. When cured at 30ºC, the phenalkamine presented the lowest moisture uptake ($\approx$5%) whereas the phenalkamide ($\approx$6,3%) performed amongst the conventional curing agents (7% $\pm$1) [10].

2. Methods

2.1. Specimens preparation

Samples of CNSL hardeners were provided by Cardolite Corporation. Conventional infusion resin and hardeners were purchased from Gurit. The specimens were prepared by mixing thoroughly the resin and the different hardeners according to the mixing ratios shown on Table 1, obtained from the data sheet of each material. The mixtures were poured into silicone molds prepared in accordance to ASTM D638 standard in order to obtain (Type 5) cured specimens and left to cure at room temperature for 24h [11].

Table 1. Specimens' compositions and final biobased content.

Hardener	Mix ratio resin:hardener (g)	Approximate final biobased content (%)
Conventional	100:27	0
Ultra Lite 2009	100:55	24
LITE 3060	100:55	32
LITE 3100	100:79	36

Some samples were then post-cured in a fan assisted oven at different times and temperatures (NPC: non post-cured, 16h60: 16 hours at 60ºC and 5h80: 5 hours at 80ºC). The producer of the conventional resin system suggests post-curing at 50º for 16 hours. However, the post-curing temperatures were chosen so they would be closer to the glass transition temperature of the system ± 10ºC. Over the glass transition temperature, the material is in a rubbery state and thus the molecules within would have a higher mobility for undergoing crosslinking.

2.2. Mechanical testing.

In order to compare the elastic modulus of the specimens, as well as their strain at break, mechanical tensile tests were performed in an electromechanical testing machine Instron 4204, where a tensile load was applied to the specimens until failure. In accordance with ASTM D638 standard [11], the elastic modulus or YM (E) is defined by the deformation or strain a material suffers due to an applied stress, elaborated in the following equation:

$$E = (F / A)/(\Delta L / L_0)$$

Where F is the tensile load applied to the specimen, A is the cross section area of the specimen before deformation, ΔL is the variation in length of the specimen and L_0 the initial length.

2.3. Hygrothermal ageing

The moisture absorption was evaluated based on ASTM D5229 standard; five samples of 0.9g ± 0.1 were placed in distilled water at 40ºC for four weeks, the weight variation of the samples was monitored twice a week [12].

3. Results and discussion

3.1. Mechanical testing.

The elastic modulus obtained from the mechanical testing are given on Table 2. The conventional hardener gave the system a very brittle behaviour whereas hardener 3060 presented a yield point, a plastic deformation region, and a higher extension to failure.

Table 2. Elastic modulus of epoxy systems cured by conventional and biobased hardeners.

Hardener	NPC (GPa)	16h60 (GPa)	5h80 (GPa)
Conventional	2.16 ± 0.06	1.92 ± 0.04	1.83 ± 0.06
Ultra LITE 2009	0.35 ± 0.02	0.84 ± 0.05	0.64 ± 0.01
LITE 3060	1.37 ± 0.03	1.48 ± 0.06	1.42 ± 0.03
LITE 3100	0.18 ± 0.03	0.57 ± 0.05	0.47 ± 0.04

Hardeners 2009 and 3100 did not withstand high loads but presented an outstanding strain, as shown in Fig. 2. After post curing at 60ºC for 16h, the conventional system showed an increase in tensile strength however, the strain to failure also increased. All the CNSL-based hardeners increased the tensile strength of the post-cured epoxy system and reduced the strain to failure, hence improving YM in all cases reported.
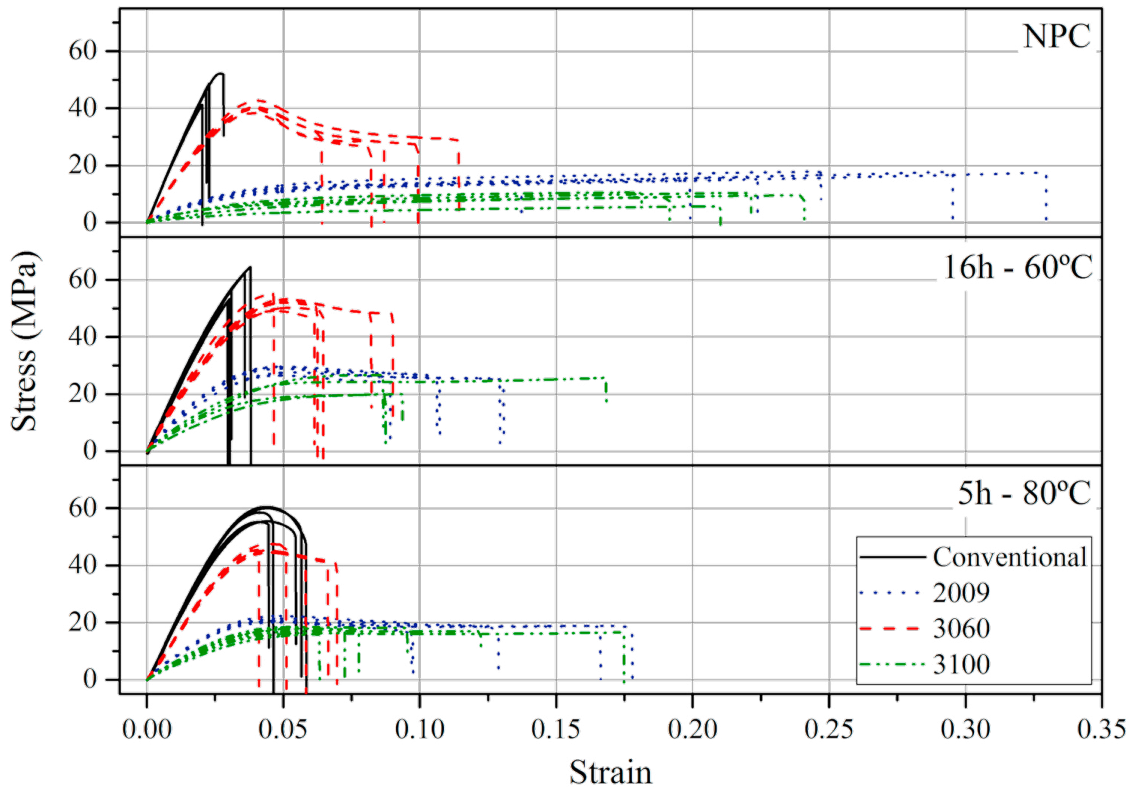

Fig. 2. Tensile testing results.

Hardeners 2009 and 3100 had their YM expressively enhanced after post-curing whereas hardener 3060 presented a much slighter improvement. The conventional hardener had its YM reduced. The temperature employed in the post-curing process was 10ºC higher than the recommended temperature. At an even higher temperature, employed for the second post-curing condition (80ºC – 5h), the YM was reduced even more. The change in the elongation at break is also evidenced according to the different curing temperatures, shown in Fig. 3.
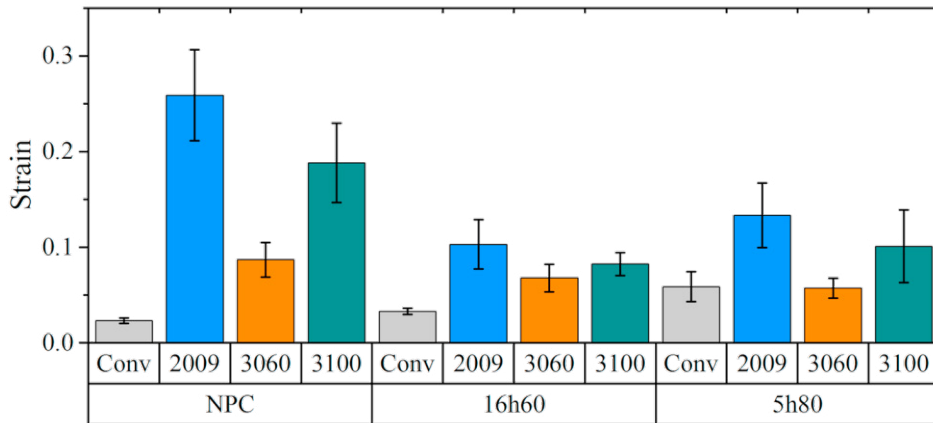
Fig. 3. Elongation at break.

The only samples that showed increase in the extension were the ones cured with conventional hardener, which increased the resin ability to absorb energy before failure. According to the hardener's data sheets, hardener 3060 is solvent free and has 1,3-clyclohexenedimethanamide as an additive, which is a primary amine and thus, more reactive than the secondary m-phenylenebis(methylamine) and 2,4,6-tris(dimethylaminomethyl)phenol amines present in hardener 3100. As the secondary amines are less reactive, the post-curing process might have supplied extra energy for the curing completion. Hardener 3060 also had its properties improved after post-curing but in a much slighter amount, that can be explained by the more reactive primary amine present and the solids content. Hardener 2009 also improved after post-curing, but mostly due to its solids content, especially when compared to 3100.

3.2. Hygrothermal ageing.

Conventional and 3060 hardeners presented very similar behaviors for all the curing and post-curing conditions, as shown in Fig. 4. Both post-curing procedures improved the properties of the system by reducing the amount of water absorbed.
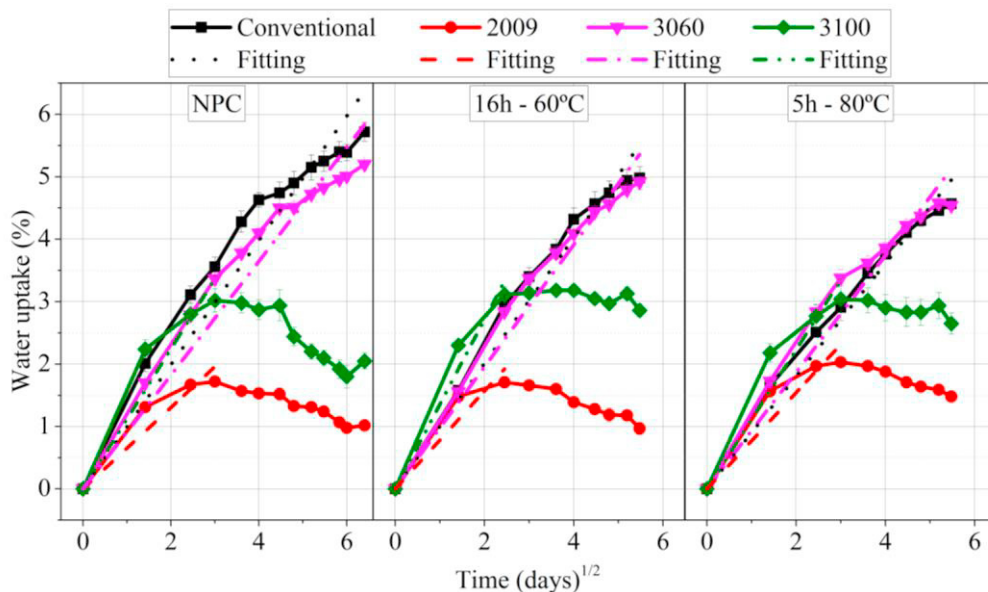

Fig. 4. Moisture uptake for different curing and post-curing procedures.

Hardener 3100 had the fastest initial rate of absorption and was not affected by the curing process, apart from the end of the period when post-curing was not employed. It quickly reached equilibrium in the post-cured conditions but it starts to lose moisture when not post-cured. Hardener 2009 had the best performance in all the situations and presented the smallest amount of water absorption. The moisture uptake curves were linearly fitted to zero, based on ASTM C1585, the fitting slope can be used to express the absorption rate [13], as shown in Table 3. For hardeners 2009 and 3060, the initial linear part of the curve was used to obtain the rates.

Table 3. Moisture uptake rate.

Hardener	NPC Slope	R^2	16h60 Slope	R^2	5h80 Slope	R^2
Conv	0.996	0.988	0.904	0.995	1.006	0.993
3060	0.912	0.988	0.935	0.989	0.978	0.994
2009	0.653	0.962	0.773	0.960	0.785	0.947
3100	1.123	0.967	1.117	0.972	1.359	0.981

Both Conventional and 3060 hardeners showed similar results regarding the absorption rate, as well as a better fitting quality (R^2). Although hardeners 2009 and 3100 showed similar results throughout the different curing and post-curing procedures, it is evidenced by their R^2 that more data points are necessary for understanding their rate behavior. The slowest absorption rate presented by the conventional system was achieved when post-curing temperature and time were close to the ones suggested by the supplier, which is 50ºC for 16h.

Further, the moisture uptake variation was compared to the behaviour shown by the Conventional hardener.
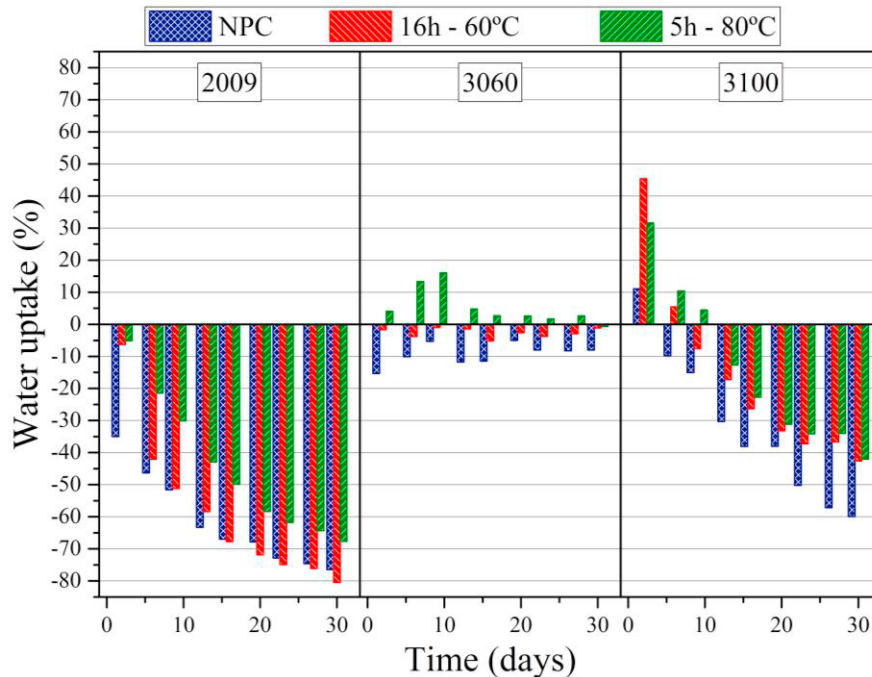

Figure 5. Moisture uptake of CNSL hardeners compared to Conventional hardener.

Hardener 2009 had the best performance, 80% less moisture uptake than the conventional hardener after the evaluation period when post-cured at 60ºC for 16h. Hardener 3060 performed slightly better when compared to the conventional hardener, apart from when a high post-curing temperature was employed. The high temperature used for the post-curing at 80ºC at 5h was detrimental for all the CNSL hardeners with regards moisture uptake. In some cases, post-curing at 60ºC for 16h affected the moisture uptake performance.

4. Conclusion

The hardeners derived from cashew nut shell liquid employed in this work had shown an outstanding performance regarding the reduction in moisture uptake however, the properties presented were, in some cases, isolated. Hardeners 2009 and 3100 reduced dramatically the moisture uptake but their mechanical properties in terms of stiffness are not comparable to conventional and 3060 hardeners. Furthermore, post-curing was detrimental to their performance regarding moisture uptake. Hardeners 2009 and 3100 gave the system a much higher extension before breaking (flexibility), this fact can make them suitable for impact absorption and damping. The post-curing of the specimens cured using the conventional hardener reduced moisture uptake, these improvements were much slighter for hardener 3060. On the contrary, hardener 3060 performed similarly to the conventional hardener, showing great stiffness as well as a 10% reduction in moisture uptake when not post-cured if compared to the conventional hardener. That alone implies conventional hardener can be replaced by 3060 giving up to 32% of sustainable content to the final system, and moreover energy saving post-curing might not be required depending on the final properties.

Acknowledgements

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