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The properties and suitability of commercial bio-based epoxies for use in fiber-reinforced composites

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Abstract

Environmental concerns about fiber composites are leading manufacturers to consider bio-based alternatives to petroleum-derived epoxies. Such a substitution is hindered by a lack of information, so commercially available bio-based epoxy systems have been compared, their mechanical properties measured, and fiber composites produced by vacuum infusion. Most high bio-based content resins for infusion use conventional curing agents. Bio-based content is generally added using Epicerol, but also other bio-based precursors. A diglycidyl ether of bisphenol A system produced using Epicerol achieves 20 % bio-based content, but achieves higher contents when Epicerol is used in diluents. Fully bio-based monomers can be deleterious to the mechanical properties and glass transition temperature (T_g), so are used sparingly. The most-promising systems (28 % to 43 % bio-based) compare well to conventional epoxies, possessing good strength, stiffness, toughness, and a reasonable T_g. These partially bio-based epoxies offer an immediate lower-carbon alternative for vacuum-infused composites in marine, sports equipment, and wind energy.

KEYWORDS

biopolymers and renewable polymers, composites, glass transition, mechanical properties, thermosets

1 | INTRODUCTION

Epoxies are thermoset polymers possessing notable mechanical and chemical properties, namely high strength, high stiffness, good creep resistance, low shrinkage, and excellent chemical resistance. Therefore, they are widely applied as the matrix material for fiber reinforced polymers (FRPs) in engineering applications.[1] The potential for FRPs to displace the use of metal alloys in weight-sensitive and high-performance applications is well known, as they have superior specific strength and stiffness. In certain applications, FRPs can be deemed a 'green' material due to their weight saving (e.g. by improving fuel efficiency or electric vehicle range); however significant improvements in the environmental impact of composites can still be achieved.

The scope of the present work is focused on assessing the current potential to replace petroleum-based epoxy matrices with commercially available bio-based alternatives. Bio-based polymers are a promising route to achieve a reduction in environmental impact; their production will often have a lower carbon footprint and they

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are an effective way to sequester carbon. These renewable materials are sourced from a predictable supply chain, which usually precedes stable pricing. Some bio-based alternatives also offer lower toxicity. Currently, the costs of bio-based epoxies are higher than fossil-fuel-based epoxies, due to lower production volumes. Some applications are well suited to using bio-based epoxies, for example, winter sports equipment due to a low T_g requirement and improbability of in-service failure as rental skis are frequently serviced, repaired, and replaced. In this sector, it is already economically viable to make the switch.[2]

For resin systems used to produce composites via infusion, it is essential to have a suitably low viscosity and long time until gelation (pot life) to allow the resin to infuse through the dry fiber stack before gelation occurs. Many commercially available infusion systems are room temperature curing which is convenient for low-volume manufacturers, who do not desire the additional complexity of controlling the temperature of the resin and the mold. A lower viscosity resin will infuse faster, increase the wetting of the fibers, and improve the fiber volume fraction, which are beneficial to the manufacturing and properties of the resulting composite. A low viscosity resin also provides the ability to toughen the matrix with micro- or nano-sized particles such as core-shell rubber (CSR) particles or silica nanoparticles, which can increase the viscosity but greatly improve the fracture performance of the resulting material, for example, Hsieh et al.[3] To reduce mixture viscosity, diluents, and low viscosity amine curing agents are often incorporated into a resin system alongside DGEBA, as is the case for many systems in this study. The addition of low molecular weight diluents based on glycols, such as, butanediol diglycidyl ether (BDGE) and hexanediol diglycidyl ether (HDGE), to DGEBA can yield good properties for use in fiber composites.[4] At low quantities of diluent, below 20 % of DGEBA, systems can exhibit increased strain to failure and increased toughness, with little effect on other mechanical or thermo-mechanical properties. All the systems used during the present study were amine cured; therefore, discussion on bio-based formulations will focus on this curing chemistry. Finally, the T_g of the cured resin must be significantly above the service temperature, as the mechanical properties are considerably reduced in the rubbery region.

Bio-based content is generally defined as the percentage of naturally occurring carbon in the material, as measured using radiocarbon dating methodologies.[5] This method is widely implemented because it is simple to perform and gives a good indication of the material's origins. However, a more comprehensive method could consider atomic origin and atomic efficiency, but implementing this would be challenging, e.g. due to logistics and intellectual property. Ignoring the origins of heavier elements, for example, oxygen could encourage synthesis methods, which do not obey 'sustainable chemistry' yet achieve high bio-based content. For bio-based epoxies to be truly sustainable, reactants and their precursors must be selected, synthesized, and processed following 'The Twelve Principles of Green Chemistry', as presented by Anastas and Warner.[6] There is no single global standard for determining bio-based content or minimum quota of renewable material to advertise a product as bio-based, instead, the standards are set by each labeling (accreditation) scheme. In general, only materials with bio-based constituents greater than 20 % are recognized, although requirements vary by material and application. The US Department of Agriculture (USDA) labeling system states that epoxies must contain a minimum of 25 % bio-content.[7] Currently, very few commercially available bio-epoxies contain a total bio-content of greater than 30 %, but even this quantity can notably reduce greenhouse gas emissions.[8]

In the last decade, there has been a large increase in scientific publications on bio-based epoxies and commercially available products. Many fully bio-based systems have been reported at laboratory scale, but these are usually more difficult to process with inferior material properties.[9–16] Generally, manufacturers have favored adding bio-based content to epoxy resin or as reactive diluent rather than to the curing agent, as the curing agent is critical to a systems' pot life, viscosity and cure cycle, modifying it has a great impact on the composite manufacturing process. It accounts for a smaller proportion of the final material than epoxy and hence has a lower impact on bio-content. Developing curing agent systems is a lengthy iterative process. Synthesis and separation of primary amines is challenging and often requires development of specialized catalysts.[17] Baroncini et al.[18] and Ding and Matharu[19] present comprehensive reviews on bio-based curing agents for epoxies.

The methods used to make epoxy resins from fatty acids, alcohols, and sugars are well-known,[20,21] and it is possible for chemicals of these groups and their reactants to have 100 % bio-based carbon content. Resin systems containing aromatic groups exhibit superior mechanical and chemical properties, hence the popularity of DGEBA-based resin. DGEBA is produced via reaction of bisphenol A (BPA) with epichlorohydrin. As BPA has been listed as potentially harmful to reproductive health, several sources of bio-based aromatic molecules have been suggested to replace BPA in epoxy resins; including cardanol, vanillin, rosin, lignin, tannins, and limonene.[18,22–25] Particularly encouraging results have been achieved using vanillin-based epoxies derived from lignin, an abundant waste product of the paper industry.[9]

Cardanol, derived from cashew nut shell liquid (CNSL), has already been incorporated into commercial products.

The widespread adoption of natural feedstock as precursors for thermoset polymers faces some significant obstacles. Suitable feedstock can hold more value in other applications, such as, food, beverages, pharmaceuticals or fragrances; especially aromatic substances. Innate variation in the purity of reactants leads to higher amounts of side reactions and by-products, which may require more reactant-, labor- and/or energy-intensive processing to produce the same quantity of the desired product. For polymers, it is generally desirable to minimize branching and use only bi-functional end-terminated monomers; which allows polymer chains to be more closely packed with a controlled, homogenous cross-linking and reduces steric hindrance. It is very common for natural oils, sugars and alcohols to have highly-branched structures. Side branching and lower-purity components tend to reduce the homogeneity of the polymer network and hence the material properties.

Epicerol is a commercially-available bio-based drop-in for epichlorohydrin, which uses glycerol as it is pre-cursor. The glycerol is a waste product of bio-fuel production, which allows Epicerol to be a cost-effective alternative. If all epichlorohydrin were Epicerol in standard DGEBA, 6 of 21 carbon atoms would be bio-based per molecule. In a 100:33 mixture of resin to hardener with no bio-content in the curing agent, this amounts to a 21.5 % bio-based system. Reaction of low molecular weight aliphatic diols with Epicerol is a more effective way to increase the bio-content. For example, if produced using Epicerol, BDGE and HDGE would possess 60 % and 50 % bio-based content respectively, and in the future enzymatic production of diols from bio-based feedstock could enable these to be fully bio-based.[26,27] Clearly, if reacted with natural alcohols or sugars a fully bio-based epoxy molecule is produced. Inclusion of low quantities of such reactive diluents could enhance the bio-based content considerably with lower impact on performance. Therefore, it is not unreasonable to suggest that these methods have been employed in most commercial bio-based systems.

It is possible that existing commercial products are synthesized from bio-based feedstocks but have decided not to certify or publicize. It can be difficult to trace the route of each ingredient and some companies wish to keep their synthesis methods secret. Certain industries may not find this term desirable to use due to confusion of definitions (e.g. bio-degradable), or poor reputation due to low performance or high variability. For bio-based polymers to be successful in the future, it is important for them not to gain a bad reputation. The authors of this paper are aware of at least one company, which currently uses Epicerol without advertising the bio-content of their product.

The current study assesses the suitability of existing commercial bio-based epoxy resin systems for use as the matrix for FRPs. Several commercial bio-based epoxy systems have been selected based on their high bio-based content and suitability for use in the production of vacuum-infused fiber composites. The approaches to increase the bio-content of these epoxies are identified, and their resulting T_g, tensile, compressive and fracture properties are measured and compared to conventional DGEBA epoxies cured using standard epoxy curing agents. For manufacturers employing thermoset composites in their products, bio-based epoxies present a good opportunity to reduce the environmental impact of their product with minimal alteration to their product and its manufacturing process.

2 | EXPERIMENTAL

2.1 | Materials

A total of nine bio-based systems were selected for this study. Table 1 shows the selected systems and their abbreviation, mixture ratio, bio-content and categorization of curing agent. Composition data was gathered by evaluating the material safety datasheet (MSDS) and technical data sheet (TDS) of each resin system.[28–47] Using this method, any ingredient deemed not to pose a potential risk cannot be identified, including harmful substances at very low concentrations.[48] Only the named components of 0A1B (Formulite 2500A + 2401B) summed to less than 100 %, indicating a slightly lower toxicity.

For curing agents that are mixtures, ingredients accounting for at least 5 % have been listed in order of percentage content. Sicomin resins were provided by Matrix Composites, UK; all other materials were provided directly by their manufacturers. All materials were used as received. The resin appearance, mixture viscosity, and curing schedule for each system are presented in Table 2.

During this study, comparisons were made with conventional (petroleum-derived) epoxy systems,[4,49–52] the system abbreviations are presented in Table 3. HY917 and HE600 are accelerated methylhexahydrophtalic acid anhydride curing agents, whereas isophorone diamine (IPD) and polyoxypropylene diamine, with molecular weight (M_r) = 230 kg/kmol, (D230) are amine curing agents; both common constituents of low-viscosity infusion systems.

TABLE 1 Summary of bio-based resin systems, abbreviations and categorization of bio-content and curing agent, as specified in MSDS,[28–38] TDS or brochure,[28,39–44] or correspondence (phr = parts per hundred of resin by weight)

		Epoxy			Curing agent					
Abb.	**Supplier**	**Name**	**Bio-based?**	**Bio-based diluent?**	**Name**	**phr**	**Bio-based?**	**Mixture bio-based percentage (%)**	**Bio-content source**	**Amine type**
0A02	Cardolite (Belgium)	Formulite 2500A	Yes	Yes	LITE2002LP	51	Yes	46.8	CNSL	aromatic
0A1B	Cardolite (Belgium)	Formulite 2500A	Yes	Yes	Formulite 2401B	30	Yes	36.6	CNSL	cycloaliphatic & aromatic
INRS	Entropy Resins (USA/ Spain)	SuperSap INR	Yes	No	SuperSap INS	33	No	19	PO	cycloaliphatic & aliphatic
AMPRO	Gurit (UK)	AMPRO BIO	Yes	Yes	AMPRO BIO Slow	29.3	Yes	>40[a]	CNSL, PO	cycloaliphatic, aliphatic & aromatic
ECO	Resoltech (France)	1800 ECO	Yes	Yes	1804 ECO	26	No	33	PO	cycloaliphatic & aliphatic
GP22	Sicomin (France)	Greenpoxy 56	Yes	Yes	SD8822	31	No	43	PO	cycloaliphatic & aliphatic
GP24	Sicomin (France)	Greenpoxy 56	Yes	Yes	SD8824	21	No	42	PO	aliphatic & aromatic
IG22	Sicomin (France)	Infugreen 810	Yes	Yes	SD8822	31	No	29	PO	cycloaliphatic & aliphatic
IG24	Sicomin (France)	Infugreen 810	Yes	Yes	SD8824	22	No	31	PO	aliphatic & aromatic

[a]Exact value withheld.

TABLE 2 Resin system appearance, viscosity, and applied cure schedule; as specified in TDS or brochure[28,39–44]

Abb.	Mixture appearance	Mixture viscosity (mPa.s)	Curing schedule (ramp = 1 °C/min)
0A02	Transparent (orange tinted)	3450 at 25 °C	25 °C for 8 h, 100 °C for 2 h
0A1B	Transparent (orange tinted)	700 at 25 °C	25 °C for 4 h, 100 °C for 2 h
INRS	Transparent	200 at 25 °C	120 °C for 20 h
AMPRO	Transparent (orange tinted)	1100 at 25 °C	25 °C for 24 h, 50 °C for 16 h
ECO	Translucent	258 at 23 °C	50 °C for 3 h, 100 °C for 3 h, 150 °C for 3 h
GP22	Transparent	—	25 °C for 24 h, 40 °C for 24 h
GP24	Transparent (green tinted)	—	25 °C for 24 h, 60 °C for 16 h
IG22	Transparent	320 at 20 °C	25 °C for 24 h, 40 °C for 24 h
IG24	Transparent (green tinted)	200 at 20 °C	25 °C for 24 h, 60 °C for 16 h

TABLE 3 Abbreviations for comparative standard epoxy systems

Abb.	Supplier	Epoxy resin (diluent)	Curing agent	References
LYHY	Huntsman	LY556	HY917	49
LYIPD	Dow/ACROS	DER 331	IPD	50
LY230	Huntsman	LY556	D230	51
LYHDEHE	Huntsman/Dow/Evonik	LY556 (HDGE)	HE600	4
LYHDEIPD	Huntsman/Dow/Evonik	LY556 (HDGE)	IPD	52

2.2 | Manufacture

For each system, the epoxy and curing agent were measured using a balance (± 0.01 g) and stirred by hand until visibly mixed, with exception of 0A02 (Formulite 2500A + LITE2002LP), which was mixed at 80 rpm for 10 min using an overhead stirrer fitted with a radial flow impeller. All resin systems were degassed under a vacuum of −1000 mbar at ambient temperature. Degassing was performed until bubble formation subsided or for the longest duration allowable within the system's pot life. The mixtures were poured into vertical steel molds, 3 mm or 6 mm thick, which had been cleaned with acetone and coated in release agent, Frekote 700NC (Henkel, UK), and cured. The cure cycles followed the recommendations of the TDS, brochure or via correspondence with the manufacturer.[40–47] GP22 and GP24 were subjected to the respective cure cycles of IG22 and IG24. Where options were presented, the cure schedule was selected to achieve a good balance of stiffness, strength and ductility.

2.3 | Test methods

2.3.1 | Uniaxial tension

Dumbbell-shaped specimens were machined from 3 mm thick cast plates using a table saw and a table router. The dumbbell specimens were 5 mm wide with a 25 mm gage length. Uniaxial tensile tests were performed using an Instron 3366 universal testing machine. Each test was performed at room temperature in accordance with BS EN ISO 527,[53] using a displacement rate of 1 mm/min. The load and strain were measured using a 10 kN load cell and a clip-on extensometer respectively. At least five repeat tests were performed for each epoxy system. The tensile Young's modulus (E_t), tensile strength (σ_{yt}) and strain to failure (ε_f) were calculated. The value of σ_{yt} is taken as the mean of the maximum stress of the tested samples. The ε_f values were calculated from the extensometer data.

2.3.2 | Plane strain compression (PSC)

Plane strain compression tests were performed in accordance with the method outlined by Williams and Ford.[54] Square, 40 mm × 40 mm, specimens were machined from 3 mm thick cast plates of epoxy using a table saw. The specimens were polished to a 6 μm surface finish using a Struers LaboPol-21 polishing machine with 6 μm monocrystalline diamond suspension (MetPrep, UK). A set of parallel dies of 12 mm width were fitted to an Instron 5585H universal testing machine with a 250 kN load cell. At least two repeats tests were performed for each material, at a displacement rate of 0.1 mm/min with the specimens lubricated

using high temperature grease (Castrol, UK). For each system, values were calculated for the equivalent compressive stress ($\bar{\sigma}_{yc}$), equivalent strain of first crack ($\bar{\varepsilon}_{c1}$) and equivalent strain of final crack ($\bar{\varepsilon}_{cf}$).

2.3.3 | Dynamic mechanical analysis (DMA)

The glassy storage modulus (E'_G), glass transition temperature (T_g), and rubbery storage modulus (E'_R) were measured in dual cantilever mode using a dynamic mechanical analyzer (DMA Q800, TA Instruments) in accordance with BS EN ISO 6721-5.[55] A minimum of two 60 mm × 10 mm × 3 mm specimens were tested for each system, and the results were very repeatable. The tests were performed between 30 °C and 150 °C, with a heating rate of 2 °C/min, frequency of 1 Hz and amplitude of 30 μm. The T_g was taken to be the corresponding temperature of the peak tan δ; E'_G was taken at 30 °C and E'_R at (T_g + 30) °C.

2.3.4 | Single edge notched bend (SENB)

Specimens of 60 mm × 12 mm were machined from 6 mm thick cast plates. A 45° notch was machined at the centre of each specimen using a horizontal mill. Specimen preparation, testing, and analysis were performed in accordance with ASTM 5045–14.[56] A steel razor blade dipped in liquid nitrogen was used to tap a sharp pre-crack in the specimen prior to testing. The specimens were subjected to a 3-point bend test with a span of 48 mm. The load was measured using a 10 kN load cell, and the test was performed at a displacement rate of 1 mm/min. The results were used to calculate the fracture toughness (K_{IC}) and fracture energy (G_{IC}). For $G_{IC,LEFM}$ the Poisson's ratio was taken to be 0.35, which is a standard value for epoxy.[57] $G_{IC,energy}$ was calculated using the area under the load extension curve, accounting for compliance. At least six repeat tests were performed for each material.

3 | RESULTS AND DISCUSSION

3.1 | Specimen preparation

During the manufacture of plates for mechanical testing, it was apparent that some systems did not possess a pot life and viscosity, which were highly suitable for resin infusion. The Cardolite resins (0A02 and 0A1B) had a high viscosity compared with the other systems. This is likely to be due to higher molecular weight curing agents and increased entanglement of monomers due to the long-branched chains inherent in cardanol. The system 0A02 possessed such a high viscosity that it was impossible produce a homogenous mixture while stirring by hand. The high viscosity increased the time required for degassing and increased the difficulty of pouring the resin into the steel mold.

The curing agents SD8824 (used in the GP24 and IG24 systems) and AMPRO Bio Slow (used in the AMPRO system) were both highly reactive with a short pot life of below 30 min for 100 g. This caused difficulty in achieving full degassing of the mixture, and air bubbles were noticeable in AMPRO. In some cases, SD8824 would uncontrollably exotherm during degassing or pouring, producing smoke. The short pot lives of both systems make them unsuitable for such an infusion process as a relatively large quantity of mixture is required during infusion.

The ECO system was the only mixture which appeared translucent rather than transparent, see Table 2, an effect of the diluent used. During manufacture, it was apparent that there were two distinct phases present and therefore the resin was shaken and degassed prior to addition of the curing agent. It is possible that the diluent was not entirely miscible with the DGEBA after storage. The bio-based content appears to be due to glycerol glycidyl ether (GGE) which could constitute a 100% bio-based ingredient, according to BS ISO 16620-5,[5] if synthesized using Epicerol.

3.2 | Mechanical properties

The measured mechanical and thermo-mechanical properties of the bio-based resin systems and comparative standard (petroleum-derived) epoxy systems are shown in Table 4. As the chemistry differs from system to system and the compositions are not completely known, it is difficult to draw direct conclusions and comparisons about the exact nature of the polymer networks. However, all the systems are based upon DGEBA and use amine curing agents, so it is possible to compare the relative effects of their bio-based content and curing agent type to conventional epoxy systems.

3.2.1 | Tension and compression

For each system, the results of a typical uniaxial tension and plane strain compression test are presented in Figure 1 (a) and (b), respectively. The tensile and PSC results show good agreement with each other in terms of the relative yield strength, see Table 4. For example, GP22 has σ_{yt} = 72.5 MPa and $\bar{\sigma}_{yc}$ = 89.0 MPa, while 0A1B has σ_{yt} = 68.0 MPa and $\bar{\sigma}_{yc}$ = 84.4 MPa, respectively. As

TABLE 4 Mechanical and thermo-mechanical properties of bio-based epoxy systems compared with conventional systems,[4,46–49] mean ± standard deviation shown

Abb.	T_g (°C)	E'_G (GPa)	E'_R (MPa)	E_t (GPa)	σ_{yt} (MPa)	ε_f (%)	$\bar{\sigma}_{yc}$ (MPa)	$\bar{\varepsilon}_{c1}$ (mm/mm)	$\bar{\varepsilon}_{cf}$ (mm/mm)	K_{IC} (MPa m$^{1/2}$)	$G_{IC,energy}$ (J m^{-2})	$G_{IC,LEFM}$ (J m^{-2})
0A02	71.9 ± 0.2	2.00 ± 0.01	5.9 ± 0.3	2.29 ± 0.08	48.0 ± 0.9	4.3 ± 1.0	56.4 ± 0.7	0.64 ± 0.01	0.90 ± 0.03	0.59 ± 0.05	141 ± 20	133 ± 22
0A1B	98.7 ± 0.1	2.61 ± 0.06	6.7 ± 0.5	3.09 ± 0.05	68.0 ± 0.5	4.9 ± 0.4	84.4 ± 0.9	0.39 ± 0.04	0.83 ± 0.03	0.68 ± 0.04	141 ± 15	134 ± 15
INRS	118.4 ± 1.5	2.38 ± 0.01	8.4 ± 0.8	3.23 ± 0.06	67.8 ± 12.9	4.2 ± 2.0	88.6 ± 0.3	0.32 ± 0.04	0.78 ± 0.03	0.96 ± 0.10	225 ± 32	251 ± 53
AMPRO	66.5 ± 0.3	1.94 ± 0.02	2.8 ± 0.3	2.20 ± 0.08	42.6 ± 0.4	7.9 ± 1.8	61.0 ± 0.4	0.46	1.10	0.64 ± 0.06	177 ± 15	165 ± 29
ECO	59.3 ± 0.2	2.46 ± 0.16	3.3 ± 0.3	2.38 ± 0.11	37.7 ± 5.4	3.8 ± 3.4	68.7 ± 0.7	0.79 ± 0.02	1.08 ± 0.01	0.81 ± 0.05	197 ± 27	241 ± 31
GP22	75.1 ± 0.1	3.10 ± 0.03	8.8 ± 0.3	3.45 ± 0.19	72.5 ± 0.4	3.6 ± 0.2	89.0 ± 0.6	0.53 ± 0.03	1.03 ± 0.03	0.94 ± 0.07	213 ± 33	228 ± 36
GP24	78.4 ± 0.1	3.03 ± 0.12	11.4 ± 2.8	3.28 ± 0.09	65.6 ± 0.5	5.7 ± 0.6	80.9 ± 0.8	0.45 ± 0.06	0.81 ± 0.02	2.16 ± 0.06	1258 ± 94	1246 ± 64
IG22	75.4 ± 0.6	3.01 ± 0.00	7.3 ± 0.5	3.57 ± 0.09	75.7 ± 0.3	3.6 ± 0.3	90.9 ± 2.0	0.66 ± 0.02	1.16 ± 0.03	1.14 ± 0.06	285 ± 26	318 ± 34
IG24	81.8 ± 0.4	2.62 ± 0.01	11.6 ± 0.4	3.09 ± 0.14	61.6 ± 1.2	6.8 ± 2.0	72.7 ± 1.3	0.60 ± 0.02	0.74 ± 0.16	2.39 ± 0.06	1835 ± 162	1628 ± 82
LYHY	151 ± 1	2.9	13.6	3.27 ± 0.1	88 ± 1	4.7 ± 0.3	105.6 ± 0.3	0.47 ± 0.21	0.86 ± 0.01	0.61 ± 0.05	102 ± 11	106 ± 10
LYIPD	162	—	—	2.65 ± 0.05	58 ± 6	4.7 ± 1.0	—	—	—	0.78 ± 0.11	—	200
LY230	96 ± 0	—	—	2.94 ± 0.11	67 ± 3	5 ± 0	96 ± 1	—	—	0.73 ± 0.13	302 ± 39	163 ± 55
LYHDEHE	127	—	—	2.93 ± 0.12	—	—	—	—	—	0.76 [a]	—	173 ± 33
LYHDEIPD	133 ± 2	—	—	2.32 [a]	—	—	—	—	—	0.66 ± 0.1	192 ± 23	165 ± 47

[a]Value back-calculated.

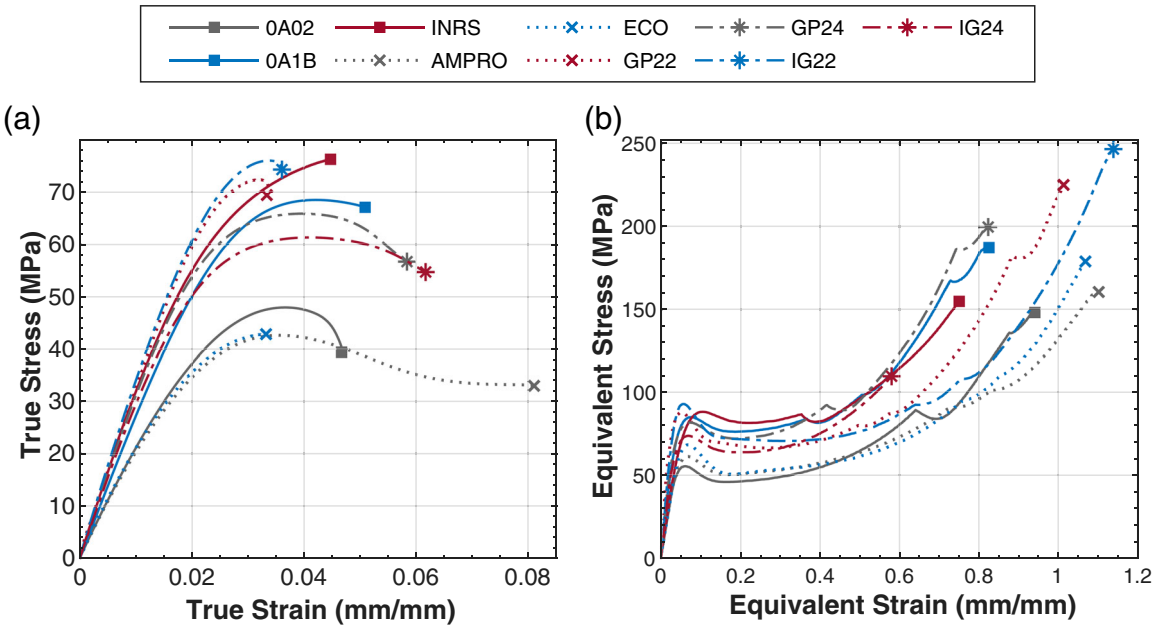


FIGURE 1 Tensile true stress vs. true strain from uniaxial tensile test (a), and equivalent compressive stress vs. equivalent strain from plane strain compression (b) [Color figure can be viewed at wileyonlinelibrary.com]

epoxies are brittle materials, they exhibit a much lower strain to failure in tension than in compression, as edge defects and voids play a more significant role in failure in tension. In both tension and compression, GP22, IG22, and INRS, were the systems with the highest yield strength. GP22 and IG22 did not tend to surpass their yield point in tension, but produced repeatable tensile results, whereas INRS showed large variability in σ_{yt} and ε_f. The worst performing resin in tension was ECO; it is suspected that the diluent was not well dispersed and that areas of high diluent concentration behaved as stress concentrators. All other systems generally failed within the strain-softening region after yield in tension.

In compression, all the systems exhibit a strain-softening region in the PSC test. This indicates that all the systems have some ability to be toughened by the addition of a particulate filler.[58] The materials, which exhibit large strain softening regions, show the largest potential to toughen by the addition of tougheners.[59] Of the tested systems, IG22, GP22, and ECO are most likely to benefit from the addition of tougheners, while INRS, 0A1B, and 0A02 are the least likely. All the systems demonstrate strain hardening or orientation hardening behavior, after the strain softening region.[58] Additionally, all systems showed a good resistance to the first crack, no cracking occurred until the epoxies had deformed significantly beyond their yield point. However, large variations were observed in the values of the strain to first crack, $\bar{\varepsilon}_{c1}$, the strain to failure, $\bar{\varepsilon}_{cf}$, and the respective slope of their strain hardening region. The most notable performing systems by these measures were ECO, GP22, and IG22, see Figure 1.

3.2.2 | Thermo-mechanical

Typical DMA results for each system are presented in Figure 2. The glassy storage modulus, E'_G, values show a similar trend to E_t, as would be expected, with values ranging from 2 GPa to 3 GPa. The E'_R values are lower by approximately 3 orders of magnitude, as is common for an epoxy polymer network. In the rubbery region, E'_R gives a good indication of the crosslink density. INRS, IG24, and GP24 exhibit the highest E'_R, whereas 0A02, ECO, and AMPRO exhibit the lowest. The diluents used in the latter systems have clearly reduced the crosslink density, it is possible that this is due to blocking of functional groups by pendant chains, steric hindrance or that the systems are resin rich. For the systems with SD8822 as curing agent, there is a noteworthy increase in storage modulus above T_g, this may be explained by an increase in crosslinking (degree of cure) during the test as the original post-cure was performed at only 40 °C. This curing agent formulation includes aromatic amines, which are more stable and require higher activation energy and curing temperatures. The 0A02 samples darkened uniformly during the DMA test, which is an indication of further crosslinking occurring.

The highest T_g belongs to the epoxy with the lowest bio-content, INRS, believed to be from only a substitution of epichlorohydrin for Epicerol in DGEBA. It would be anticipated that pure DGEBA systems with amine curing agents would have a T_g above 80 °C.[50,60] Therefore, in the other systems, the methods used to include additional bio-content have had a negative impact on this property,

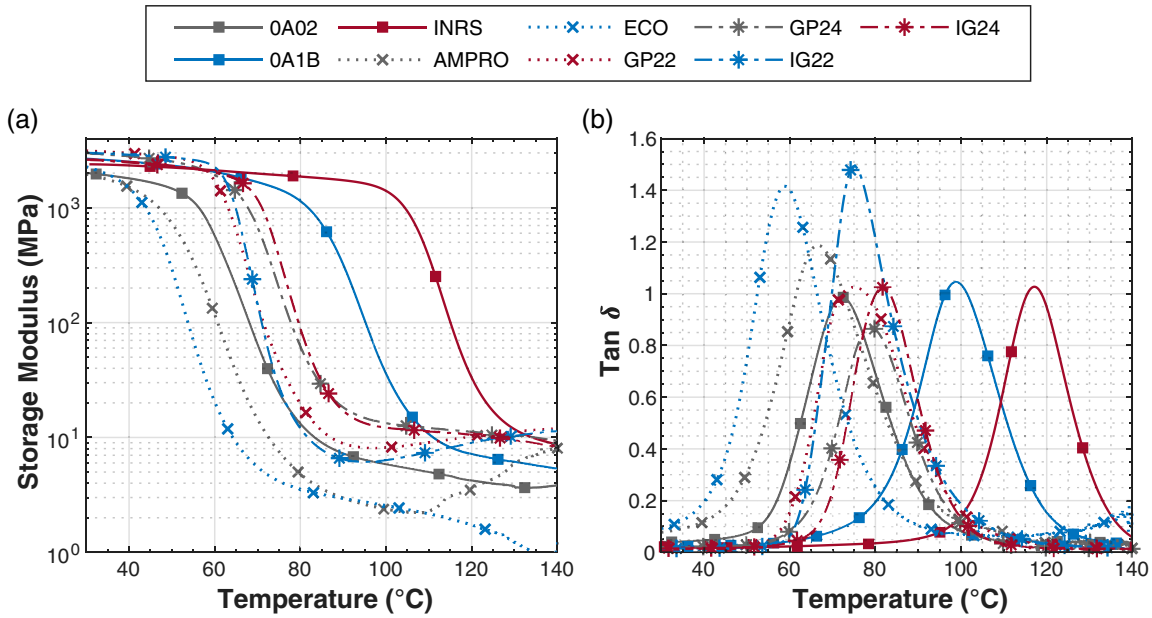


FIGURE 2 Storage modulus (a), and tan δ (b) vs. temperature for the bio-based epoxy systems from dynamic mechanical analysis [Color figure can be viewed at wileyonlinelibrary.com]

but to differing extents. Diluents, required in infusion resin systems to reduce the viscosity, normally reduce the T_g. As can be seen in Figure 2, INRS and 0A1B have the most desirable T_g out of the tested systems, at 99 °C and 118 °C. In contrast, ECO and AMPRO have relatively low values of T_g, at 59 °C and 67 °C, see Table 4, experiencing the onset of T_g at around 40 °C. This temperature is readily experienced as the ambient temperature in warm climates and therefore such a low onset is undesirable. The remaining systems all have their T_g in the region of 70 °C to 80 °C. This would be too low for structural aerospace components, but could be considered suitable for applications, such as, transport, sports equipment, or wind turbine blades.

The width of the tan δ curve for the sample gives an indication of the homogeneity of the polymer network. The peaks of GP24, IG24, and INRS are narrower than those of the other systems, see Figure 2, indicating a more uniform polymer network. The height of the peak tan δ can be related to the damping capacity of the material, so IG22, ECO, and AMPRO might be expected to perform well in a vibration-sensitive application. As ECO and AMPRO have low E'_R and suspected low crosslink density, it is not a surprise that they have a large viscous contribution.

3.2.3 | Fracture toughness

The fracture toughness values of unmodified epoxies are commonly in the range of 0.5 MPa $m^{1/2}$ to 1 MPa $m^{1/2}$, with a fracture energy between 100 J m^{-2} and 200 J m^{-2}.[61] The values for all the bio-based systems are within or above this range, which indicates that, in general, the addition of the bio-content has not negatively impacted the fracture properties, although they tend to show a lower T_g than the standard epoxy systems used for comparison. As the tests were performed at ambient temperature of 23 °C, systems with a T_g closer to this value will exhibit a higher toughness as it is easier to overcome intermolecular bonds and deform plastically. The INRS and Sicomin epoxies have better fracture properties compared to ECO and those utilizing CNSL content. The GP24 and IG24 systems possessed very large values of $G_{IC,energy}$, of 1258 J m^{-2} and 1835 J m^{-2}, respectively. Systems can exhibit a larger fracture toughness depending on the network structure, types of pendant groups, unreacted end-groups and unreacted monomers; and how these affect the deformation of the polymer under stress.

The fracture toughness and T_g are plotted against bio-based content in Figure 3. Note that the bio-based content value for AMPRO is shown as 40 % because the exact value cannot be disclosed. For both measures, it is clear that no overarching trend exists with increasing bio-based content; and this is also the case for all other mechanical properties. Bio-based systems generally exhibited greater K_{IC} than the conventional systems, but only the Sicomin systems (GP22, GP24, IG22, and IG24) and 0A1B possessed similar E_t and σ_{yt} values, while the bio-based systems had lower $\bar{\sigma}_{yc}$. In almost all cases, the additional bio-based content appears to come at the expense of T_g, as only two systems, INRS and 0A1B outperform LY230, the

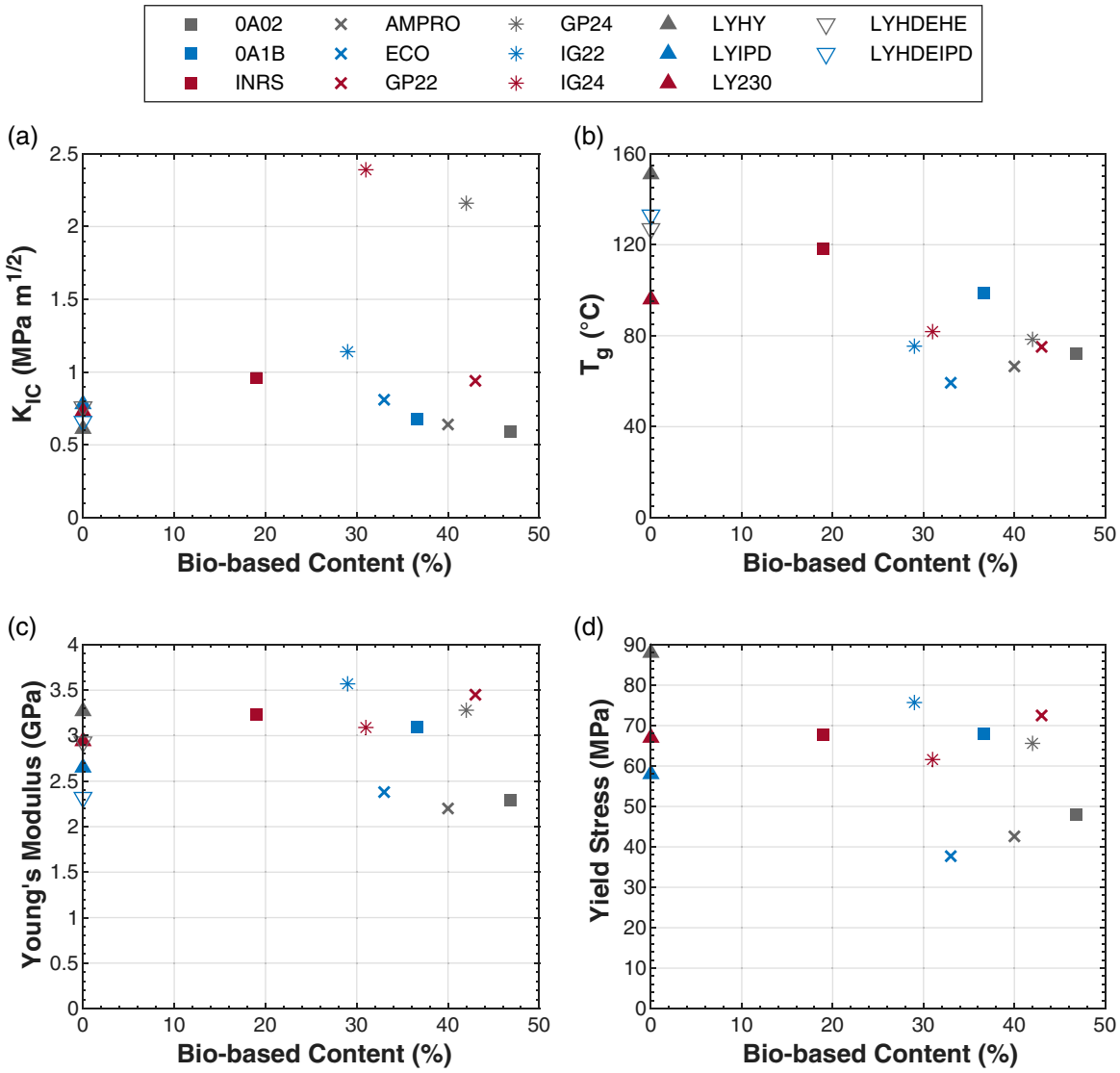


FIGURE 3 Fracture toughness (a), glass transition temperature (b), tensile Young's modulus (c), and tensile yield strength (d) vs. bio-based content for the epoxy systems [Color figure can be viewed at wileyonlinelibrary.com]

conventional system with the lowest T_g. The bio-based systems GP22, IG22, and 0A1B exhibit the best combinations of ease of processing, and good mechanical and thermomechanical properties for their bio-content.

3.3 | Bio-based content

Currently, the most successful method to add bio-content is to replace epichlorohydrin with Epicerol during the reaction with BPA and aliphatic diols to produce DGEBA and reactive diluent, respectively. It can be noted from this study that resin manufacturers have successfully applied this method to incorporate partially bio-based aliphatic diglycidyl ethers as diluent. This allows a significant proportion of bio-based content to be introduced while maintaining chemically-similar resins and reactive diluent, which can be cured by existing optimized curing agents. However, this method has a limit to the bio-content it can introduce, and so going forwards it is important to develop bio-based alternatives to DGEBA and amine curing agents. This method yields the highest percentage of bio-based content when applied to produce low molecular weight (short chain) glycidyl ethers. Low AHEW curing agents are also utilized to maximize the percentage of bio-based content in the system, although these can often be more reactive and toxic. Epoxy resins with more functional groups would yield higher bio-content using this method, but if the diluent does not effectively form a polymer network then this could be detrimental to the material properties, as is believed to be the case of GGE in the ECO system.

A final point to consider is that for all systems in this study, both resin and curing agent are provided by the same supplier. This provides security in the way that the products are used and their performance. Of the systems used, only one supplier provided details of the epoxide equivalent weight (EEW) and amine hydrogen equivalent weight (AHEW). If these were provided, higher bio-content systems could be produced, and more direct comparisons with conventional systems could be made. This would also enable greater freedom to formulate bio-based systems with mixtures of epoxy resins or curing agents, enabling users to match more closely the performance of existing petroleum-based systems.

4 | CONCLUSIONS

In the current socio-political climate, companies operating in many sectors are looking to reduce their environmental impact. For those using thermoset polymer composites, bio-based epoxies provide such an opportunity. In this study, approaches that manufacturers have taken to increase the bio-content of epoxies have been identified. Most high bio-based content resins for infusion appear to be produced with conventional curing agents and adding bio-based content to the resin or reactive diluent; generally using Epicerol but also using other bio-based precursors, such as, CNSL and glycerol. Use of only Epicerol for production of DGEBA can lead to around 20 % bio-based content in an epoxy system, but larger increases can be achieved if used to produce diluents such as low molecular weight glycidyl ethers. Some diluents used by manufacturers appear 100 % bio-based, according to carbon content, but are used more sparingly as these generally have a deleterious effect on the resultant mechanical properties and T_g. The most promising systems tested, GP22, IG22, and 0A1B possessed good strength, stiffness, toughness and a reasonable T_g with bio-based contents of 28 %, 43 %, and 36.6 %, respectively. Producing fully bio-based resin systems presents a challenge, but these results show that bio-based epoxy systems show very good potential for use in composite materials and provide manufacturers with an immediate lower-carbon alternative for vacuum-infused composites, for example in marine, sports equipment, and wind energy applications.

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CONFLICT OF INTEREST

The authors declare no potential conflict of interest.

AUTHOR CONTRIBUTION

Joseph S. Terry, formal analysis; investigation; validation; visualization; writing–original draft.
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