N°1455 / PC

TOPIC(s) : Polymers or composites / Clean reactions

The use of a natural acid mixture in the fabrication of eutectic hardener for green cross-linking of epoxy resin

AUTHORS

Mona JAMALI MOGHADAM SIAHKALI / UNIVERSITY CÔTE D'AZUR, FACULTÉ DES SCIENCES ET INGÉNIERIE EQUIPE ARÔMES, PARFUMS, SYNTHÈSES,, 28, AVENUE DE VALROSE 06108 NICE CEDEX 2,, NICE

Jonathan TELLERS / UNIVERSITÉ CÔTE D?AZUR, FACULTÉ DES SCIENCES ET INGÉNIERIE EQUIPE ARÔMES, PARFUMS, SYNTHÈSES,, 28, AVENUE DE VALROSE 06108 NICE CEDEX 2,, NICE

Nicolas SBIRRAZZUOLI / UNIVERSITÉ CÔTE D?AZUR, FACULTÉ DES SCIENCES ET INGÉNIERIE EQUIPE ARÔMES, PARFUMS, SYNTHÈSES,, 28, AVENUE DE VALROSE 06108 NICE CEDEX 2,, NICE

Philippe WILLEMS / ORINEO ? ORIGINAL RENEWABLES, ACACIASTRAAT 14, B-3071 ERPS-KWERPS, BELGIUM, ERPS-KWERPS

Bôke TJEERDSMA / ORINEO ? ORIGINAL RENEWABLES, ACACIASTRAAT 14, B-3071 ERPS-KWERPS, BELGIUM, ERPS-KWERPS

Corresponding author : Nathanael GUIGO / Nathanael.GUIGO@univ-cotedazur.fr

PURPOSE OF THE ABSTRACT

There are numerous readily available and economically viable bio sources of epoxy matrices based on unsaturated vegetable oils. However, it is challenging to find a convenient green hardener that crosslinks the epoxy resin at low temperatures while being simple to process and cost effective without posing a health risk. A potential alternative hardener are carboxylic acids, However, due to their high melting point, efficient mixing of these acids with epoxy resin is impossible, resulting in heterogeneous cross-link density and high curing temperature, and poor network.

To address this issue, an innovative eutectic hardener concept was developed [1,2]. The preparation of a liquid hardening system in which citric acid (CA), tartaric acid (TA), and malic acid (MA) that are naturally available, potentially multi-functional, non-toxic, and inexpensive acids are combined with a liquefier to form a eutectic mixture. This liquid mixture at room temperature strongly facilitates the interaction with epoxy resin and this feature allows room temperature cross-linking. This also holds true for combination of the natural acids.

As shown in Table 1, mixtures containing a low amount of difunctional acid, i.e. 25 mol % TA to CA will lead to cross-linked sample with an increased stiffness, tensile strength, and toughness compared to the sample prepared with 100 % CA. This can be explained by the lower steric hindrance and better mobility of a difunctional acid to crosslink the polymer matrix (Fig. 2B). The addition of 25 mol% MA mixed to CA mixtures increases reactivity resulting in a higher glass transition temperature (Tg) and reasonable tensile properties in the final product. On the other hand, using mixtures with a higher mol% of MA complicates obtaining clear samples without inclusion of too many air bubbles.

These fully biobased and non-toxic systems cured with eutectic hardeners is leading to flexible materials. Such a flexibility could be used as an advantage for flexible coatings (e.g. on textile), for decorative sheets for interior applications.

Acknowledgements

This work benefited from financial support from the French government, managed by the National Research Agency (ANR) under the UCAJEDI Future Investments project with reference number ANR-15-IDEX-01 " and financial support of ?La Maison de la Chimie?.

Key words:

Eutectic mixture | Carboxylic acids | Bio-based thermoset polymer | Epoxy resin Bibliography:
[1] J. Tellers, M. Jamali, P. Willems, B. Tjeerdsma, N. Sbirrazzuoli, N. Guigo, Green Chem.2021, 23, 536-545.
[2] J. Tellers, P. Willems, B. Tjeerdsma, N. Guigo, N. Sbirrazzuoli, Green Chem., 2020, 22, 3104-3110.

FIGURES

Sample	Tensile Data				Shore Hardness		Swelling	Gel
	E (MPa)	σ_Y (MPa)	ε_B (%)	Toughness (J m^{-3})	Type A	Type D	Ratio (%)	Fraction (%)
CA100	33±4	6±1	51±4	0.64±0.11	85±4	24±2	88.1±6	89±1
CA75MA25	55±10	4.6±0.9	55±8	0.65±0.16	78±3	19±2	105.9±6	89±4
CA50MA50	17±3	2.8±0.7	57±10	0.44±0.16	71±3		118.4±3	90±3
CA25MA75	14±4	2.3±0.4	59±6	0.38±0.09	65±2		125.4±23	86±2
MA100	8±1	1.7±0.5	59±10	0.24±0.08	55±2		146.4±8	81±4
CA75TA25	243±26	7.4±0.5	30±2	0.75±0.08	92±3	38±3	82±6	90±2
CA50TA50	20±3	3±0.6	62±9	0.44±0.12	68±3		124±11	83±3
CA25TA75	5±2	1.1±0.1	73±8	0.19±0.05	47±5		151±10	78±2
TA100	3±0.5	0.8±0.3	68±4	0.19±0.02	47±2		158±18	73±2

With E = Young's modulus; σ_Y = Tensile Strength at Yield Point; ε_B = Strain at break.

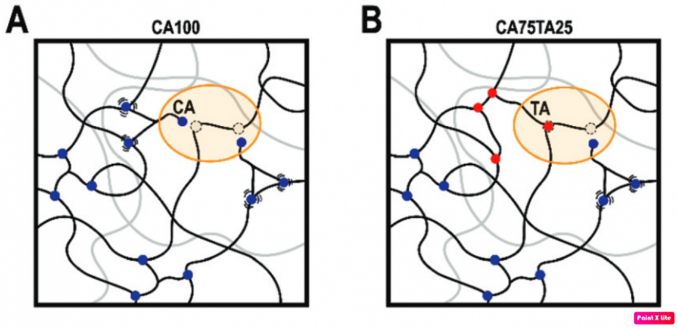

FIGURE 1

Tensile data, solubility data, Shore Hardness of thermosets cured with eutectic hardener

Table1

FIGURE 2

(A) Hindered mobility of CA moieties after the vitrification of the sample leading to unconnected entities; (B) Illustration on how low amount of TA can help in cross- linking inaccessible oxirane moieties. These images are from the reference [1].

Figure 1

KEYWORDS

Eutectic mixture | Carboxylic acids | Bio-based thermoset polymer | Epoxy resin

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