Low fire, smoke and toxicity SMC and BMC using novel latent catalyst activated phenolic resins

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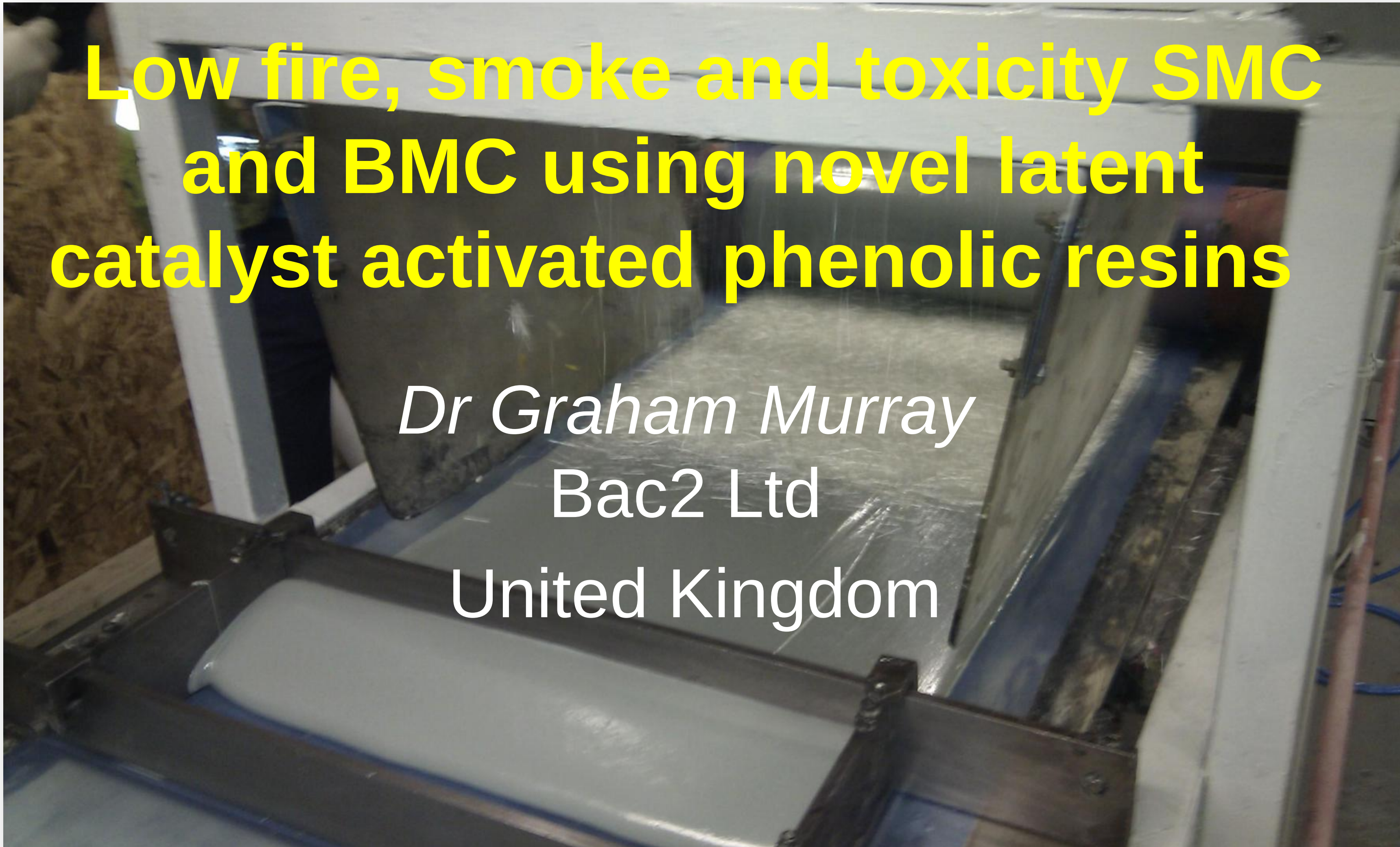


Background

Bac2 Ltd is a privately owned and funded SME based in Hampshire, England.

Bac2 has been producing phenolic resin based conductive composites for cleantech applications such as compression moulded bipolar plates for fuel cell stacks. Much of the development work has centred around catalyst technology to improve the processing properties of phenolic resins.

The fuel cell plate development resulted in Bac2 securing Intellectual Property based on novel latent acid catalysts, prefixed CSR, which can be applied to phenolic resin technology (and other resin types) outside of the fuel cell industry.

This presentation is focused on the use of Bac2's CSR catalysts in the development of sheet and bulk moulding compounds to impart process control over phenolic resins with established low fire, smoke and toxicity properties.

Development of CSR Latent Acid Catalysts

Bac2 developed a binder system and process to manufacture composite bipolar plates using a combination of graphite and a phenolic resin based binder in an acid catalysed condensation reaction.

Phenolic polymers are highly suited to the fuel cell operating environment due to their excellent chemical resistance and heat stability. A well recognised problem when working with acid catalysed phenolic resins, however, is controlling the reactivity of the catalysed system which can be highly exothermic and reactive resulting in an increased risk of batch errors and yield reduction.

Throughout the development of Bac2's bipolar plate products a constant search was made for a suitable latent catalyst which could retard the acid reactivity of the pre-mix to allow storage of the moulding compound for periods measured in months rather than minutes or hours.

Development of CSR Latent Acid Catalysts

The problem with the most common latent catalyst salts, such as ammonium sulphate or ammonium chloride, is that they require high temperature (180^{O}C) to rapidly breakdown and release the acid.

Weaker bases such as primary and secondary amines form less stable salts and the acid is slowly released at room temperature, shortening storage life.

The ideal latent acid catalyst should be:

1. Stable at room temperature enabling a storage life of an acid catalyst/phenolic resin mix to extend to weeks or months.

2. Heat activated at temperatures well below 180^{O}C offering opportunities to improve production speeds and lower energy costs

Development of CSR Latent Acid Catalysts

Bac2's CSR latent acid system provides stability and rapid heat activation at moderate temperatures. The key component is the base, hydroxylamine.

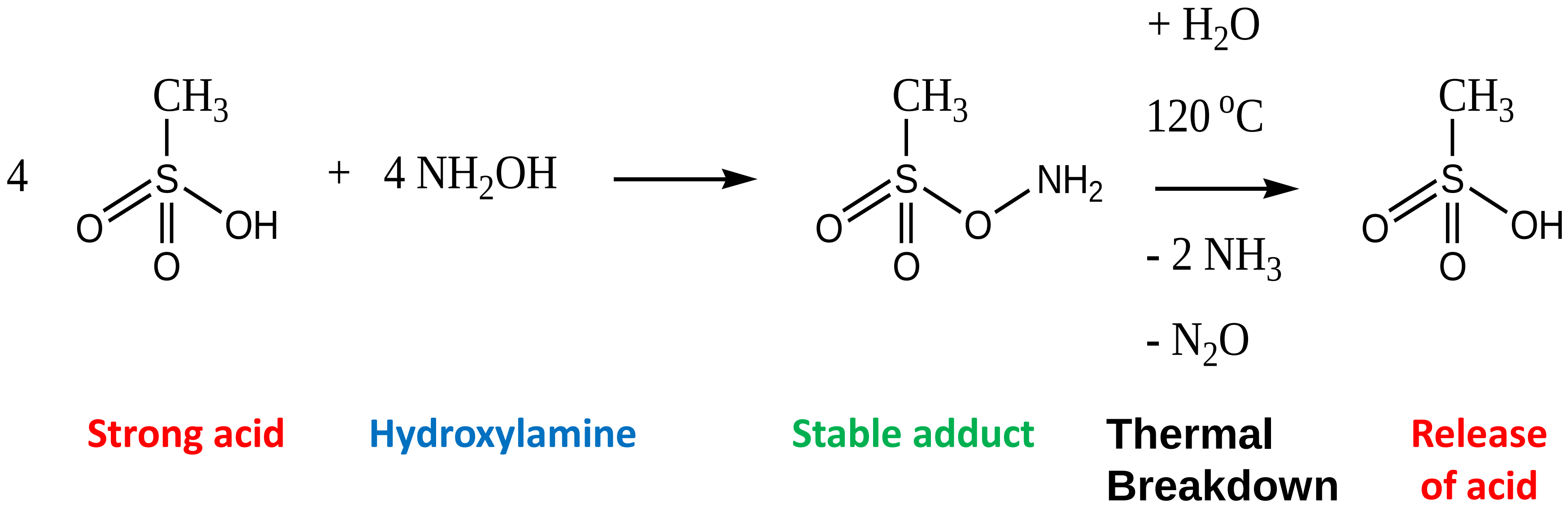
$$4\ NH_2OH \xrightarrow{120^oC} N_2O + 2\ NH_3 + 3H_2O$$

Hydroxylamine

Unlike all other bases, hydroxylamine is thermally unstable and decomposes instantly around 120^{o}C leaving the acid completely free to begin the catalysis.

Development of CSR Latent Acid Catalysts

Hydroxylamine can form a stable adduct with many acids eg,



On decomposition of hydroxylamine the acid is completely freed and the polymerisation reaction proceeds rapidly

Development of CSR Latent Acid Catalysts

Hydroxylamine salts are not obvious latent catalysts. They are commonly used as accelerators due to their reactivity towards formaldehyde which releases an acid eg.

$$HCHO + NH_2OH{:}HCl \rightarrow CH_2{:}NOH + H_2O + \mathbf{HCl}$$

To counter this reaction Bac2 has developed blendable CSR formulations **CSR20 and CSR100** which allow the adjustment of the hydroxylamine content to mop up any free acid generated from free formaldehyde.

Based on International Patent Application **WO 2010094979 (A1)**

Development of CSR Latent Acid Catalysts

The table below gives an indication of the reactivity of CSR latent catalysts compared to common ammonium salts. The resin used was an aqueous resole, solids 65%).

Catalyst	% based on resin	Hot plate gel time		
		90°C*	120°C	140°C
None	-	>20min	>20min	15min
Ammonium Sulphate	5 (solid)	>20min	14min	4min
Ammonium Nitrate	8 (52%aq)	9min	6min	3min
CSR20	5 (45%aq)	1min 45s	30s	20s
CSR20/CSR100 (1:1)	5 (42%aq)	3min	50s	35s
CSR100	6 (40%aq)	5min	2min	1min 20s

*CSR catalysts can be activated below 100°C which is important in low pressure processes

Process Control in Wider Applications

The development of CSR latent catalysts enabled Bac2 to formulate graphite/ phenolic based BMC with a storage life of over 12 months. A decision was made to introduce CSR technology to wider phenolic applications.

Composites	Industrial
Bulk Moulding	Abrasives
Sheet Moulding	Filters
Pultrusion	Laminates
Pre-pregs	Coatings

The applications listed involve processes where a CSR latent catalyst can offer benefits of storage stability, faster production speeds and lower energy consumption.

The following slides describe how CSR can be used in phenolic BMC and SMC to produce moulding compounds with low FST properties

Phenolic Resin Based Mouldings for the Rail Industry
http://www.firete.com/en/detail_271.html

Test	**Performance**
Oxygen Index, BS 2782-method 14 ASTM D2863, NES 714	Ignitability > 55%
Temperature Index	> 420°C
BS 476 Pt 6	RHR I <6, L< 12 **- Class 0**
BS 476 Pt 7	Flame spread - **Class 1**
Cone Calorimeter	RHR 128kW/m² Qe 50 kW/m² effective heat of combustion 22.3 MJ/kg SEA 182 m²/kg Qe 50 kW/m²
3m Cube, Smoke Test. BS 6853	Ao On < 1.0 Ao Off < 1.5 - **Category 1**
NBS Smoke Box ASTM E 662	DM NF 55 F 91
NES 711	Smoke Index 4
NES 713	Toxicity Index < 5
NF F 16-101	Flame spread M1, Smoke & Toxicity F1

CSR Latent Catalyst for Low FST Phenolic BMC and SMC

Typical fire properties of a commercial Phenolic based laminate (Data by courtesy of Caleb Technical Products, UK)

Test	Performance
Oxygen Index, BS 2782-method 14 ASTM D2863, NES 714	Ignitability > 55%
Temperature Index	> 420°C
BS 476 Pt 6	RHR I <6, L< 12 **- Class 0**
BS 476 Pt 7	Flame spread - **Class 1**
Cone Calorimeter	RHR 128kW/m² Qe 50 kW/m² effective heat of combustion 22.3 MJ/kg SEA 182 m²/kg Qe 50 kW/m²
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CSR Latent Catalyst for Phenolic BMC

With many years experience working with graphite based BMC the switch to glass filled BMC needs to take into account the main differences in the moulding compound properties. The key processing considerations are:

Beginning with a phenolic resin with proven FST properties. Good glass wetting properties and an effective release agent are essential. Selecting the CSR blend for the required shelf life of the BMC is a feature of the catalyst.

The glass content and filler material will influence the flow in the mould and the resulting mechanical properties. Tool venting during the early stage of moulding will eliminate blisters due to the formation of condensates and volatiles.

CSR Latent Catalyst for Phenolic SMC

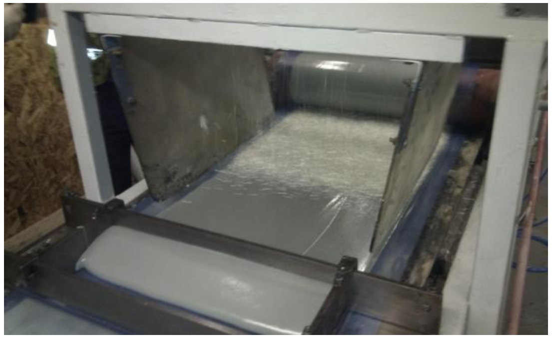
As with phenolic BMC it is desirable to select a phenolic resin for SMC with certified FST properties. The resin/CSR/filler combination needs to be formulated so it can be the transferred from a mixing vessel to the baths dispensing the resin layer onto the upper and lower plastic sheeting where the chopped glass is then added.

A uniform resin spread is key and wetting of the chopped glass very important.

If the resin layer is too low viscosity, there is a high possibility it will be squeezed out of the sheet roll as the pressure increases.

The pictures on the right show a pilot SMC line and the production of a CSR/phenolic resin/filler formulation being transferred to the bath and doctor bladed onto the plastic outer layers. The glass can be seen in the centre picture being dropped onto the resin layer.

The SMC is then rolled and stored at room temperature until required for moulding.



CSR Latent Catalyst for Phenolic SMC

Phenolic SMC is slightly more complex than BMC, in that it is necessary to include a thickening stage after the sheet roll has been formed. This enables the moulder to unroll the sheet, cut to size and strip the plastic outer layers without the resin being runny or tacky. If the sheet thickens too much it can become unusable.

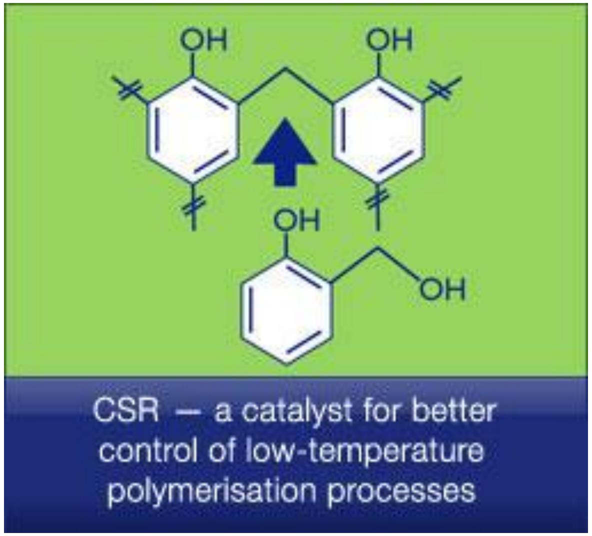
To introduce a thickening stage to Phenolic SMC, the usual practice is an addition of an oxide of magnesium or calcium.   A drawback of this is that the sheet often hardens to a level where it is difficult to prepare for moulding.

When using a latent catalyst, it is not possible to include a basic oxide as the acid is neutralised.
However, Bac2 found that with the correct blend of CSR latent catalysts, a thickening stage can controlled with a flexible, non tacky sheet stored for up to 4 weeks at room temperature.

CSR Catalyst

Summary

- Bac2 has developed hydroxylamine based CSR latent catalysts
- **CSR latent catalysts enable control of latency and shelf life**
- CSR latent catalysts are heat activated at moderate temperatures

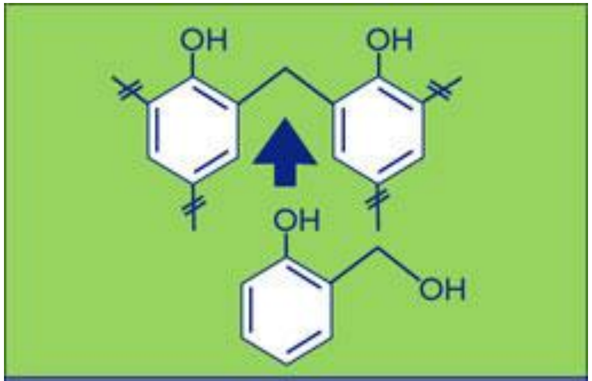


CSR Catalyst

Summary

Latent Catalysts from Bac2

- **CSR20 and CSR100**
  - aqueous
  - blendable to tune latency and reactivity
- **CSR800**
  - non aqueous for evaluation with epoxy, acrylic and polyester



CSR — a catalyst for better control of low-temperature polymerisation processes

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