Amino-borate complexation for controlling transport phenomena of penetrant molecules into polymeric matrices

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Short Abstract

The development of new high performance materials, coatings, composites and adhesives relies on insight into the origin of performance on a molecular level. This research explores a new type of epoxy-amine-borate (EAB) hybrid material for control of penetrant solvent molecules into cross-linked thermoset polymer networks. The properties of these materials are explored through material and mechanical testing and model studies are used to probe the mode-of-action through which EAB materials deliver their improved performance properties.

Introduction

Coatings, composites and adhesives made from epoxy resins are of huge commercial importance supplying a market predicted to be worth over $14.26 billion by 2024 [1]. Within the research field of epoxy resin thermoset coatings, controlling and preventing ingress of small molecules through materials is critical in the development of new, more durable, high performance materials. Advances within the understanding and application of new technologies in this field can positively impact a wide range of important industrial applications across the coatings industry.

The absorption of small molecules into cross-linked polymer networks is linked to physical properties such as free-volume and cross-link density where the relative penetrability of small molecules are related to their inherent molecular volume (i.e. ability to 'fit' into the free volume pores within a polymer network) [2][3]. It has been previously demonstrated that manipulation of the average free-volume pore size can be an effective route to preventing solvent ingress into a cross-linked polymeric matrix [4][5]. Small molecule absorption is also influenced by molecular affinity or 'solubility' of the penetrating small molecule within the polymer network [6]. In this case, solvent uptake rate is related to how favourably solvent molecules interact with the host polymer matrix (e.g. through hydrogen bonding, dipole-dipole interactions or other intermolecular force) in addition to molecular volume considerations [7]. The coatings industry is challenged with achieving broad-spectrum chemical resistance across a wide range of penetrant molecules or cargoes for the development of new chemical resistant coatings [8].

This paper reports a new hybrid material based on epoxy-amine coating technology that undergoes modification during and immediately after the primary cure process. These materials are based on the reaction of exploitable chemical functional groups generated during the cure process (Scheme 1) [9][10]. Exploitation of these functional groups may offer new, unexplored opportunities for control of transport phenomena of penetrant molecules into coatings, films and membranes.
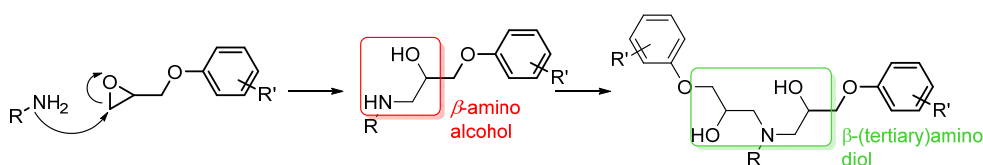
Scheme 1: The formation of β-amino alcohol functionality from the reaction of an amine with an epoxide

Experimental

For the synthesis of epoxy-amine cross-linked polymer networks that are representative of those used in high performance chemical resistant coatings the following materials were selected. D.E.N. 431 which is a widely used commercial Novolac epoxy resin was supplied by Olin Epoxy (formally DOW Chemicals) and is a semi-liquid resin with a number average functionality of ~2.8 [11]. As a reactive partner/'curing agent' 4,4'-methylenedicyclohexanamine (4,4'-MDH) was selected due to its wide commercial use as a curing agent for epoxy resins in coating applications (Figure 1).
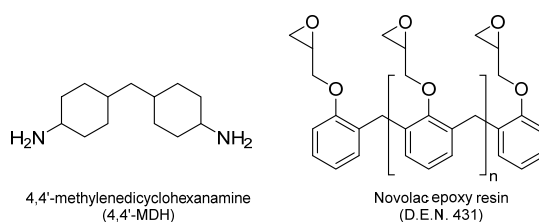

Figure 1: The structure of 4,4'-methylenedicyclohexanamine (4,4'-MDH) and Novolac epoxy resin (D.E.N. 431).

Experiemental methods for material characteristion include solvent uptake procedures via immersion studies, kinetic data obtinaed by near infra-red spectrometry, thermal analysis by DSC, DMTA and TGA, free volume studies *via* Position annihilation lifetime spectroscopy and structural characterization of the molecular network structure by single crystal X-ray diffraction.

Results & Discussion

To explore the concept of post cure network modification of epoxy-amine thermoset coatings, films based on D.E.N 431 and 4,4'-MDH were prepared. The initial formulation studied (**F1**) included co-curing accelerators 1-methylimidazole (1-MI) and 2-ethyl, 4-methylimidazole (2-Et-4-MeI) as is standard practice in commercial coating compositions [12]. This benchmark epoxy-amine thermoset material was used to study the impact that trialkylborate esters can have when used to create an epoxy-amine-borate (EAB) hybrid material. Of particular interest was the solvent uptake behaviour of the EAB hybrid material in comparison to the epoxy-amine parent system. A homologous series based on trimethyl-, triethyl-, triisopropyl- and tributyl-borate (i.e. C1 to C4) were prepared, where the borate esters were incorporated at 5 mol% into the D.E.N 431/4,4'-MDH **F1** formulation and cured according standard procedures under controlled conditions. This resulted in a set of transparent, hard uniform films for each of the 5 test formulations (parent **F1** formulation plus four EAB hybrid materials) and resulting films were immersed for 28 days in VAM and EDC. The penetrant solvent absorption behaviour was evaluated and the results from these five test materials are illustrated in Figure 2 (left graph). It was observed that the EAB hybrid materials significantly outperformed the epoxy-amine parent material in this test. The weight percentage (wt%) increase in the mass of the test samples on immersion in VAM and EDC dropped significantly when trialkylborates were included in the formulation. This is most clearly exemplified when comparing Entry 1 (parent) with Entries 3 and 4 in Figure 2. This chart shows that the use of either triethylborate or triisopropylborate in the synthesis of an EAB hybrid material was highly effective at preventing penetrant solvent ingress into the resulting cross-linked polymer network. In the highest performing example for the EAB hybrid material based on triethylborate (Entry 3, Figure 2, left graph), the saturated solvent equilibrium concentration of VAM and EDC dropped to 50.2% and 36.4% of the values seen with the epoxy-amine parent control. To put result into context, the parent epoxy-amine control (Entry 1, Figure 2, left graph) was itself selected due to its

established excellent performance as a material for chemical resistant coatings. Further optimisation of this formulation showed that the solvent uptake performance of the EAB hybrid material could be decreased even further resulting in saturated solvent equilibrium concentration for the test solvents VAM and EDC of 40.6% and 26.5% respectively, compared to the parent epoxy-amine system (Entries 1 and 3, Figure 2, right graph). A further more detailed study of the coatings immersion behaviour was then conducted to re-enforce this result, the reults of which are are discussed in the full paper.
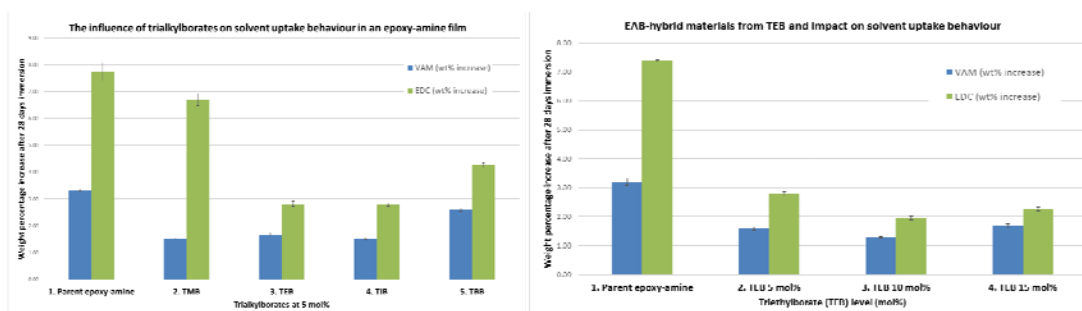

Figure 2: The reduction in absorption of VAM and EDC through the use of EAB hybrid materials vs. a parent epoxy-amine control (left) and the relationship between mol% of triethylborate and reduction in solvent uptake in a D.E.N. 431/4,4'-MDH formulation (right)

An investigation was conducted in an attempt to understand the mode-of-action by which these new EAB hybrid materials prevent the ingress of small molecules into epoxy-amine cross-linked polymer networks. Kinetics studies using near infra-red indicated the absence and any significant acceleration effect from the Lewis acidic triethylborate through Lewis-acid mediated catalysis of the epoxy-amine reaction. Equally, it also indicated the lack of significant complexation of the triethylborate with the Lewis basic amine groups on the MeCHA model curing agent which would result in a deceleration of the reaction rate [13]. Having established that triethylborate does not interact directly with the epoxide or amine starting materials to any observable extent, the study focussed on understanding the mechanism through which EAB hybrid materials are formed and at what stage of the cure process this occurs. To explore this areas a number of model compounds were synthetized and characterized to structurally represent the functional groups present within a cured epoxy-amine coating. Cyclohexylamine **1** was used as a model for 4,4'-MDH and reacted with both 1 equivalent and 2 equivalents of phenyl glycidyl ether (a model for a Novolac epoxy resin) to give the desired model β-amino-alcohol **3** and tertiary-β-amino diol intermediate **5** (Scheme 2).
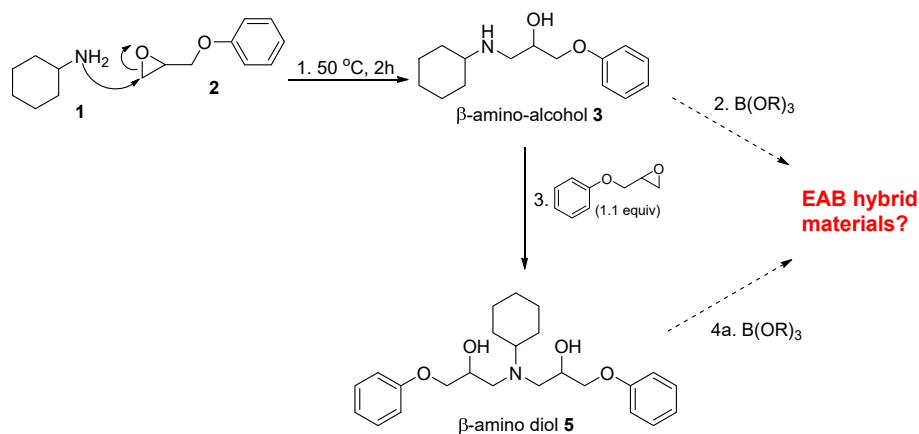
Scheme 2: The synthesis of model β-amino-alcohol compounds and complexation experiments with trialkylborate

An extensive investigation was then conducted using both these model compounds and the cured EAB hybrid and epoxy-amine parent thermoset coatings. Using thermal analysis (DSC, DMTA and TGA), free volume studies *via* position annihilation lifetime spectroscopy (PALS) and structural characterization by single crystal X-ray diffraction, a sound and evidenced mechanism for the formation of EAB hybrid materials was established and details of the internal network structure elucidated. This allowed a viable hypothesis for the improved solvent uptake behaviour to be discussed, supported by strong mechanistic evidence.

Conclusions

In conclusion, we have reported a new epoxy-amine-borate (EAB) hybrid material prepared through the network forming reaction of trialkylborate esters, an amine curing agent and a Novolac epoxy resin. Triethylborate has proven to have the ideal chemical reactivity for post-cure modification of a cross-linked epoxy-amine polymer network, reacting highly selectivity with the emerging β-amino alcohol functional groups in a latent fashion. It has been demonstrated that this chemo-selective reaction does not interfere with the primary cure mechanism between the epoxy-functional Novolac resin and the amine functional curing agent. Without this high level of chemo-selectivity the network structure and resulting properties of the epoxy-amine thermoset material would be significantly compromised. Experimental evidence including solvent uptake studies, model reactions, single crystal X-ray diffraction and positon annihilation lifetime spectroscopy, strongly supports the hypothesis that the reduction in solvent ingress in the new EAB hybrid materials originates from the formation of well defined and structurally characterised complexes that develop within the curing epoxy-amine network. It is proposed that the removal of both *H*-bond donor (i.e. OH groups) and Lewis basic functionality (i.e. NH_2 groups) from the polymeric matrix network reduce the affinity of polar solvent molecules with the EAB hybrid material resulting in an overall reduction in solvent uptake behaviour.

This discovery could have potentially wide-ranging applications for the development of high performance materials, composites, plastics and adhesives. This is particularly important in applications where engineering materials, high performance coatings and adhesives are exposed to aggressive chemical and where it is critical to prevent loss of material integrity and performance. Applications include Aerospace and Automotive composites, as well as coatings for the global transport and storage of solvents and chemicals across the chemical, oil and gas industries can benefit from this insight. Further work to understand the full scope and potential of this technology is ongoing but it is hoped that the insight into the mode-of-action of these materials will fuel further exploration of chemo-selective post cure modification of thermoset materials.

Acknowledgements

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[11] Number average functionality (Fn) is defined as the epoxy equivalent weight (EEW) of the resin in g/mol^{-1}/number average molecular weight (Mn) as determined by gel permeation chromatography vs a polystyrene standard i.e. EEW/Mn = Fn

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