Recycling of thermoset resins
via the development of a solvent trigger de-curing system

Magali Rego[1,2], James Bruce[1], Peter Taylor[1], Alan Taylor[2]
[1] School of Life, Health and Chemical Sciences, The Open University, Walton Hall, Kents Hill, Milton Keynes MK7 6AA, UK
[2]NSIRC, TWI Ltd., Granta Park, Cambridge CB21 6AL, UK

Background

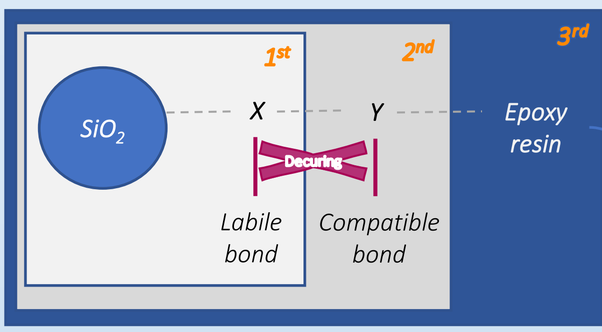
Irreversible covalent crosslinked thermoset epoxy system

- Material of choice in the aerospace, automotive, windmill, and sporting goods industries as adhesive and coating
- Great thermomechanical stability and chemical resistance but complex multi-step and energy demanding processes to recycle epoxy-based composites
- Epoxy-based composites represent most of polymer waste products

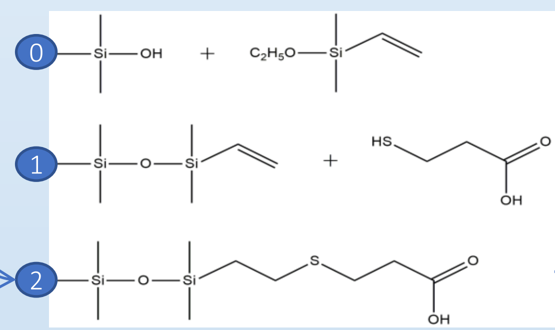
Aim and Objectives

- Introduce reversible crosslinking mechanism into thermoset epoxy system and create a closed-loop recycling alternative for highly cross-linked epoxy materials
- Functionalise silica additive and tune chemical surface properties to obtain a versatile recoverable monomer
- Determine silane distribution and orientation of the silica additive

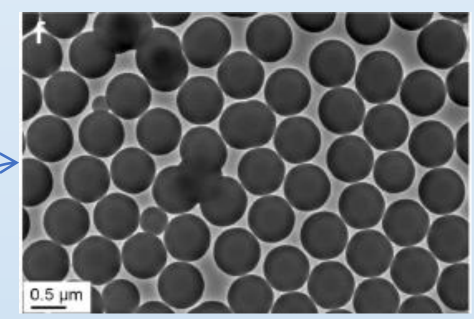
Methodology/Approach



Functionalised **fumed silica** (1st and 2nd step), incorporated into resin (3rd), depolymerized under a specific system and monomer recovery (decuring target).
X group: Thiol or Vinyl groups
Y group: Carboxyl or Amine



(0) Controlled hydrolysis and condensation of alkoxysilane;
(1) sulphur labile bond with catalyst;
(2) final functionalised silica surface to incorporate into the resin.
X - Alkoxysilanes and **Silazanes**

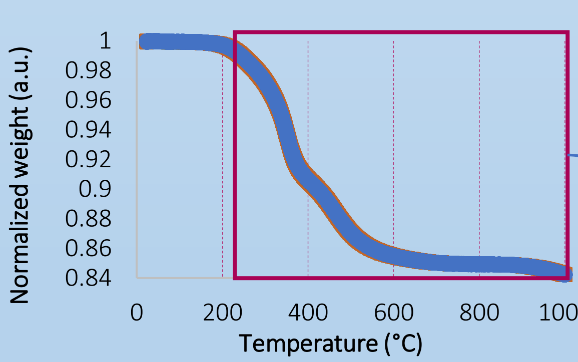


Stöber silica synthesis has pure, uniform and discrete resultant materials, with control over the surface chemistry, particle size, and complex structures[1].
TWI was involved in the development of the synthesis protocol

Nanomaterial characterization

1st step functionalization

- Protocol functionalisation of fumed silica with 3-mercaptopropyl-trimetoxisilane and imidazole as catalyst in anhydrous toluene solvent. Time of reaction, quantity of silane and catalyst considered as factors to be studied.



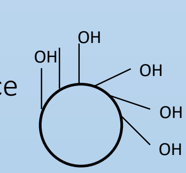
Example of sample thermogram from thermal gravimetric analysis TGA program run from 25-1000 °C under N_2 atmosphere, 5 °C/min.

Quantify silane distribution on silica additive

Not a straightforward calculus

After the grafting reaction there are many side products generated, such as silane monomers, homocondensates and possibly different grafted silane layer arrangements[2].

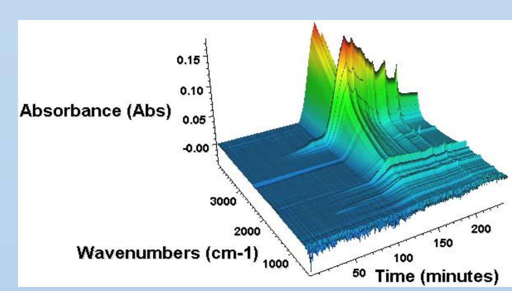
- Rod like
- Parallel to surface



2.30 - 8.74 μmol/m^2 of grafted silane calculated by TGA for the mercaptosilane functionalisation protocol (close to values 3 – 6.9 μmol/m^2 calculated by Posthumus[3])

Future work

- Silanol density determination with solid-state ^{29}Si NMR
- TGA-FTIR analysis of previous functionalized fumed silica



Example of a sample infrared spectra analysis with TGA-FTIR, program run from 25-1000 °C under N_2 atmosphere, 5 °C/min; infrared collection 400 – 4000 cm^{-1} at a rate of 20 scans/min

- Select conditions for the next functionalisation protocols

References

[1]Bourebrab, Marion A. et al, Influence of the initial chemical conditions on the rational design of silica particles, Journal of Sol-Gel Science and Technology 2018, 88(2): 430–441, DOI: 10.1007/s10971-018-4821-9, http://creativecommons.org/licenses/by/4.0/
[2]Spyrogianni, Anastasia et al, The silanol content and in vitro cytolytic activity of flame-made silica, Journal of Colloid and Interface Science 2017, 507:95-106, DOI: 10.1016/j.jcis.2017.07.096
[3]Posthumus, W. et al, Surface modification of oxidic nanoparticles using 3-methacryloxypropyltrimethoxysilane, Journal of Colloid and Interface Science 2004, 269(1):109-16, DOI: 10.1016/j.jcis.2003.07.008

Acknowledgments

Magali Rego would like to acknowledge TWI Ltd. and NSIRC for providing access to the facilities and equipment necessary; Also thankful for Lloyds Register Foundation for mentorship and financial support for this PhD work study.

Email contact: magali.goncalves-rego@open.ac.uk