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BIO-BASED EPOXIES: MECHANICAL PROPERTIES AND FREE VOLUME PERSPECTIVES.

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Abstract

Epoxy resins have been used as composite matrix materials for over half a century, enabling lightweight materials for a variety of applications. Their properties including high strength, chemical resistance, and ease of processing feature them as prime candidates for composite applications. Currently, high performance epoxy monomers are derived from non-renewable feedstocks, which presents a problem for future generations and technologies regarding sustainability. Many bio-based alternatives have been investigated, but properties fall short of high-performance industry standards due to a lack of appropriate chemical groups. Herein 3 bio-based epoxy monomers, with potential to replace high-performance standards, are compared against 3 petroleum derived industry standards. Industrial high performance aromatic diamine crystalline hardener is used to synthesise resin systems. Tensile, flexural and fracture toughness properties are investigated following ASTM standards. Beyond a practical investigation of the physical properties of these resins a comparison of chemical structure to mechanical properties is made. Free volume investigations using positron annihilation lifetime spectroscopy (PALS) were performed, and can be used to explain to some degree the observed properties of the resin systems.

1. Introduction

Composite materials have revolutionized industries such as aerospace, automotive, and maritime – enabling lightweight structures to reduce costs and increase performance.[1,2] Epoxy thermoset matrices are most widely employed in structural applications including fuselage, wings, and the majority of F1 race car monocoques and chassis. Epoxy monomers are currently derived from non-renewable petroleum-based feedstocks, which may present a challenge in the future due to diminishing supply and increasing costs.[3] Additionally, many epoxy monomer feedstocks are toxic. The most widely used monomer is derived from Bisphenol A, a chemical that has faced decades of scrutiny for its disruptive hormone-mimicking effects and its ability to find its way into our bodies.[4,5] Therefore, there is great interest in investigating renewable, less-toxic feedstocks for new epoxy formulations.

The investigation and characterization of new materials is an extensive process while developing high performance sustainable resin systems, mainly due to their low abundance, high costs and quantity required for ASTM standard tests. Despite much work investigating sustainable epoxy resin systems, very few delve into their potential towards large scale composite manufacturing. Much work has been done to characterize renewable epoxy monomers, and some investigates higher performance candidates, including work by Mija et al and ourselves which show PHTE to have generally higher T_g and better mechanical properties compared to BADGE system.[6,7] Other work investigating RTE shows T_g above 320°C and tensile strength 20% higher than BADGE.[8,9] VDE investigations have mainly produced resins with low T_gs below 100°C.[10] Recent work by Zaidi et al highlights the potential for vanillyl alcohol derived epoxy through complete curing and decomposition kinetics analysis.[11] Whilst the current research suggests PHTE, RTE and VDE could all have a role in replacing non-renewable epoxy monomers, they have not been incorporated into a high-performance system. DDS aromatic diamine hardener is routinely used in aerospace structural applications. Bio-based epoxies cured with this hardener will give the best example so far of the potential of these renewable epoxy monomers. Additionally, literature often fails to investigate the reasons for given mechanical properties, which ultimately lies in the network structure of the resin systems. This network structure is composed of the crosslinked epoxy and hardener components, which depending on their chemical structure (ratio of aromatic to aliphatic groups, permanent dipoles, crosslink density) impart stiffness, brittleness, ductility and other mechanical characteristics to the resin. The network structure has a second, non-atomic element and that is the free-volume of the resin system.[12] Larger free volumes have been linked to increases in strength and fracture toughness, and decreases in stiffness.[13] A higher free volume gives more space for molecular movement. When a network is being stressed it can rearrange slightly to distribute the stress more evenly throughout the material. For fracture toughness free volume pores can lead to stress concentrations. It's generally understood that increases in free volume lead to decreases in fracture toughness for this reason.[14]

2. Materials and methods

2.1 Materials

Phloroglucinol triglycidyl ether (PHTE), Vanillin diglycidyl ether (VDE) and Resveratrol triglycidyl ether (RTE) were purchased from Specific Polymers. Bisphenol A diglycidyl ether (BADGE) was purchased from Sigma Aldrich. Tactic 742 ® (T742) and 4,4-DDS diamine hardener (Aradur 9664-1 micronised powder) was obtained from Huntsman, Switzerland. Trimethylolpropane triglycidyl ether (TPTE) was purchased from Merck Sigma.

2.2 Methods

2.2.1 Specimen preparation

All samples were prepared using a metal sandwich mold to manufacture dog bone samples for tensile testing, and a resin plate from which flexural, SENB and PALS samples were prepared. The epoxy and DDS hardener were mixed at room temperature. PHTE, VDE, T742 and RTE resins were heated to 80°C in an oven, and then mixed in a speedmixer at 2200 rpm for 5 mins under a vacuum pressure of 40 mbar. TPTE and BADGE showed lower viscosities and were immediately mixed in the speedmixer without a preheating step. Mixed resins were poured in the molds with care taken to avoid trapped air.

Tensile specimens were prepared according to ASTM D638 ”Standard Test Method for Tensile Properties of Plastics.”. A Type 5 specimen was selected. Flexural samples were prepared according to ASTM D790 ”Standard Test Methods for Flexural Properties of Unreinforced and Reinforced Plastics and Electrical Insulating Materials”. Fracture toughness SENB samples were prepared according to ASTM D5045 ”Standard Test Methods for Plane-Strain Fracture Toughness and Strain Energy Release Rate of Plastic Materials”.

Curing cycles for the resins were determined using DSC studies. For BADGE, PHTE, T742 and RTE this was 180°C for 2 hrs, 220°C for 1 hr. For VDE and TPTE a curing cycle of 160°C for 2 hrs, 180°C for 1 hr was used.

PALS samples were cut from a larger epoxy plate, the surfaces cleaned 3 times with isopropanol and 3 times with acetone, before sandwiching a small sample of ^{22}Na (radioactive sodium). PALS data was collected for 48 hours for each resin system. The positron emission spectrum is interpreted, and tau3 component corresponds to the positron existing in free space within the material is determined. Using the Tao-Eldrup relation a free volume was derived.

Tensile tests were performed on a Zwick 10 kN universal testing machine with a 10 kN loadcell. Flexural tests were performed on a Zwick 20 kN universal testing machine with a 20 kN loadcell. Fracture toughness tests were performed on a Zwick 10 kN universal testing machine with a 100 N loadcell.

3. Results and Discussion

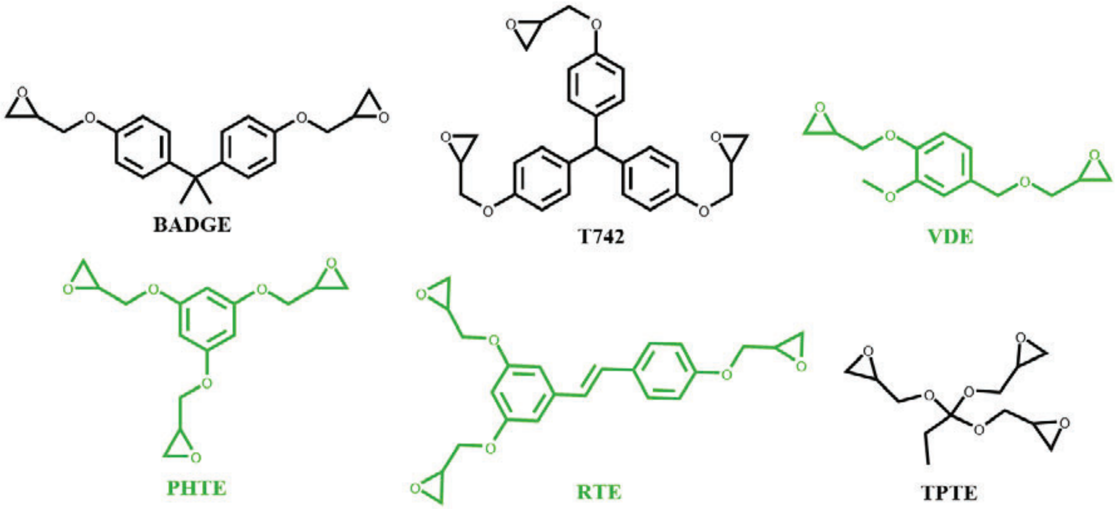

Figure 1 Idealised chemical structures of each epoxy monomer

3.1 Predicted behavior from chemical structure

From the chemical structures (Figure 1) we can predict to some degree the mechanical properties of the epoxy resins, and make a prediction about the free volume of each resin system. The ratio of aromatic:aliphatic atoms in the resins will play a large role in the free volume and mechanical properties of the resins. Therefore this ratio was calculated for each resin system overall (including DDS hardener) by calculating the aromatic and aliphatic atoms in each monomer, and converting this to a ratio by incorporating molar ratios of epoxy:DDS. A higher ratio of aromatic:aliphatic atoms should lead to stiffer resins with lower strength. Effect of aromaticity on free volume is not as intuitive - on one hand aromatic phenyl units can pi-pi stack which would reduce free volume. On the other hand the rigidity of aromatic units may hinder packing of the network and therefore increase free volume. Additionally, the bi-functionality of BADGE and VDE should lead to less crosslinked networks and larger free volumes.

Table 1 Data recorded for each of the resin systems outlining their mechanical properties, free volume size, density and functionality. Aromatic:aliphatic ratio was calculated taking all atoms in epoxy and hardener component into account.

Resin system	Tensile modulus (GPa)	Tensile strength (MPa)	Flexural modulus (GPa)	Fracture toughness (MPa.m$^{1/2}$)	Free volume (Å)	Density (kg/cm$^{2)}$	Aromatic:Aliphatic atoms
BADGE	1,30	72,09	2,50	0,51	2,62	1217	1,16
T742	2,57	63,36	3,37	--	2,48	--	1,35
VDE	2,17	113,31	3,78	1,33	2,30	1318	0,75
PHTE	1,79	48,04	3,76	0,99	2,28	1333	0,76
RTE	2,31	39,04	3,09	0,79	2,44	1308	1,20
TPTE	1,91	103,42	3,41	--	2,37	--	0,41

3.2 Mechanical properties

The flexural testing via a three-point bending set-up reveals a flexural modulus distribution for the resin systems of BADGE < RTE < T742 < TPTE < PHTE < VDE. BADGE shows the lowest flexural modulus followed by RTE. The other 4 resins show similar values, ranging from 3,37-3,78, an 11% spread between these 4 moduli. VDE and PHTE have the highest flexural modulus suggesting they are the stiffest of the 6 resins tested. Tensile testing reveals tensile modulus distribution between the resins of BADGE < PHTE < TPTE < VDE < RTE < T742. T742, RTE and VDE have the highest tensile modulus suggesting they are the stiffest materials here, and BADGE and PHTE have the lowest suggesting they are less stiff and more flexible. The tensile strength values increase in the order RTE > PHTE > T742 > BADGE > TPTE > VDE. For RTE and T742 we can conclude that these resins are stiff but highly brittle as they have considerably low strength values. PHTE seems to be less stiff but also brittle. VDE and TPTE stand out in terms of strength, with VDE showing a 63% increase in strength at failure as compared to BADGE. SENB testing was performed on 4 resin systems. The initial results show that all 3 bio-based resins have significantly higher fracture toughness values than BADGE, with VDE showing a 2.6x increase in fracture toughness (Table 1).

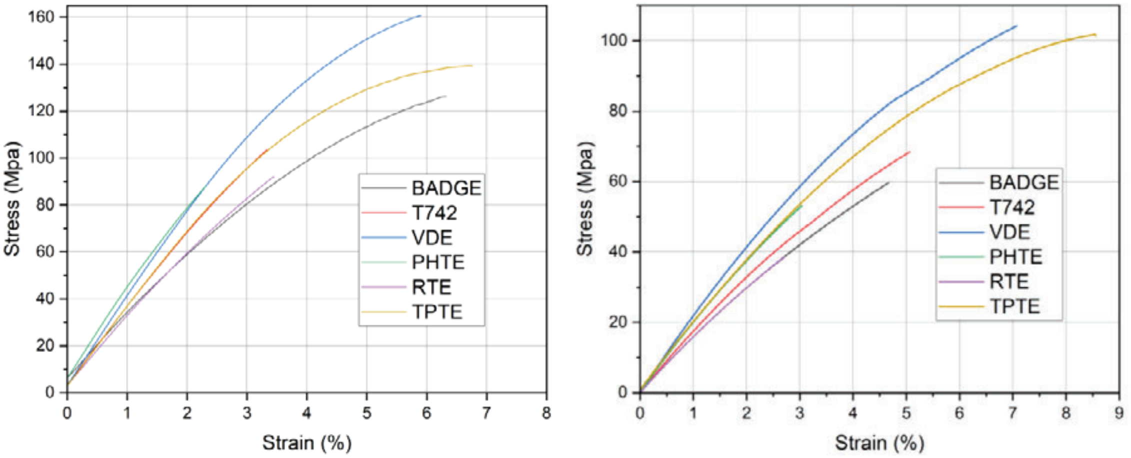

Figure 2 a) Average flexural test results for all 6 resins. b) Average tensile test results for all 6 resins. RTE curve greatly overlaps with BADGE curve.

3.3 PALS results

The PALS data suggests that PHTE, VDE and TPTE have the lowest free volumes of the systems, followed by RTE, T742, and BADGE having the highest. These results are not all intuitive – for example VDE is only difunctional and therefore has lower crosslink density than the 4 trifunctional epoxy systems. In this case we would expect VDE to have free volumes larger than PHTE and TPTE, and comparable to BADGE.

3.4 Discussion

From figure 4 we can see that plotting free volume data and flexural modulus data, we see an inverse relationship between the two to a high degree. PHTE and VDE show the lowest free volume and the highest flexural modulus. TPTE, RTE and BADGE also follow this trend – an increase in free volume leads to a lower flexural modulus. T742 slightly deviates from this trend, which could be due to the highly aromatic nature of the monomer, imparting stiffness. The tensile results for VDE and TPTE can be explained by their fairly linear structures, allowing for more ductility. This ductile behavior tends to increase strength as linear units can rearrange and distribute the applied force more evenly across the polymer network. Stiffer networks i.e. RTE and T742 cannot dissipate applied force as well due to a less mobile network, and therefore generally have a lower strength and lower toughness.

As outlined in the introduction, research has suggested that a lower free volume will lead to a stiffer polymer due to the network having less free space within which to move. This stiffness and lack of mobility also leads to a decrease in strength, as any applied force cannot dissipate as effectively throughout the network in the form of molecular movement. In contrast, larger free volumes (less

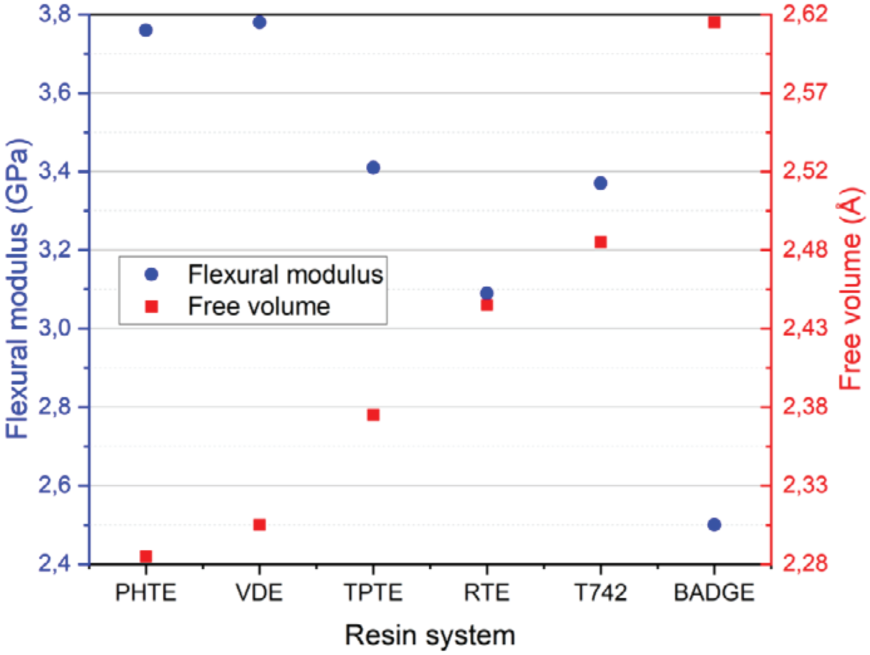

Figure 3 Flexural modulus and free volume of resin systems. The stiffer materials (PHTE, VDE) have a shorter positron lifetime, suggesting a smaller overall free volume.

tightly packed, less dense networks) leads to a decrease in stiffness as there is increased molecular mobility, and an increase in strength as the network can flex and distribute any applied force more efficiently. The PALS data suggests that BADGE should have the lowest stiffness as it has the highest free volume content. Conversely, PHTE and VDE should have the highest stiffness as they have the lowest free volume, which indeed is the trend that we see. Whilst the free volume and flexural modulus data support each other, the question of why VDE has these properties is still not obvious from its chemical structure.

When we compare tensile modulus with free volume the same trend is not observed – there seems to be no correlation between free volume and tensile modulus. This could be explained by the different modes of deformation that the material experiences under tension and flexion. During flexural testing the sample experiences both tensile and compressive deformation, and during tensile testing it only experiences tension. The polymer networks will react differently to these different scenarios. And indeed, beyond free volume perspectives there is also the different effect on linear vs aromatic units in each system.

4. Conclusions

We found that, in the case of these 6 high-T_g (>100°C) epoxy-amine systems, flexural modulus does correlate with free volume to a high degree. Tensile modulus and strength seem to be less dependent on the free volume, which suggests that deformation in compression relies more heavily on free volume characteristics. The effect of chemical structure on mechanical properties has been somewhat elucidated, with more highly aromatic thermoset resins displaying higher stiffness.

This research has also showcased some properties of 3 biobased epoxy resins in a high-T_g system. In particular vanillyl alcohol diglycidyl ether (VDE) showed the highest tensile strength, flexural modulus, and fracture toughness of all the resin systems, with a 60% increase in strength at failure and a 160% increase in fracture toughness when compared to BADGE. The reasons for this are not evident in the free volume studies or from the chemical structure of the VDE monomer. It could be the case that the balance of aromaticity, linearity, and crosslink density in the VDE:DDS formulation leads to some synergistic effects in which molecular packing is tight (low free volume and high modulus) but network mobility is still high to enable high strength. More research into the processing behavior and fracture toughness of these biobased resins should be investigated, as well as more thorough thermal and rheometric investigations. To prevent trivial investigations of biobased resins, more-thorough LCAs should be performed on the investigated bio-based feedstocks to assess their potential at industrial scale.

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