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# Vanillin-derived epoxy resin as a high fracture toughness high stiffness matrix for carbon fibre reinforced structural composites

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The following study cements vanillin's position as a leading replacement for BPA-based epoxy resins in high performance epoxy-amine composite applications. Diglycidyl ether of vanillyl alcohol (DGEVA) is cured with a high-performance aerospace grade crystalline diamine hardener 4,4-diaminodiphenyl sulfone (4,4-DDS) yielding a resin with a  $T_g$  of 140 °C according to DMA, high bending stiffness of  $3.84 \pm 0.02$  GPa, and high mode I fracture toughness of  $1.33 \pm 0.23$  MPa m<sup>1/2</sup>, as evidenced by ASTM standard tests. Initial kinetic and rheological evaluation of DGEVA-DDS highlights its potential to act as a drop-in epoxy system for many industrial composite manufacturing processes with minor processing adjustments. Resin is characterized by means of cure kinetics, thermomechanical properties and physical properties deciphering a route for carbon fibre reinforced composite manufacturing. The results show superior performance of the neat DGEVA-DDS system in mechanical tests including up to 38% greater strength, 60% stiffness, 160% fracture toughness, and minor increases when translated to composite materials as compared to BADGE-DDS.

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## Sustainability spotlight

This study confirms vanillin as a leading renewable alternative to BPA-based epoxy resins for high-performance composites. A bio-based epoxy resin from diglycidyl ether of vanillyl alcohol (DGEVA), cured with the aerospace-grade diamine hardener 4,4-diaminodiphenyl sulfone (4,4-DDS) demonstrated a high glass transition temperature (140 °C), high bending stiffness ( $3.84 \pm 0.02$  GPa), and remarkable fracture toughness ( $1.33 \pm 0.23$  MPa m<sup>1/2</sup>). Compared to traditional BPA-based epoxy systems (BADGE-DDS), the vanillin-based resin exhibited up to 38% greater strength, 60% increased stiffness, and 160% higher fracture toughness. The resin's ease of integration into existing composite manufacturing processes supports responsible production (UN SDG 12), sustainable industrialization (UN SDG 9), and contributes positively towards climate action (UN SDG 13).

## Introduction

Epoxy resins are a cornerstone of modern sports, automotive, and aviation industries through their employment as fibre reinforced matrix materials.<sup>1</sup> High performance fiber reinforced polymer composites (FRPCs) utilise carbon fibres with a high- $T_g$  matrix material, often an epoxy monomer mixed with either an amine or anhydride curing agent.<sup>2</sup> To enhance the sustainability of composite materials the plastic matrix must be sourced renewably from a bio-resource.<sup>3,4</sup> Indeed many leading companies in varied industries are taking concrete steps towards a more bio-based portfolio.<sup>5</sup> However, many scalable renewable epoxy monomers are aliphatic in nature, with thermomechanical properties unsuitable for high-performance and structural applications. Additionally, some aromatic bio-based

monomers display high viscosities and low-scalability as drawbacks.<sup>6,7</sup>

Lignin is a complex, highly aromatic network polymer present in wood in high percentages. It is also a byproduct of the paper industry and is therefore available in large amounts.<sup>8</sup> Vanillin is a non-toxic phenol that can be produced from the catalytic cracking of lignin in high yields.<sup>9</sup> Through a simple reduction reaction its vanillyl alcohol derivative is synthesised, and epoxidation with bio-based epichlorohydrin yields a potentially 100% bio-based epoxy monomer.<sup>10</sup> This diglycidyl ether of vanillyl alcohol (DGEVA) has been utilised numerous times to produce partially bio-based thermosets and vitrimers.<sup>11</sup> Many of these vanillin-based network polymers exhibit mechanical properties suitable for high-performance applications with  $T_g$  ranging from 114–178 °C (DSC) and moduli in the range of 10 GPa,<sup>1</sup> already making it a potential candidate for many applications.<sup>12</sup> Positively, its precursor vanillin is also non-toxic in large quantities, which cannot be said for BADGE precursor bisphenol A which has been well-documented to disrupt hormone systems in human beings.<sup>13–16</sup> Whilst DGEVA

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Fig. 1 (a) Chemical structures of DGEVA epoxy and DDS hardener. (b) TGA of cured resins. (c) Isothermal DSC thermograms and corresponding modelling fits. (d)  $E_a$  evolution vs. degree of cure for both resin systems. (e) Degree of cure vs. time at isothermal temperatures.

23 °C, 50 °C and 80 °C respectively (Fig. 2b). Shear viscosities for BADGE-DDS were at least 4 times higher at any given temperature and showcase the potential for DGEVA-DDS for certain manufacturing techniques such as vacuum infusion at a lower temperature than BADGE-DDS. In this study we define the gelation point as the crossover of  $G'$  and  $G''$  at 1 Hz, as suggested in other studies.<sup>36–38</sup> Gel-point times at various temperatures were recorded and show faster gel-times for DGEVA-DDS, which is surprising given that the kinetic modelling showed a higher average activation energy for DGEVA-DDS. The average activation energy up to the theoretical point of gelation ( $\xi = 0.53_{\text{DGEVA-DDS}}$ ,  $0.57_{\text{BADGE-DDS}}$ , calculated using Flory–

Stockmayer theory) is slightly higher for DGEVA-DDS at 72.6 vs. 70.2 kJ mol<sup>-1</sup>, so the lower gel-point values for DGEVA-DDS are surprising. Nonetheless, DGEVA-DDS offers ample processing time with a gel-point of 6 hours at 120 °C.

Combining rheological investigations and derived reaction kinetics enables us to calculate the degree of cure at gelation ( $\xi_{\text{GP}}$ ) for the reference system and thus quantify the degree of cure necessary to form a percolated network. For this, the temperature profile recorded during the rheometer measurements is used to solve eqn (S1) to (S4) and determine  $\xi_{\text{GP}}$  (Table 2). Fig. 3 presents the measurement values and the calculated cure progression. As it takes approximately 1 minute to load the





Fig. 2 (a) DMA temperature sweep in the three point bending setup of both systems. Heating rate = 1 K min<sup>-1</sup>. (b) Viscosity vs. temperature profiles of both systems.

Table 1  $T_g$  comparison of epoxy-amine resins utilising vanillin-based epoxy monomers with common diamine hardeners. All  $T_g$  values are derived from the onset of the storage modulus decrease in DMA measurements<sup>a</sup>

Vanillin-based epoxy	Amine hardener(s)	$T_g$ [°C]	Ref.
Diglycidyl ether of vanillyl alcohol (DGEVA)	DDS	140	This work
Diglycidyl ether of vanillyl alcohol (DGEVA)	IPDA	97	32
Diglycidyl ether of vanillyl alcohol (DGEVA)	PACM	100	33
Diglycidyl ether of vanillyl alcohol (DGEVA)	TETA, TREN, DETA, EDA	~40	34
Vanillin mono-epoxy (Schiff-base epoxy network)	DDM	136 <sup>a</sup>	35
Diglycidyl ether of methoxyhydroquinone	IPDA	132	32

<sup>a</sup>  $T_g$  from DSC.

Table 2 Parameters obtained from the kinetic modelling of the reaction according to Kamal and Sourour (eqn (S3) and (S4))

$m$	$n_1$	$n_2$	$A_1$ [log(s <sup>-1</sup> )]	$E_1$ [kJ mol <sup>-1</sup> ]	$A_2$ [log(s <sup>-1</sup> )]	$E_2$ [kJ mol <sup>-1</sup> ]
1.05	1.39	4.74	3.52	53.17	7.29	85.99

sample and start the measurement, we assume an initial degree of curing of 0.01 (Table 3).

The average  $\xi_{GP}$  for the BADGE-DDS formulation is above the value reported in the literature  $\xi_{GP} < 0.5$ .<sup>39</sup> The exceptionally high values for the lower curing temperatures may be due to the absence of a term in the kinetic model describing the curing reaction's diffusion effect (and slowdown). The kinetic model was calibrated at curing temperatures, ensuring  $T > T_{g,\infty}$  during nearly the whole reaction process, so that it does not capture any effect of diffusion which might become relevant, especially at the lower temperatures. The theoretical calculations give consistently lower values compared to the average value of the experiments. The divergence between measurements and theoretical consideration may be attributed to a slight divergence between the recorded and the actual temperature present

within the resin specimen. Still, the differences are within the standard deviation of the measurements. Slight deviations between theory and experiments are common<sup>40</sup> and might be explained by a substitution effect in the amine group, with the secondary amine reacting at a slower rate than the primary amine, particularly for aromatic diamines,<sup>41</sup> which leads to higher conversions before gelation occurring due to linear chains forming preferentially over microgels. Intramolecular cyclization could also contribute to this increased experimental  $\xi_{GP}$ .<sup>40,42</sup> Although the standard deviations are comparably high, the results indicate that gelation of the DGEVA-DDS formulation occurs at an earlier stage of curing as compared to BADGE-DDS. In practical terms, this results in a smaller timeframe for the injection and fiber impregnation process, which could be mainly a drawback for infusion processes of large components





Fig. 3 (a) BADGE–DDS gel point times of 37, 120 and 490 minutes at 120, 150 and 180 °C respectively. (b) DGEVA–DDS gel-point times of 21, 79 and 372 minutes at 120, 150 and 180 °C respectively.

Table 3 Calculated  $\xi_{GP}$  for the two resin systems

	$\xi_{GP}$			Average	Theoretical
	120 °C	150 °C	180 °C		
BADGE–DDS	0.68	0.60	0.56	0.57	0.61 ± 0.06
DGEVA–DDS	0.60	0.51	0.47	0.53	0.54 ± 0.07

with long flow paths requiring a long processing window. This relation becomes more tangible comparing the time scales: at 180 °C, gelation occurs after 21 minutes for the DGEVA and 37 minutes for the BADGE formulation.

DMA is a non-destructive technique to obtain thermo-mechanical information on a material.<sup>43</sup> Comparing DGEVA–DDS against BADGE–DDS we saw that the vanillin-based samples showed a higher initial storage modulus of 3.76 GPa compared to 2.44 GPa for the BADGE system, similar to mechanical testing moduli reported further on (Fig. 2a).  $T_g$  of DGEVA–DDS is considerably lower than that of BADGE–DDS at 140 °C compared to 220 °C for BADGE–DDS; however this is still an acceptable  $T_g$  for many high-performance applications; however further investigations on wet  $T_g$  should be performed.<sup>44</sup> From TMA analysis (Fig. 4a) we can derive the coefficient of thermal expansion (CTE) of a material. The CTE is an important parameter for matrix materials as it informs us about a parts expansion across a temperature range which can greatly affect the stability and loading on larger composite structures.<sup>45</sup> CTE for DGEVA–DDS is 58.12  $\mu\text{m per m per }^\circ\text{C}$  compared to 84.45  $\mu\text{m per m per }^\circ\text{C}$  for BADGE–DDS resin. This means that DGEVA–DDS expands less than BADGE–DDS upon heating, which can be advantageous in composite materials, or where parts routinely undergo thermal cycling of some kind.<sup>46</sup> Lower CTE leads to reduced residual stresses, which become evident during cooling processes after complete curing.<sup>47</sup>

Further resin characterisation was performed to evaluate hydrophilicity and gel-content of resin systems. The water contact angle (SI 1.3.6) was measured to be 71° indicating that DGEVA–DDS is hydrophilic. The water absorption test (SI 1.3.7) indicated a weight increase of 5.5% after 14 days, which is a large increase. Gel content (SI 1.3.8) was evaluated and shown to be 100%. These results show that DGEVA–DDS is considerably hydrophilic, and this must be taken into account when assessing its use case. Composite materials are coated prior to final applications, so the employment of a hydrophobic coating that can enhance water resistance is essential.<sup>48</sup> Density of the resin evaluated according to ASTM D792 (SI 1.3.9) was  $1.296 \pm 0.043 \text{ g cm}^{-3}$  (7% higher than BADGE–DDS) which is typical of epoxy–amine resins;<sup>49</sup> however for applications where light-weighting is of prime importance it is a cause for consideration.<sup>50</sup> Cure shrinkage was evaluated by recording the density of the uncured systems (SI 1.3.10) with DGEVA–DDS cure shrinkage calculated to be 7.0%, slightly larger than the 5.5% recorded for BADGE–DDS, which is in the usual range for epoxy resins.<sup>51</sup> Lower cure shrinkage is ideal in CFRP systems as carbon fibres shrink very little across curing temperature ranges, so with greater matrix shrinkage more residual stress is introduced in the composite material (Table 4).<sup>52</sup>

Quasistatic destructive mechanical testing in flexure, tension and SENB geometries was performed according to standards ASTM D790, D638 and D5045 respectively. Resin mechanical testing results are summarised in Table 5. Overall the results show that DGEVA–DDS is a significantly stiffer and stronger material than BADGE–DDS, whilst also having a much higher resistance to crack propagation shown by a higher  $K_{IC}$  value. These results are surprising as epoxy materials tend to become more brittle and less strong as their stiffness increases – DGEVA–DDS resin does not follow this trend.<sup>53</sup> One reason for this could be the increased linearity in the DGEVA–DDS network which will allow for more mobility and therefore energy





Fig. 4 (a) TMA displacement vs. temperature graphs for both systems. (b) Tensile stress–strain curves. (c) Flexural stress–strain curves. (d) Fracture toughness force–displacement graph. BADGE–DDS results from a previous study published by our group.<sup>7</sup>

Table 4 Material properties of DGEVA–DDS and BAGDE–DDS resin systems

	Viscosity (23 °C) (Pa s)	Gel point time at 120, 150, and 180 °C (minutes)	Cure shrinkage (%)	Gel-content (%)	$T_g$ (°C)	$E_{avg}$ (kJ mol <sup>-1</sup> )	Water contact angle (°)	Water absorption (14 days) (%)	Density (g cm <sup>-3</sup> )	CTE (µm per m per °C)
DGEVA-DDS	5.2	21, 79, and 372	7.0	100	140	82.2	71	5.50	1.296	58.12
BAGDE-DDS	34.8	37, 120, and 490	5.5	100	220	69.6	80	0.96	1.217	84.45

dissipation in the network, increasing strength and fracture toughness.<sup>54</sup> This comes at the expense of lower thermal properties as previously discussed. Previous studies show that DGEVA-DDS has significantly (12%) lower free volume than BADGE-DDS which can explain the increase in stiffness.<sup>55</sup> It has been shown previously that methoxy units increase fracture toughness of epoxies due to enhanced energy dissipation through relaxation of the methoxy group, which occurs around room temperature.<sup>29,30</sup>

The flexural modulus was determined to be  $3.84 \pm 0.02$  GPa and strength,  $165.29 \pm 3.32$  MPa, considerably higher than

those of similar commercial resin systems from data sheets (Fig. S19). Whilst these stiff and strong properties are imparted by the increased linearity in the DGEVA molecule as compared to BADGE, the presence of the phenyl ring on the DGEVA molecule allows for a suitably high  $T_g$  for many high-performance applications. Tensile strength was also relatively high at  $110.98 \pm 7.94$  MPa. On comparing flexural and tensile strength to those of the BADGE-DDS system we see a 38% increase in stiffness and 60% increase in strength in flexure, with similar values for tensile. These results are very encouraging for DGEVA's potential as a bio-based BADGE alternative. The largest



Table 5 Mechanical data for resin coupon testing

	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile modulus (GPa)	Tensile strength (MPa)	$K_{IC}$ fracture toughness ( $\text{MPa m}^{1/2}$ )
DGEVA-DDS	$3.84 \pm 0.02$	$165.29 \pm 3.32$	$2.12 \pm 0.06$	$110.98 \pm 7.94$	$1.33 \pm 0.23$
BAGDE-DDS	$2.50 \pm 0.07$	$130 \pm 2.46$	$1.29 \pm 0.03$	$72.09 \pm 25.43$	$0.60 \pm 0.03$

deviation in mechanical behaviour between the two systems is seen in the increased mode I fracture toughness ( $K_{IC}$ ) value of the DGEVA-based resin as compared to the petroleum system. A  $K_{IC}$  value of  $1.33 \pm 0.23 \text{ MPa m}^{1/2}$  was determined *via* ASTM D5045, an increase of 160% compared to that of analogous BADGE-DDS resin. High performance PEEK has a reported  $K_{IC}$  of around  $3 \text{ MPa m}^{1/2}$  whereas unmodified high-performance epoxy-amine systems rarely breach the  $1.0 \text{ MPa m}^{1/2}$   $K_{IC}$  value, making DGEVA a unique epoxy monomer in this regard.<sup>56,57</sup> Fig. 6d compares DGEVA-DDS's  $K_{IC}$  and  $T_g$  values to those of other well-known commercial epoxy-amine systems, and its advantage can clearly be seen.

CFRP samples were manufactured for both DGEVA-DDS and BADGE-DDS, and tested in 4 different geometries. Interlaminar shear, in-plane shear, and compression samples were manufactured from the same manufactured plate using biaxial fibres (Fig. 5a and b).

The in-plane shear strength (IPSS) test was chosen as the in-plane shear behaviour is independent of the fibre properties, and relates to matrix yield strength and fibre-matrix interface properties. ASTM D3518 was followed using 6 samples with fibres in a  $[\pm 45]$  orientation. The force *vs.* strain graphs (Fig. S8–S10) show the stiffer nature of the DGEVA-DDS samples, with initial elastic deformation in the linear region followed by plastic deformation in the non-linear region. A modulus of  $6.58 \pm 0.68 \text{ GPa}$  was calculated for DGEVA-DDS compared to  $5.49 \pm 0.52 \text{ GPa}$  for BADGE-DDS, a stiffness increase of 20%. Final shear strengths came out to be  $85.75 \pm 0.52 \text{ MPa}$  for DGEVA-DDS and  $81.84 \pm 4.85 \text{ MPa}$  for BADGE-DDS. A much smaller standard deviation in the DGEVA-DDS tests suggest better sample quality and homogeneity, which could be due to the lower viscosity of DGEVA-DDS allowing for the manufacturing of higher-quality laminates with less defects. Larger spreads in the BADGE-DDS samples are likely due to manufacturing



Fig. 5 (a) Schematic showing sample cutting locations in the composite plate according to standard sizes. (b) Final DGEVA-DDS composite plate. (c) and (d) DGEVA-DDS samples failing in compression *via* wedge splitting with some inter-laminar failure.





Fig. 6 (a) ILSS results. (b) IPSS results. (c) Compression strength results. (d) Fracture toughness vs.  $T_g$  for a variety of epoxy-amine systems.

defects. Compression tests were performed as it has been shown that the dominant composite failure mode in compression is plastic yielding of the polymer matrix. According to ASTM D6641 9 samples were cut from the plate at 45° to get a [0/90] configuration. Compressive strength came out as  $532.95 \pm 36.90$  MPa for DGEVA-DDS compared to  $499.02 \pm 40.26$  MPa for BADGE-DDS, a less conclusive result than the IPSS result due to significantly larger overlap in the standard deviations. Interlaminar shear strength (ILSS) tests were performed to probe the load transfer efficiency in the two systems. ASTM D2344 was followed and 10 samples were tested in the [0/90] configuration. ILSS was  $58.17 \pm 2.37$  MPa for DGEVA-DDS and  $52.53 \pm 3.72$  MPa for BADGE-DDS, giving an increase of 11% in ILSS for the DGEVA-DDS resin.

The final composite test conducted was a low-velocity impact test. For this test 3 plates for each resin were manufactured according to ASTM D7136. Impact test results are highly sensitive to different testing setups and manufacturing conditions. Through the tests it was revealed that DGEVA-DDS composites absorb similar amounts of energy compared to BADGE-DDS; however, the calculated damage initiation energy of the matrix was 21% higher for BADGE-DDS. This is due to the higher modulus and bending stiffness (10% higher) of DGEVA-DDS composites, leading to increased brittle response at high loading rates. Further impact testing results will not be discussed further as there were some inconsistencies in results between samples, but data and analysis can be found in SI Section 1.6.4.



## Conclusions

In this research we have showcased the potential for a highly bio-based high performance epoxy-amine system suitable for use as a matrix material in FRPCs. Thermal properties are lower than those of a comparable petroleum-based system but still in the high-performance range with a  $T_g$  of 140 °C and  $T_{d5\%}$  of 273 °C. Reaction kinetics have been modelled using DSC and rheology, and show properties including lower overall reactivity than BADGE-DDS but faster gel-point times across a temperature range. This is likely due to the documented effect of the methoxy group on the DGEVA molecule interacting with the hydroxyl unit from epoxy ring-opening, hampering its catalytic effect. Gel-point times for DGEVA-DDS give a large processing window for composite production and prepreg production. Water absorption tests revealed a higher affinity to water compared to BADGE-DDS. Room temperature mechanical properties are significantly higher than that of BADGE-DDS with increases of up to 38% in stiffness, 60% in strength, and remarkably 160% in fracture toughness for the pure resin system. These increases are likely due to the higher crosslink density from the smaller DGEVA molecule, tighter packing of the epoxy network structure due to increased linearity, and greater energy dissipation mechanisms through linearity and the methoxy unit which increases fracture toughness.

Manufacturing of high-quality CFRP laminates has been demonstrated using vacuum infusion and autoclave curing. Minor improvements in strength and stiffness of CFRPs were seen using the DGEVA-DDS matrix compared to BADGE-DDS in in-plane shear, interlaminar shear, and compressive tests. Low velocity impact testing shows a more-complicated story, with BADGE-DDS having a higher matrix crack initiation energy. This report highlights the potential of DGEVA to be used in higher performance composite applications, including its benefits and potential challenges when compared to conventional resin systems. Future research could focus on the effect of matrix methoxy units in the composite material through fibre-matrix adhesion studies, helping to provide a more fundamental understanding of these interactions. To provide a more critical understanding of sustainability credentials in materials science, an interdisciplinary approach incorporating LCA and economic analysis could be pursued.

## Conflicts of interest

The authors declare that they have no competing financial interests.

## Data availability

Data for this article, including all raw experimental data are available at TU Delft Open Servers at <https://doi.org/10.4121/bb769d70-40ca-4999-a77f-4f491b6cc46e>.

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