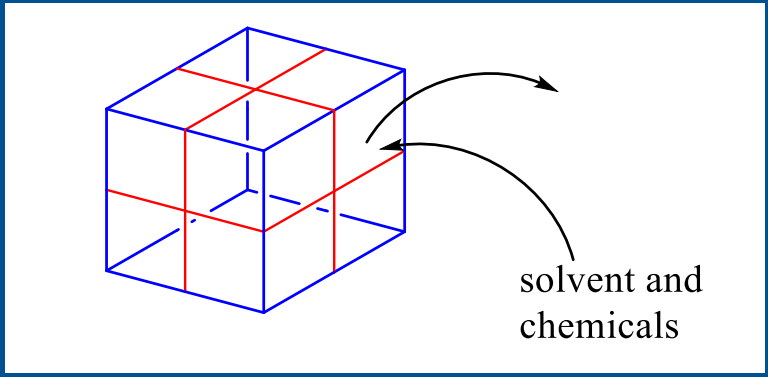
Amino-diol borate complexation for controlling transport phenomena of penetrant molecules into polymeric matrices

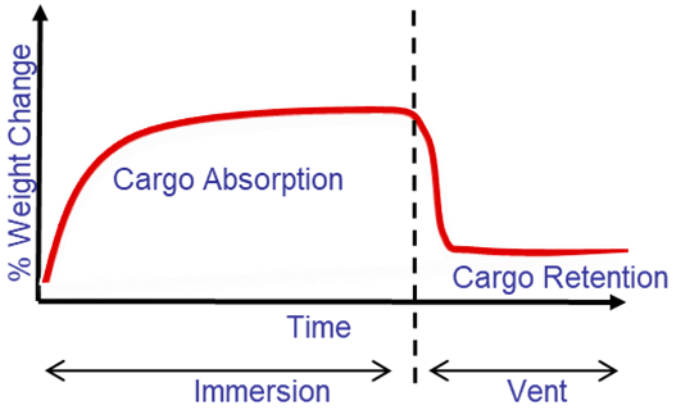
Dr. Matt Unthank
Northumbria University, Newcastle

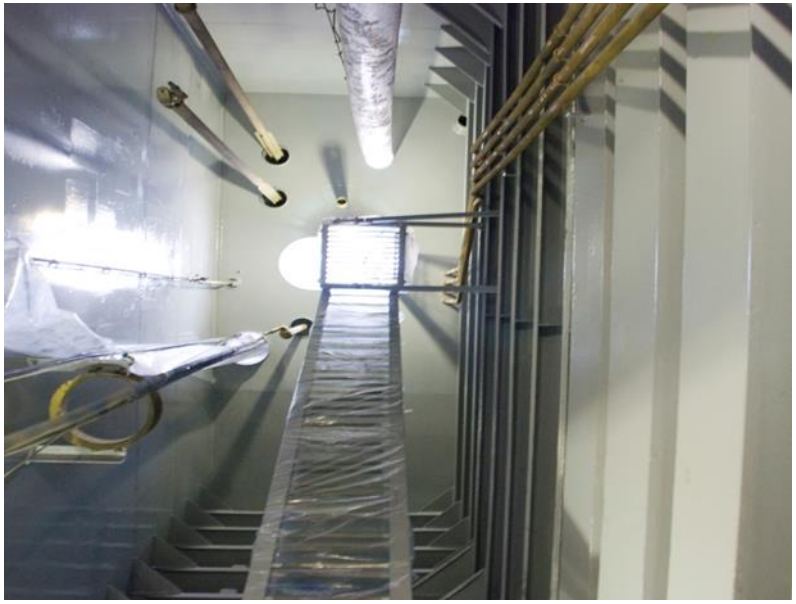
Formulating Functional Films and Coatings
19th Aug 2020



M. G. Unthank*, C. Cameron, A. Wright, D. Hughes, M. A. Alam and M. R. Probert, Amino-diol borate complexation for controlling transport phenomena of penetrant molecules into polymeric matrices, *Polym. Chem.*, **2019**, *10*, 4920

Chemical transport and storage



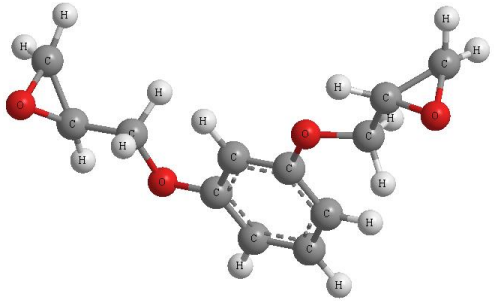


Epoxy resins for chemical resistance

Northumbria University NEWCASTLE

AkzoNobel

[1]



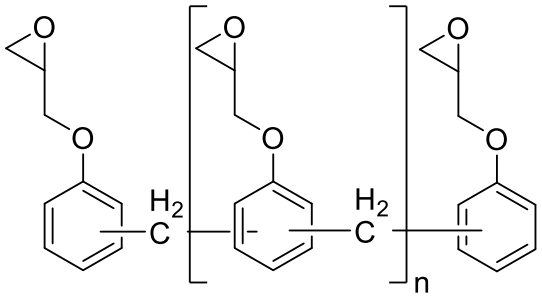
Resorcinol diglycidylether

HSE concerns relating to sensitisation

High crosslink density and chain packing

Delivers

Outstanding broad spectrum chemical resistance



Novolac epoxy resin

Improved H&S profile

Lower crosslink density, increased free volume

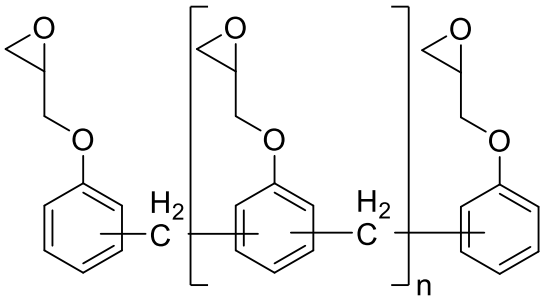
Delivers

Modest chemical resistance and high solvent uptake

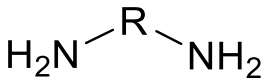
[1] https://www.echa.europa.eu/web/guest/substance-information/-/substanceinfo/100.002.716

Bench-marking chemical resistance
A practical approach

- Our interest was in exploring **new methods** and developing **new materials** for high performance chemical resistance
- This covered a wide range of potential routes from high cross-linking density coatings to organic-inorganic hybrid materials
- Much of this research was based around epoxy-amine cure chemistry due to its established leading position in the chemical storage and transport market.[2]



Novolac Resin

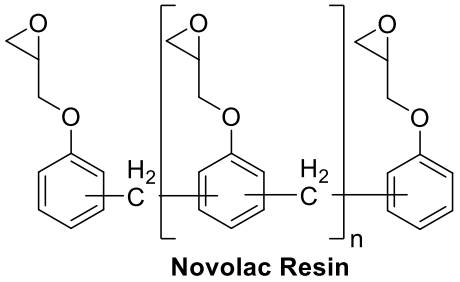


Catalysts
+
Additives

- Today I will focus on one of the new developments in this field.

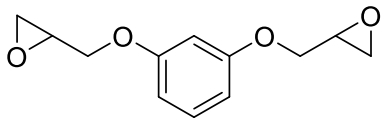
[2] ICIS Chemical Business, 13-19 October 2017, awarded 'Best Product Innovation' for AkzoNobel's Interline 9001 advanced coating system for ship's cargo tanks https://www.icis.com/resources/news/2017/10/13/10154034/innovation-awards-the-winners-revealed/

Bench-marking chemical resistance
A practical approach



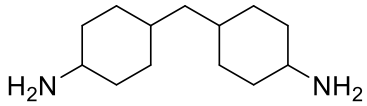
Novolac Resin

or



Resorcinol diglycidyl ether
(**RDGE**)

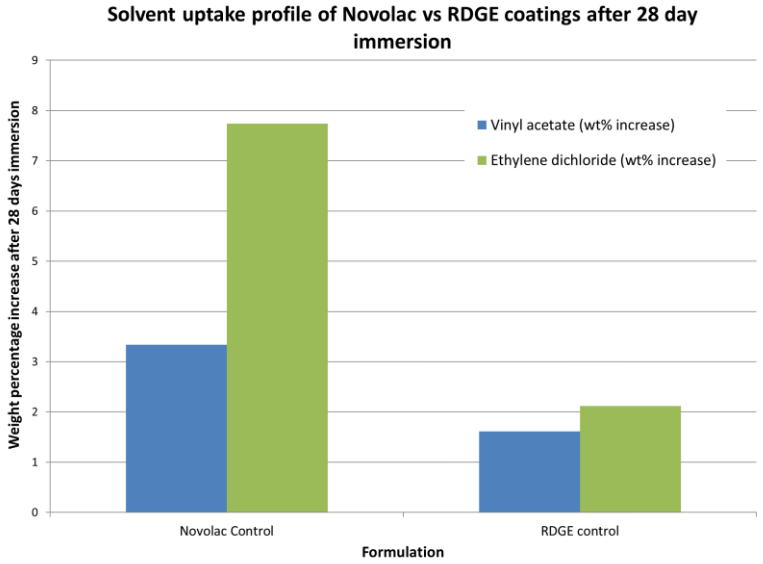
+



4,4'-methylenedicyclohexanamine
(**4,4'-MDH**)

+ alkyl imidazole catalyst

- Thin films were prepared at 100% stoichiometry with either Novolac (Olin D.E.N.431) or RDGE and 4,4'-MDH as the curing agent
- Films were applied to pre-cleaned microscope slide and cured at ambient temperature for 24 hours followed by 16 hours at 80 ^{o}C
- Resulting in hard, transparent films for chemical immersion studies

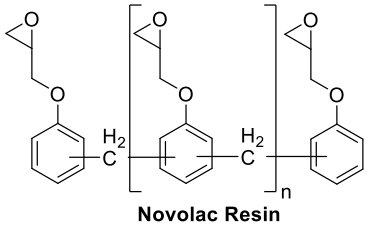


Chemical resistant coatings

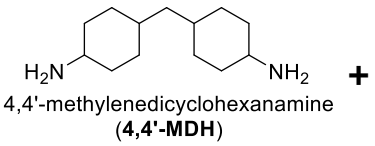
New materials research

Northumbria University NEWCASTLE

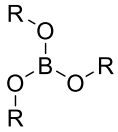
AkzoNobel



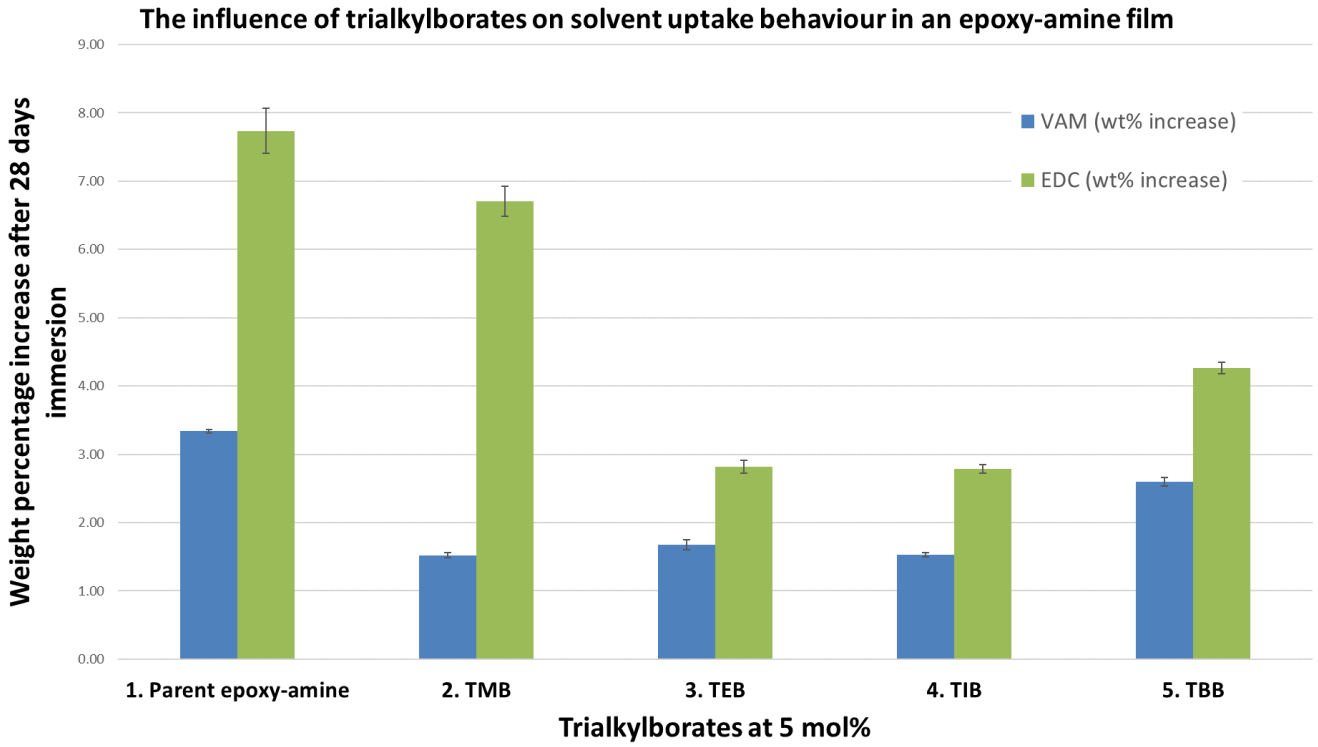
+

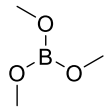


+ alkyl imidazole catalyst

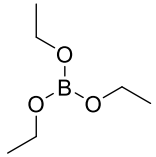


Trialkylborate esters

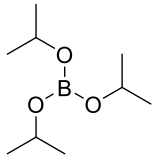




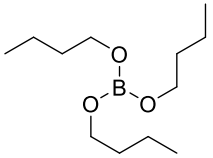
Trimethyl borate (TMB)



Triethyl borate (TEB)

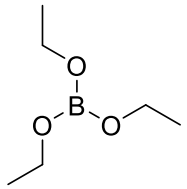


Triisopropyl borate (TIB)



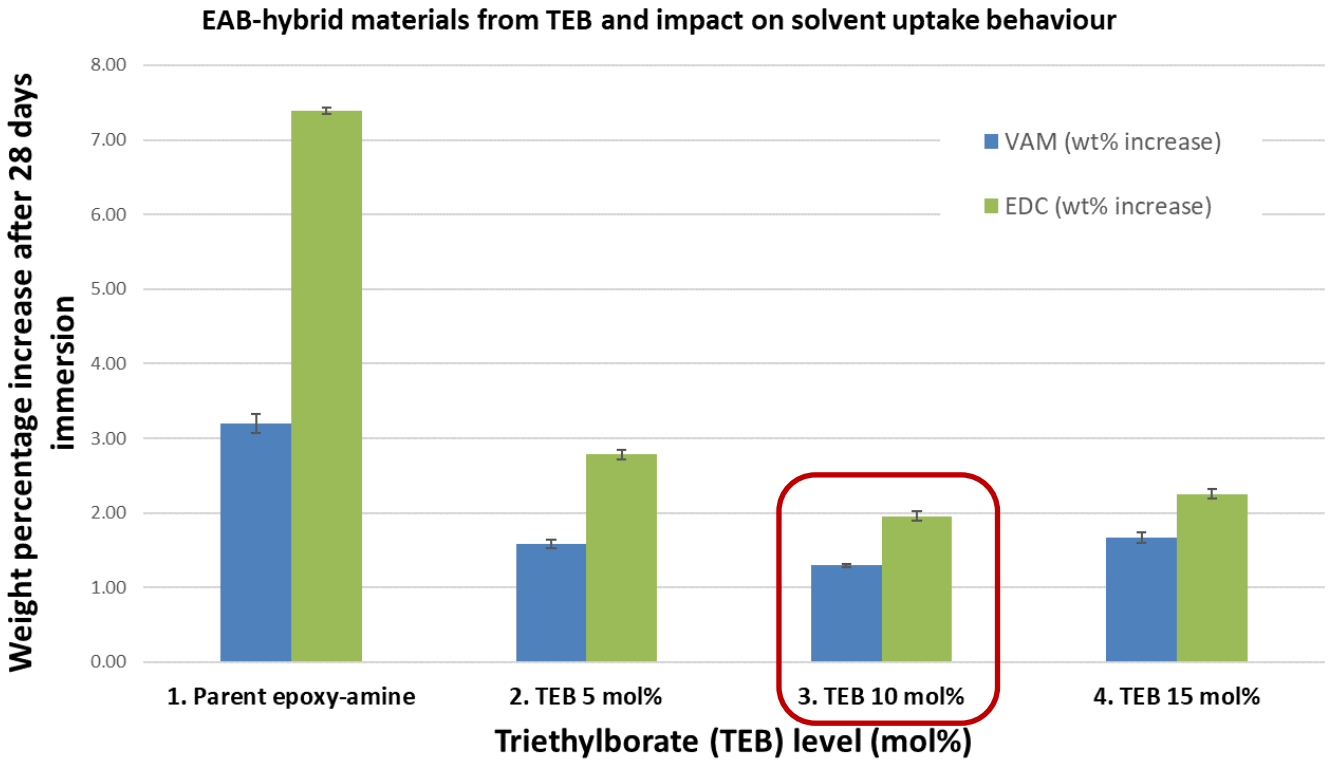
Tributyl borate (TBB)

Chemical resistant coatings
New materials research



Triethyl borate (TEB)

- Further work was conducted to explore this performance improvement
- New triplicate sets of polymer films were prepared using 0, 5, 10 and 15 mol% of triethylborate
- Resulted in saturated solvent equilibrium concentrations of **40.6% (VAM)** and **26.5% (EDC),** compared to the parent epoxy-amine system

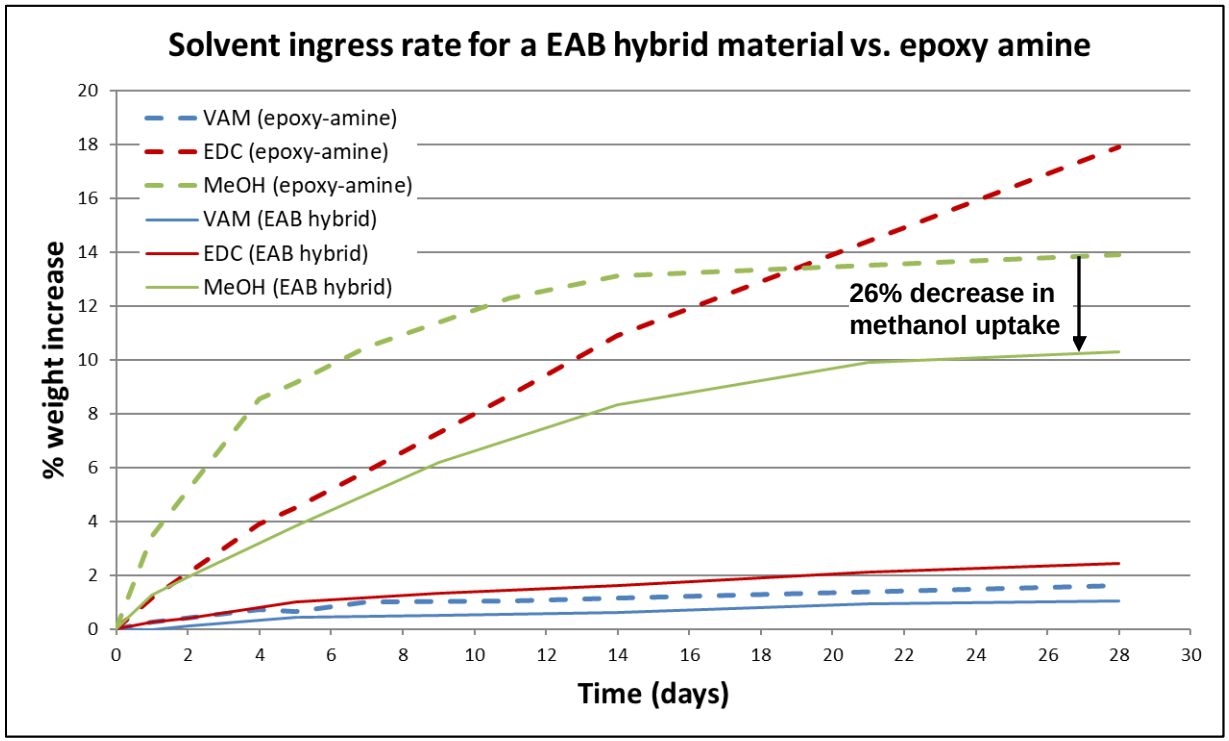


Chemical resistant coatings
New materials research

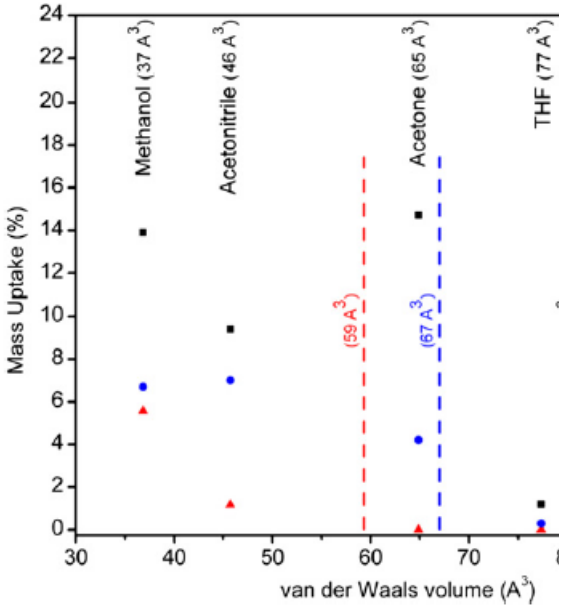
Northumbria University NEWCASTLE

AkzoNobel

- The 2-MI and 2-Et-4-MeI cure accelerators are known to play multiple roles in the cure process, which will inevitably lead to a less homogeneous polymer network.[3]
- To study and understand this effect further a simplified 1:1 stochiometric blend of Novolac resin and 4,4-MDH was tested for solvent uptake



Methanol is particularly difficult to keep out.[4]



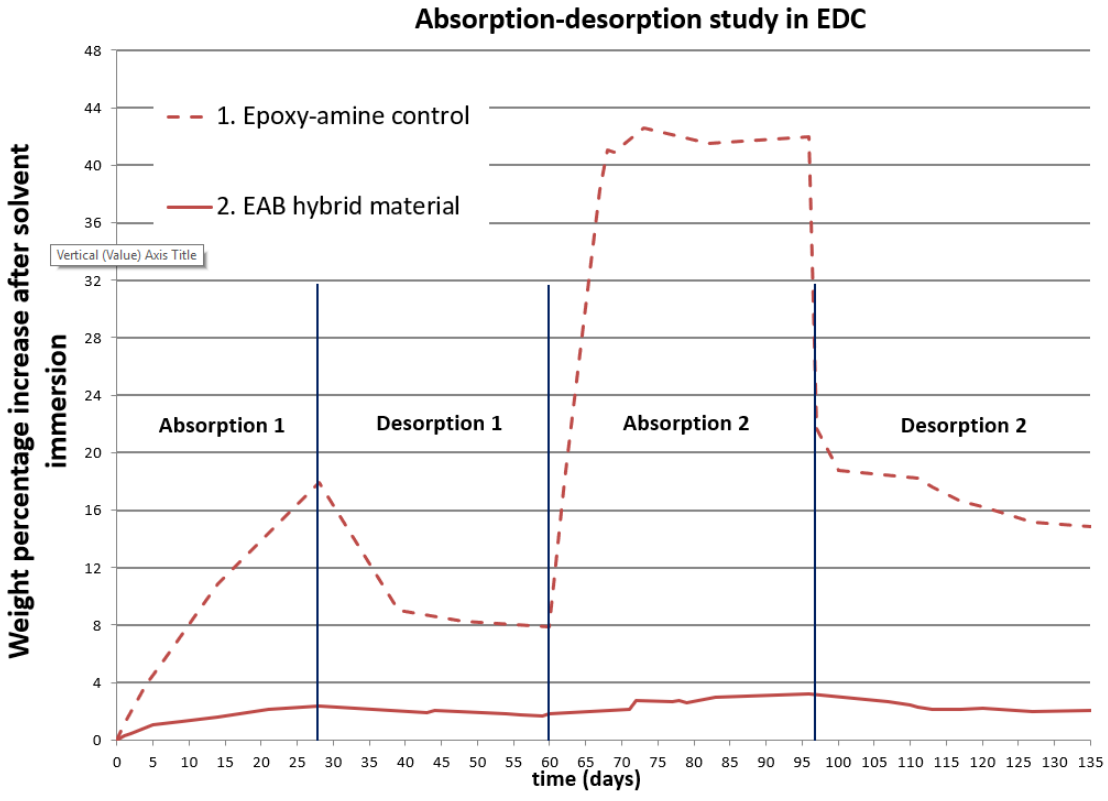
[3] a) F. Ricciardi, W. A. Romanchick and M. M. Joullié, *Polymer Chemistry*, 1983, **21(5)**, 1475; b) M. S. Heise, G. C. Martin, *J. Pol. Sci, Part C*, 1988, **26**, 153.
[4] M. Jackson, M. Kaushik, S. Nazarenko, S. Ward, R. Maskell and J. Wiggins, *Polymer*, 2011, **52**, 4528.

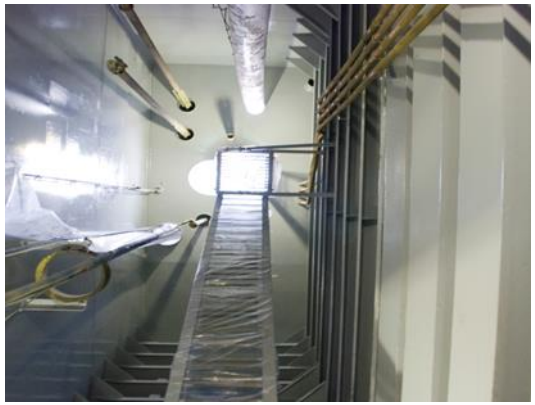
Chemical resistant coatings
New materials research

Northumbria University NEWCASTLE

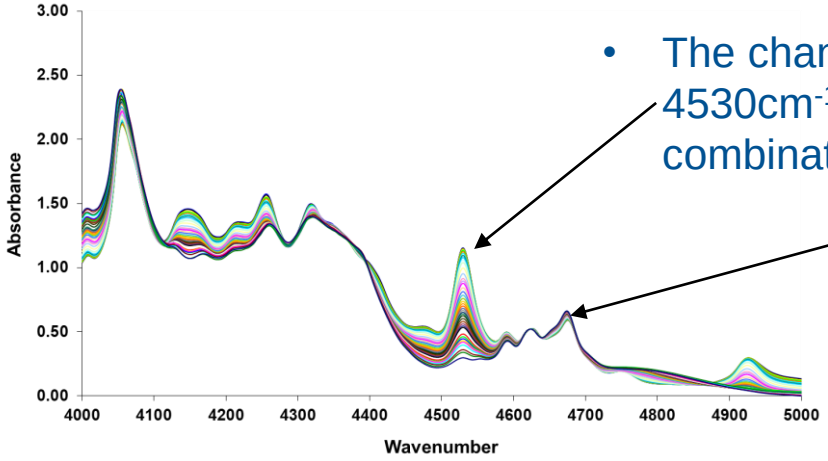
AkzoNobel

- Repeated absorption-desorption study was conducted using EDC as the test solvent mimics the ‘in-field’ conditions experienced in a coated industrial chemical storage or marine shipping transport container.

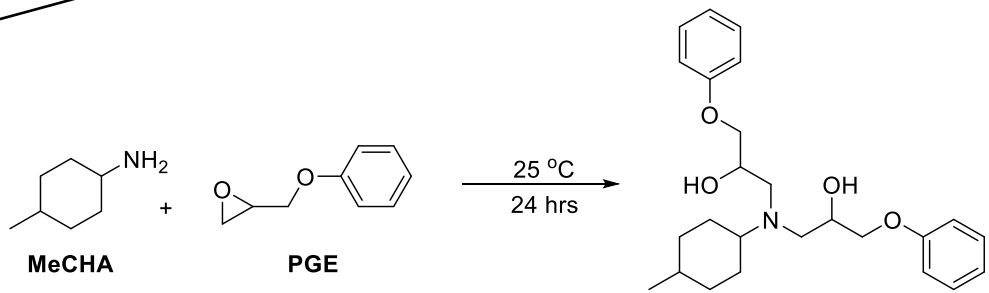


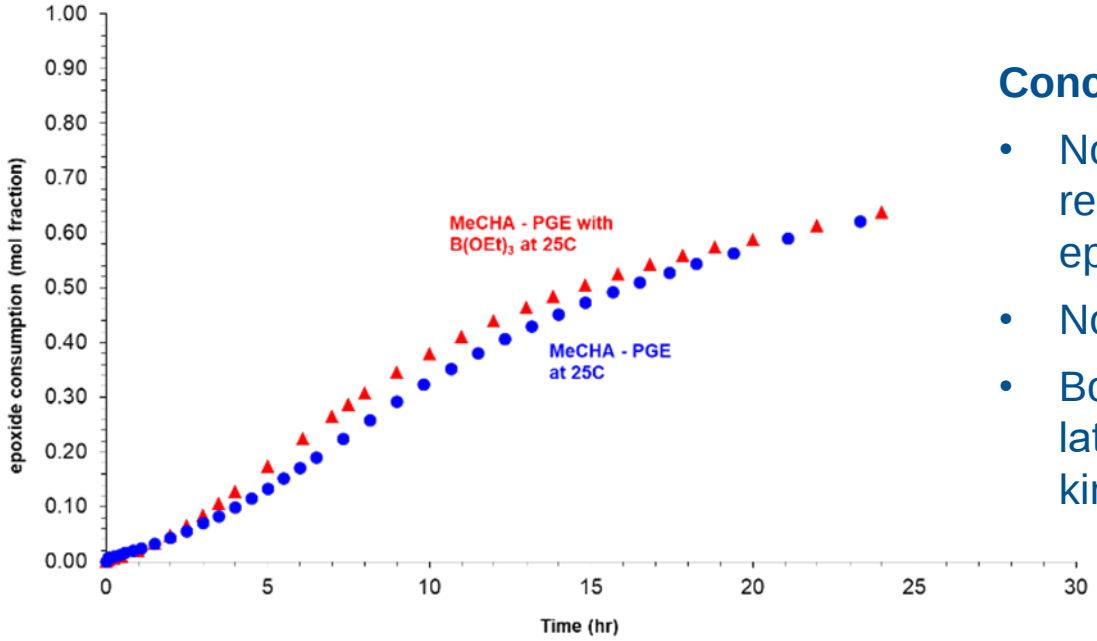


Chemical resistant coatings
Mechanistic insight



- The change in peak height of the epoxy peak at 4530cm^{-1} was measured relative to the aromatic combination band at 4676cm^{-1}.[5]



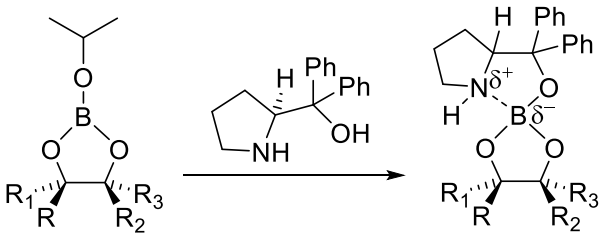


Conclusion:

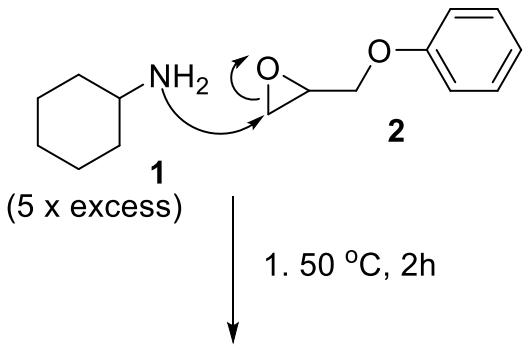
- No significant difference in either rate of reaction or final conversion (yield) of epoxide to β-amino alcohol.
- Not a catalytic effect
- Both reaction mixtures showed a slight latent period and '*S*-shaped' reaction kinetics.

[5] a) G, Nikolic, S, Zlatkovic, M, Cakic, S, Cakic, C, Lacnjevac, Z. Rajic, *Sensors*, **2010**, *10*, 684-696; b) L. Li, Q. Wu, S. Li and P. Wu, *Applied Spectroscopy*, 2008, **62(10)**, 1129.

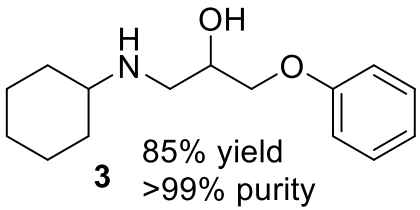
Chemical resistant coatings
Mechanistic insight

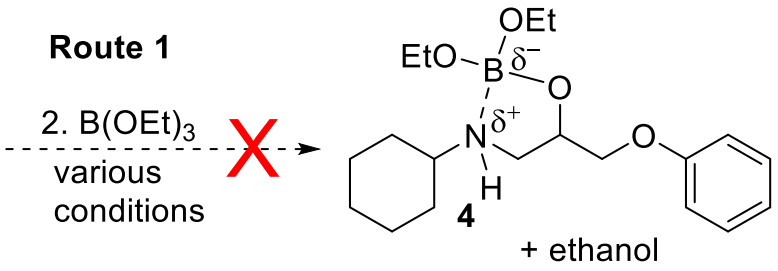


- *β*-Amino alcohols can react with trialkylborate esters to form borate complexes such as those recently reported by Ortiz-Marciales and co-workers.[6]



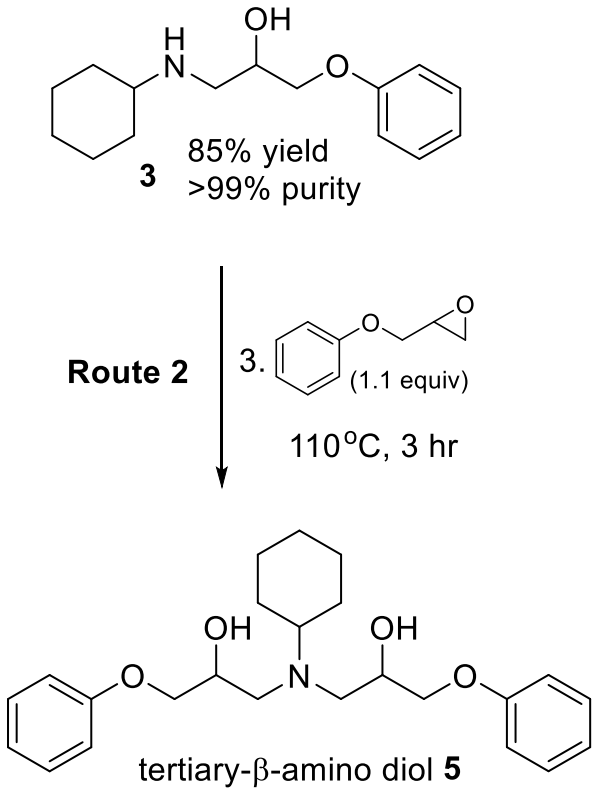
- A wide range of reaction conditions were studied
- Included catalysis, elevated reaction temperatures and continuous distillation (of liberated ethanol)
- No clear evidence for the formation of proposed borate complex **4**





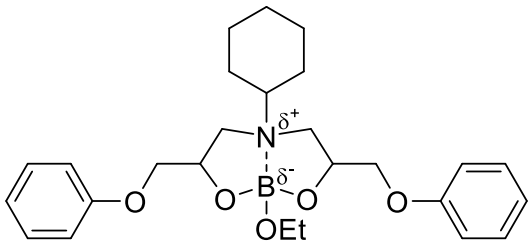
[6] V. Stepanenko, M. de Jesus, C. Garcia, C. l . Barnes and M. Ortiz-Marciales, *Tetrahedron Lett*. 2012, **53**, 910.

Chemical resistant coatings
Mechanistic insight



- In contrast to β-amino alcohol **3**, the reaction of tertiary β-amino diol **5** with triethylborate is **instantaneous** and **quantitative**.
- Resulted in the isolation of stable, white crystalline solid

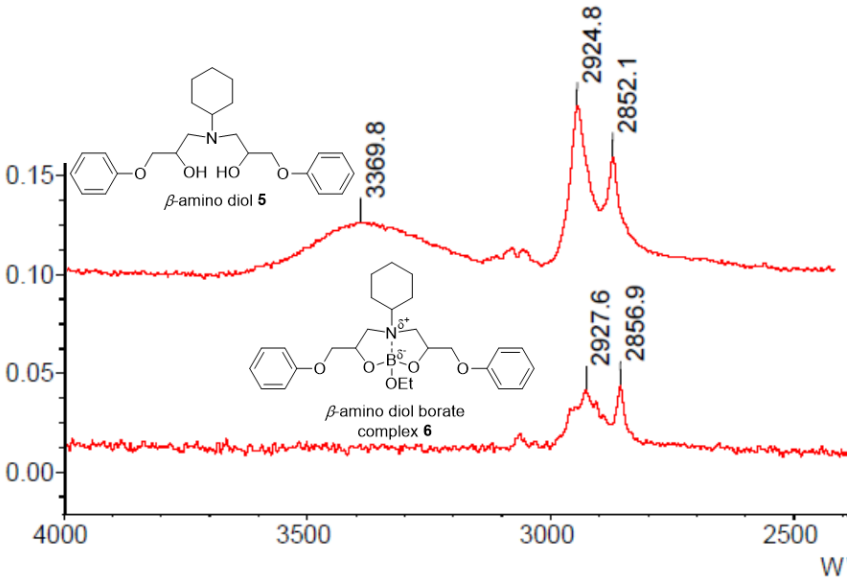
Chemical resistant coatings
Mechanistic insight

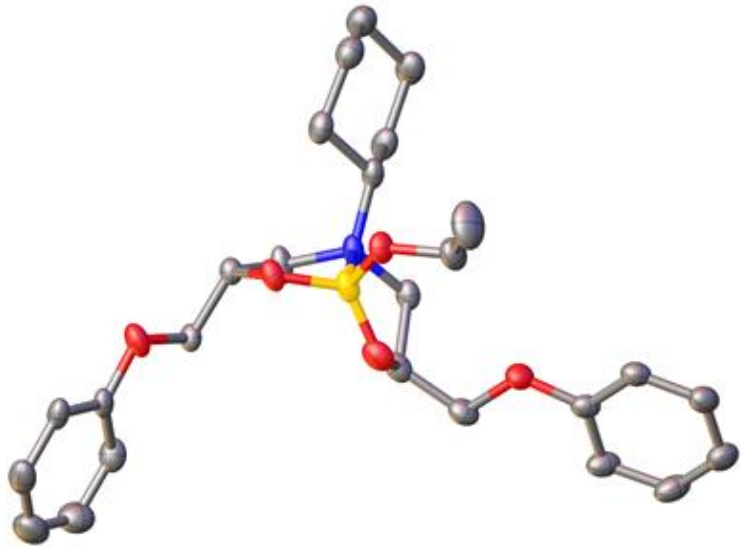


β-amino diol borate complex **6**

^{11}B-NMR = 10.30 ppm

- ^{1}H-NMR and ^{11}B-NMR supported the formation of β-amino diol borate complex **6** but spectra complicated by diastereomeric mixture.
- IR also suggested OH complexation
- Structure confirmed using single crystal X-ray diffraction.



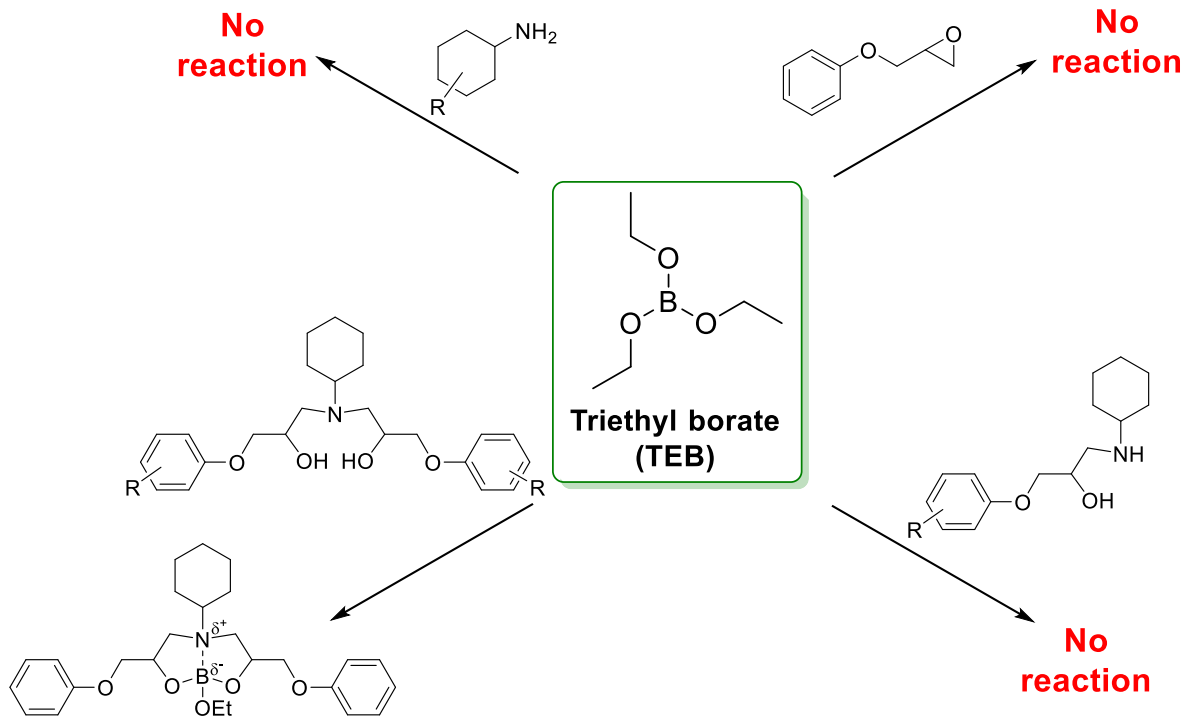


- Formation of borate complex **6** is entropically favoured due to multi-dentate 'chelate effect' of the tertiary-β-amino diol **5.**[7]

[7] H. Steinberg, D. L Hunter, *Industrial and Engineering Chemistry*, 1957, **49(2)**, 174.

Chemical resistant coatings
Mechanistic insight

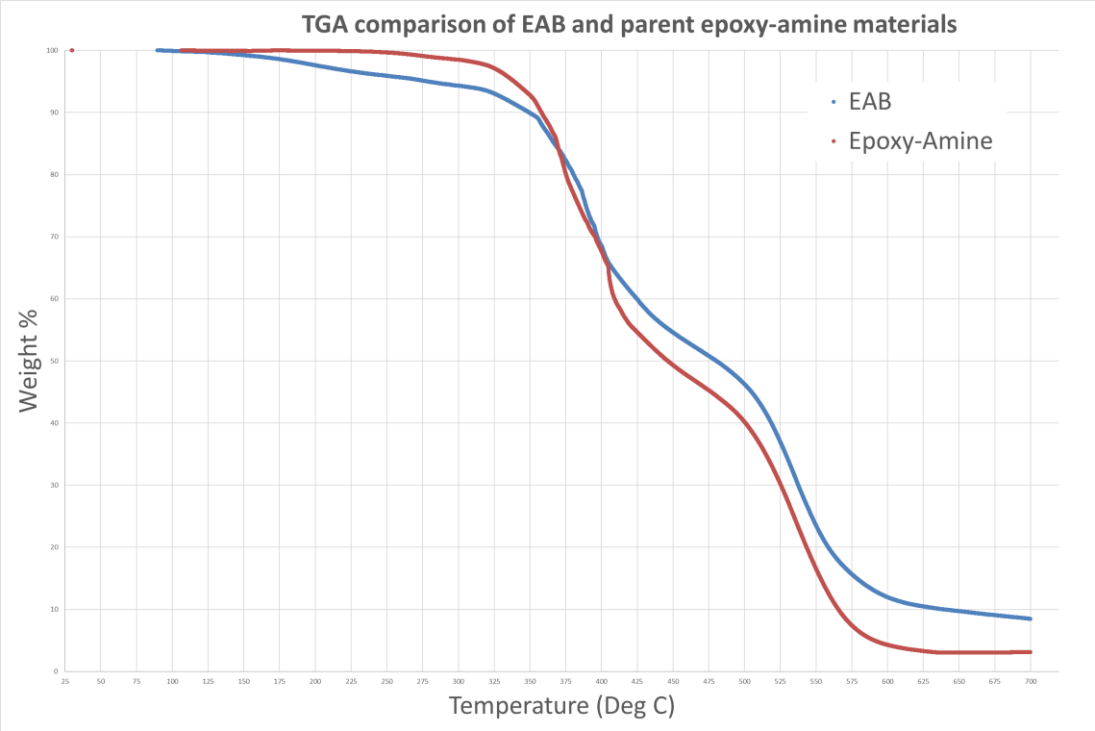
- Triethylborate therefore exhibits a **latent** and **highly chemo-selective** reactivity in the formation of epoxy-amine-borate hybrid materials



- Anything other than high chemo-selectivity would compromise the overall material properties through interference with the primary cure process (i.e. epoxy-amine).[8]

[8] a) A. R. Kannurpati, K. J. Anderson, J. Anseth and C. N. Bowman, *J. Polm. Sci., Part B: Polym. Phys*., 1997, **35(14)**, 2297; b) R. A. Pearson and A. F. Yee, *J. Mater. Sci*., 1989, **24(7)**, 2571.

Chemical resistant coatings
Mechanistic insight

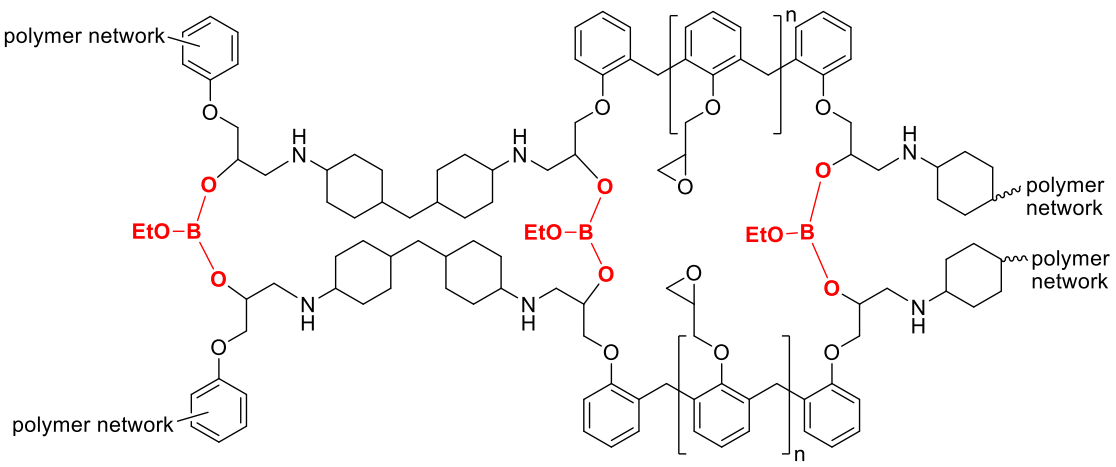


- Comparison of basic material properties such as Tg (DSC) and thermal stability (TGA) also support this hypothesis.
- Indicate that physical bulk properties such as Tg and thermal stability are very similar between the test materials

Entry	Material	Tg (°C)	Degradation temp (°C)	Residual mass (wt%)
1	Epoxy-amine	108.6	338	4
2	EAB hybrid	110.1	344	11

Chemical resistant coatings
Mechanistic insight

- All of the evidence indicates that trialkylborate esters operate via complexation of β-amino-diol functional groups rather than an independent cross-linking mechanism, e.g.

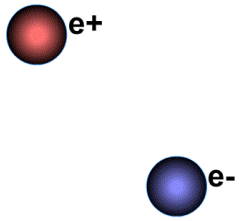


Not experimentally supported

- Within a thermoset polymer network, such a process should result in a reduction in average free-volume through increase cross-link density
- This can be probed using positron annihilation lifetime spectroscopy (PALS)

Chemical resistant coatings
Mechanistic insight - PALS

The Bristol Positron group:
Professor M. A. Alam [9]



- Positrons are emitted as a result of *β*+ decay of radioactive isotopes such as Na^{22}

Work horse

$$^{22}Na \longrightarrow {}^{22}Ne + \beta^{+} + \nu + \gamma$$

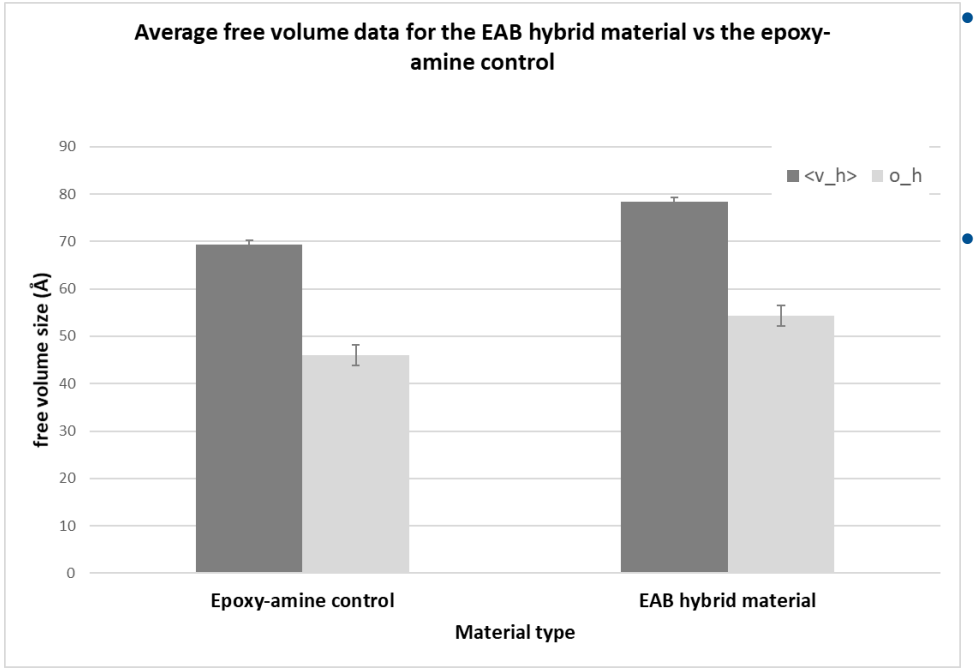
- The positron lifetime (*τ*) determined by the local electron density at the annihilation site
- Positron 'birth' is accompanied by the immediate emission of 1.28 MeV photon
- Positron 'death' is accompanied by the immediate emission of two 511keV photons
- Time between birth and death (positron lifetime) gives information on free volume in materials

Information at: http://www.positronannihilation.net/index.htm

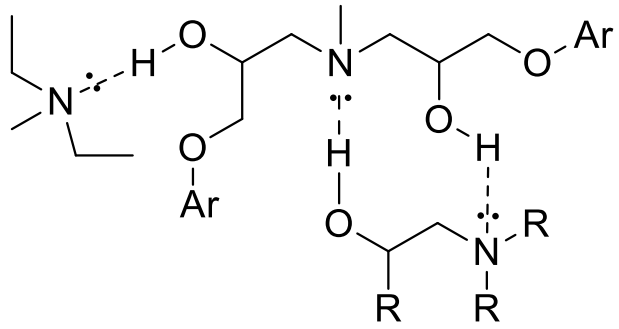
[9] a) D. Kilburn, J. Claude, T. Schweizer, A. Alam, J. Ubbink, *Biomacromolecules*, 2005, **6**, 864; b) D. Bamford, G. Dlubek, G. Dommet, S. Horing, T. Lupke, Kilburn, M. A. Alam, *Polymer*, 2006, **47**, 3486; c) D. Hughes, C. Tedeschi, B. Leuenberger, M. Roussenova, A. Coveney, R. Richardson, G. Badolato-Bonisch, M. A. Alam, J. Ubbink, *Food Hydrocolloids*, 2016, **58**, 316.

Chemical resistant coatings
Mechanistic insight - PALS

- Other groups have shown that epoxy-amine materials with a reduced average free volume pore size prevent the penetration of small molecules more effectively than those with high average free volume pores.[4,8]



- Average free volume pore size ($< v_h >$) and size-distribution (σ_h) in the EAB hybrid material **<u>are greater</u>** than those of the parent epoxy-amine material.
- Reduced free volume **<u>is not</u>** the mechanism by which EAB materials function

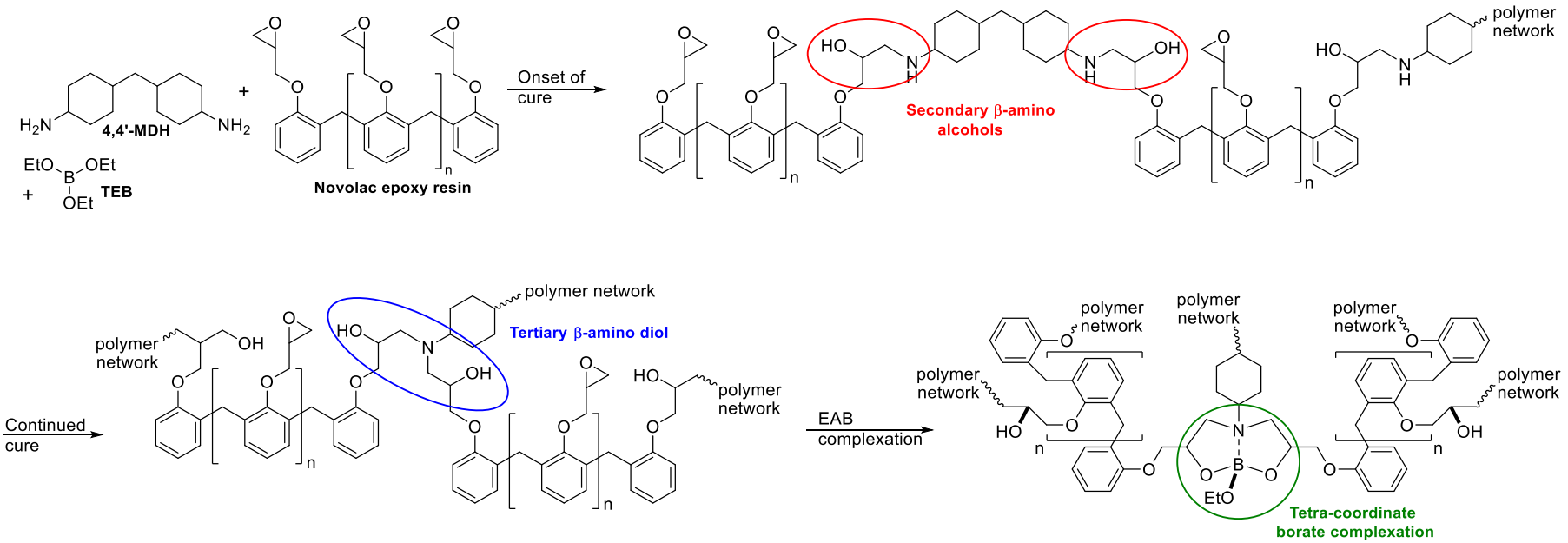


- Likely that loss of inter- and intra-molecular hydrogen bonding is responsible for the increase in free-volume
- PALS experiments and the X-ray diffraction experiments do not support a hypothesis of increased cross-linking as the origin of the EAB hybrid material performance properties.

[8] K. Frank, C. Childers, D. Dutta, D. Gidley, M Jackson, S. Ward, R. Maskell and J. Wiggins, *Polymer*, 2013, **54**, 403.

Chemical resistant coatings
Conclusions

- Experimental evidence including solvent uptake studies, model reactions, single crystal X-ray diffraction and positron annihilation lifetime spectroscopy all support the following mode-of-action:



M. G. Unthank*, C. Cameron, A. Wright, D. Hughes, M. A. Alam and M. R. Probert, Amino-diol borate complexation for controlling transport phenomena of penetrant molecules into polymeric matrices, *Polym. Chem.*, **2019**, *10*, 4920

Chemical resistant coatings
Conclusions

- We have reported for the first time,[1,2] an **epoxy-amine-borate (EAB) hybrid material** prepared through the network forming reaction of trialkylborate esters, an amine curing agent and a Novolac epoxy resin.
- The reaction of triethylborate with the developing epoxy-amine network shows **remarkable chemo-selectivity** with is key to the results material performance
- A detailed study has been conducted at to elucidate the mode-of-action through which this material functions
- Reduction in solvent ingress in the EAB hybrid materials originates from the formation of tetra-coordinate complexes between the boron atom and the β-amino diol functional groups that develop within the curing epoxy-amine network.
- Removal of both *H*-bond donor (i.e. OH groups) and Lewis basic functionality (i.e. NH_2 groups) from the polymeric network, reduces the affinity of polar solvent molecules with the EAB hybrid material resulting in an overall reduction in solvent uptake behaviour

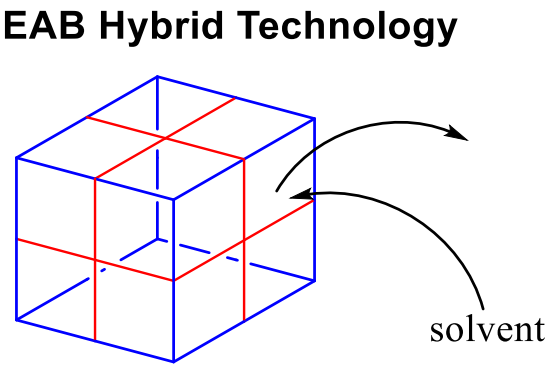
[1] C. Cameron, A. Wright and M. G. Unthank, Coating method for surfaces in chemical installations, WO 2015165808, 2015.
[2] C. Cameron, A. Wright and M. G. Unthank, J. Wood, Coating method for surfaces in chemical installations, WO 2017068015, 2017.

Chemical resistant coatings
Conclusions

- We hope these finding could have potentially wide-ranging applications for the development of high performance materials, composites, plastics and adhesives.

'Only the penitent man shall pass'
Dr. Indiana Jones, Lucasfilm, 1989

'Only the penetrant molecule shall pass'
Dr. Colin Cameron, AkzoNobel, 2012



Chemical resistant coatings
Acknowledgements

Colin Cameron (AkzoNobel, Chemical resistant coatings team)

Tony Wright (AkzoNobel, Chemical resistant coatings team)

Alistair Finnie (AkzoNobel Marine Research, Technical Expert)

Prof. M. Ashraf Alam (University of Bristol, PALS)

Dr. David Hughes (University of Bristol, PALS)

Dr. Michael R. Probert (Newcastle University, X-ray analysis)

Thanks for listening

Questions?