Pseudo B-stage phenolic SMC using novel latent catalysts

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Abstract
Despite their superior fire properties, phenolic resole based sheet molding compounds (SMC) are not commonplace due to poor storage and processing. Phenolic SMC is produced using liquid resole resins, chopped glass and filler sandwiched between an upper and lower protective film. The resin layer must thicken during storage to allow ease of cutting and handling at the moulders. To thicken the resin an addition of metal oxide is used. The resulting sheet however has to be stored below 0^oC as the sheet becomes unusable if left at room temperature for more than a few days. Bac2 Ltd has developed novel latent acid catalyst systems for use in the production of resole based products for a wide range of applications such as abrasives, pultrusion, adhesives and moulding products including BMC and SMC. Applications that involve processes that will benefit from better storage stability, faster production speeds and lower energy consumption are where CSR latent acid catalysts can be most effective.
Based on an International Patent Application WO/2010/094979, the novel feature of the CSR latent catalysts is the use of hydroxylamine as the base in association with a strong acid to give a stable adduct.

Unlike all other bases, hydroxylamine is thermally unstable and decomposes around 120^oC producing gaseous decomposition products and water vapour leaving the acid completely free to begin the catalysis. By conrolling the ratio of acid to hydroxylamine, a wide range of reactivities can be acheived and equally a tight control of storage stability.
When used in the SMC production process, the CSR catalysts enable phenolic SMC to be formed into rolls which thicken via a ***pseudo B-stage*** and require no cold storage. The ***pseudo B-stage*** thickening step is acheived without the need for metal oxide additives and after a few days at room temperature the SMC is at a consistency allowing the easy cutting, stripping and moulding of a wide range of GRP parts. The rolls can be stored at ambient temperature for up to 2 months. The sheets are cut to size and compression moulded at temperatures between 120 and 150 ^oC with minimal breathing required. Mechanical and fire properties are excellent for the newly developed phenolic moulded parts. The main challenge is to demonstrate to the composite industry that a phenolic option for storage stable SMC is available and can produce. At high volume, mechanically strong, fire safe products for many applications.

INTRODUCTION

Phenolic resole resins are typically formed from an alkaline catalysed resin synthesis in which a molar excess of formaldehyde over phenol is used. In traditional terminology the term “A Stage” is used for liquid resins or pre-polymers. When heated and partially cured the term for the phenolic polymer form is “B Stage”. When fully cured the phenolic polymer has reached the “C Stage”. In some applications such as pre-preg, “A Stage” resins are converted to the “B Stage” to allow better handling of the non-liquid form prior to moulding or forming. As the polymerisation of phenolic resins is a condensation reaction, the “B Stage” forms are less susceptible to blistering and void formation when finally heat cured.

Phenolic resoles can also be cured using acid catalysts. An acid catalyst can rapidly cure the polymer at lower temperatures but can cause processing problems. An acid catalyst will convert resin from the “A Stage” form to the fully cured “C Stage” in a strong exothermic reaction. This means the pre-mixing of resin and acid catalyst can only be used in small scale applications and carried out immediately before use.

The reactive polymerisation, however, can be controlled by using a latent or blocked acid catalyst. The latent catalyst is usually a stable salt product of an acid and a base. The choice of salt will determine the latency and the activation temperature. Strong bases such as alkali metals and alkali earth metals are not suitable candidates for a latent acid salt. Strong bases form very stable salts with strong acids and will not decompose at low temperatures. Ammonia forms stable salts, ammonium sulphate and ammonium chloride with sulphuric and hydrochloric acid respectively which will decompose, but at temperatures typically well above 200°C. Primary and secondary amines are weaker bases than ammonia and form salts with strong acids but latency is short and pot life is counted in hours.

Pseudo B-stage

Bac2 Ltd has developed a novel latent acid catalysts using hydroxylamine as the base. The hydroxylamine based latent acid catalysts **[1]** pre-fixed CSR, offer many advantages over existing catalysts. This paper covers the chemistry of the CSR latent acid catalysts and how they can be used in many phenolic resin processes demanding varying latency and different reaction speeds and temperatures. When used in the SMC production process, the CSR catalysts enable phenolic SMC to be formed into rolls which thicken via a pseudo “B Stage” and require no cold storage. The pseudo “B Stage” thickening step is acheived without the need for metal oxide additives and after a few days at room temperature the SMC is at a consistency allowing the easy cutting, stripping and moulding of a wide range of GRP parts. The paper describes the use of the latent acid catalyst to manufacture a phenolic SMC and how a number of processing challenges are overcome to produce a stable, thickened sheet, suitable for compression moulding.

SHEET MOULDING COMPOUND

Sheet moulding compound is a combination of a thermoset resin, catalyst, chopped glass, fillers and process aids formed into a sheet between two carrier layers (Fig.1). The sheet is usually produced and supplied to the customer in rolls after a number of days during which the sheet, thickens and becomes tack free. This maturation stage allows easier handling of the sheet by the moulder, to enable cutting and removal of the outer carrier layers in readiness for compression moulding.

The resins used in sheet moulding are mainly unsaturated polyester and vinyl ester for higher heat stability. Polyesters are favoured due to the well established processing techniques and there exists a wide range of process additives to control shrinkage and enhance surface finish. Standard polyester resins, however, have poor fire smoke properties and fire retardants must be included in the formulations to enable polyester moulding compounds to meet certain fire standards. Aluminium trihydrate (ATH) is a favoured fire retardant as it is free from halogens found in many alternative fire retardants. A disadvantage using ATH is that high loadings are required to meet the more stringent fire tests. The high ATH loadings can cause problems with resin processing and final product properties.

Phenolic resins are well known for their excellent low fire, smoke and toxicity (FST) properties and can be considered as an alternative to polyester in some applications demanding low FST.

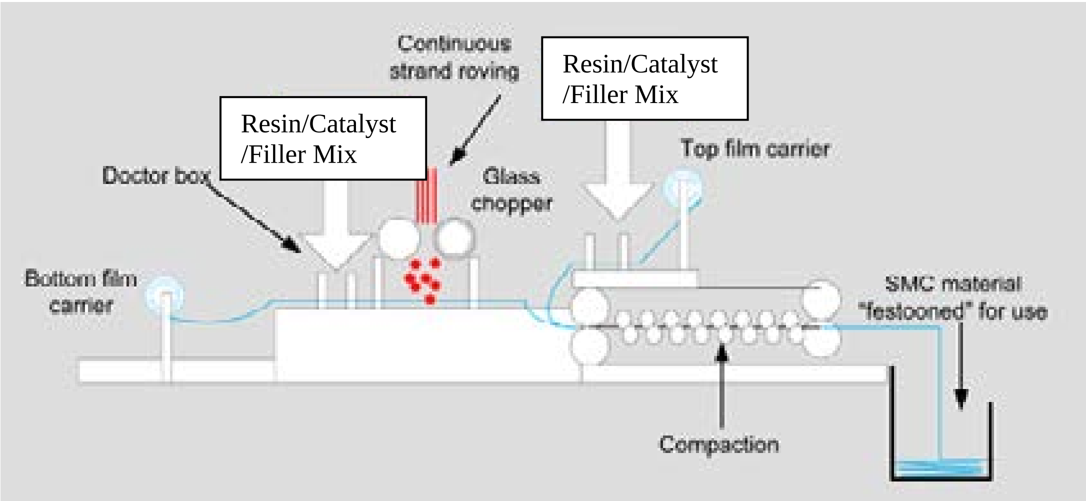
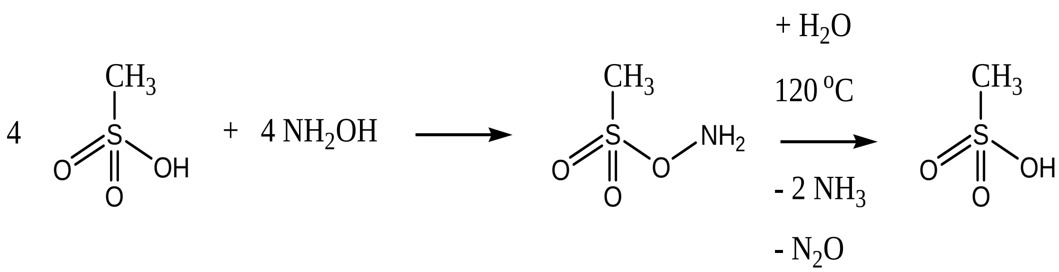


Figure 1. Sheet moulding compound production line

CATALYST CHEMISTRY

The novel feature of the CSR latent catalysts is the use of hydroxylamine as the base retarder in association with a strong acid to give a stable adduct. Unlike all other bases, hydroxylamine is thermally unstable, rapidly decomposing around at 120^{o}C leaving the acid completely free to begin the catalysis **[2]**, **[3]**.



(1)

On heating the catalyst to temperatures above the decomposition temperature of hydroxylamine the acid is freed and the polymerisation reaction proceeds rapidly. At ambient temperatures, hydroxylamine is stable and the polymerisation is controlled.

Hydroxylamine salts are not obvious latent catalysts. They are commonly used as analytical reagents [4] due to their reactivity towards formaldehyde in a reaction which generates an acid e.g.

$$HCHO + NH_2OH{:}\ HCl \longrightarrow CH_2{:}\ NOH + H_2O + HCl \qquad (2)$$

When introduced to phenolic resins the hydroxylamine salts can react with free formaldehyde in the resin. To counter this side reaction Bac2 provides blendable formulations, CSR20 and CSR100, which allow the adjustment of the hydroxylamine content to mop up acids generated from the reaction of the salt with free formaldehyde.

At room temperature the CSR catalysts can stabilise an active resole resin to give storage life from a few hours to many months depending on the blend ratio of CSR20 and CSR100 used.

CATALYST PROPERTIES

The properties of CSR20 and CSR100 are shown in Table 1. CSR100 contains a higher mol ratio of hydroxylamine to acid and when used increases the storage life of an active resin. CSR20 has a lower ratio of hydroxylamine to acid and is a more reactive form of latent acid so the latency is shorter. Both catalysts can be blended to suit the process requirements.

Table 1. Catalyst Properties

Properties		**CSR20**	**CSR100**
Form		liquid	liquid
Colour		clear	clear
Acid concentration	moles l^{-1}	3.65	2.60
Specific gravity	g cm^{-3}	1.189	1.175
Solvent		water	water

Most resole resins can be used with CSR catalyst blends, but resins with high pH (>7.5), may require higher catalyst levels. Table 2. shows how the reactivity of a neutralised phenolic resin can be increased at various temperatures. The CSR catalyst blends can be activated below 100^{o}C which is important for low pressure processes. Above 120^{o}C activation of the catalysts is very fast and more suited for high pressure moulding.

Table 2. Reactivity Data for Latent Catalyst Blends

Catalyst	**%** **based on neutralised resin**	**Hot plate gel time**		
		90°C*	120°C	150°C
None	-	>60min	>60min	15min
Ammonium Sulphate	4 (solid)	>20min	16min	9min
Ammonium Nitrate	6 (52%aq)	9min	7min	4min
CSR20	4 (45%aq)	**1min 45s**	**30s**	**20s**
CSR20/CSR100 (1:1)	4 (42%aq)	**3min**	**50s**	**35s**
CSR100	5 (40%aq)	**5min**	**2min**	**1min 20s**

STORAGE STABLE PHENOLIC SMC

Phenolic SMC is difficult to source as few SMC manufacturers supply it. There is a market demand for fire safe products particularly in the marine, mass transit, off-shore and construction sectors. Existing phenolic SMC exhibits outstanding low FST characteristics but suffers from very short storage life. The additives required to impart the "B Stage" to the SMC are usually metal oxides such as magnesium oxide. Such additives also accelerate the cure of the resins used. This means the SMC when produced requires cold storage. Once out of the freezer, the SMC has about 24-48 hours during which to use it.

Compared to polyester SMC this is a big disadvantage and moulders must change their working procedures to allow for this. When Bac2 began the development of a new phenolic SMC, this appeared to be the biggest challenge as the alkaline thickeners could not be used with an acid catalysed system. "B Staging" using heat is also not possible in the SMC process. Working with a European SMC manufacturer and using their pilot line, a number of formulations were used to produce a pseudo "B Stage" thickened phenolic SMC which can be stored at room temperature for up to three months.

Figure 2. The phenolic resin/CSR/filler mix being poured into the “doctor box”

A phenolic resin with certified FST properties (Table 4) was selected for the SMC. The resin/CSR/filler mix needs to be formulated so it can be transferred from a mixing vessel to the “doctor box” 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 is 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.

Figures 2, 3 and 4 show the 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.

Figure 3. Chopped glass added to the bottom resin layer

The chopped glass is added (Figure 3.) and the upper resin layer sandwiches the glass. The sheet is then carried through a compactor to aid the glass wetting and uniformity of the sheet thickness.

Figure 4. The phenolic SMC is formed into a roll and stored until thickened.

The SMC when produced is formed into a roll and stored at room temperature. The level and blend of catalyst can influence the pseudo “B Stage” thickening. Of the rolls made some were tack free and ready for moulding after one week (figure 5). With different catalyst blends the thickening stage could be accelerated to 1-2 days or delayed for 2-3 weeks.

Figure 5. Thickened (matured) phenolic SMC sheet, cut and ready for moulding

Optimisation work looking at storage conditions, catalyst blends, filler type and content, glass type and length, release agents, coupling agents is ongoing. The early rolls of SMC were moulded in a test tool producing 150 x 150 x 4mm flat plaques. The main aspects to observe were the flow of the material in the mould tool, the release of the moulded part, any evidence of blisters, tool venting requirements, moulded properties and fire properties.

		
Figure 6a. SMC shot	Figure 6b.Release from tool	Figure 6c. Moulded part

Figure 6. Moulding of phenolic SMC test plaques

On moulding the parts released easily and the material flowed well. It is well known that a phenolic resin polymerisation is a condensation reaction resulting in water and other volatiles forming during the moulding cycle. These volatiles need to escape from the tool and failure to vent the tool properly can lead to blisters forming in the moulded part. Surprisingly no blisters were found on the mouldings and a breathing step was not required. The tool used was well vented but there is an indication of a reduction in volatile production due to the maturation step of the phenolic SMC.

FIRE PROPERTIES

All SMC work was undertaken with a phenolic resin grade fully assessed for fire performance.

The results of the first indicative fire tests undertaken in accordance with DD CEN/TS 45545-2 Annex C are shown in Table 4. EN 45545 is expected to be the new European rail stock test procedures standard with Part 2 – Requirements for Fire Behaviour of Materials and Composites (Reaction To Fire) the relevant procedure.

Table 4 Indicative fire performance of a composite sample made with phenolic resin and CSR catalyst in accordance with DD CEN/TS 45545-2 Annex C

Test Mode 50kw/m^2 in the absence of a pilot flame	
Test Result	Target
Ds4 = 43	
Ds (max) = 68	**HL3 (interior) < 150**
VOF4 = 64	
CIT value (4 minutes) = 0.06	
CIT value (8 minutes) = 0.17	**HL3 (interior) < 0.75**

The test is carried out in a sealed chamber having a volume of $1/2m^3$. The specimen sits inside a small metal holder with one face left exposed. The sampling of fumes is made at 4 minutes and 8 minutes test duration. The concentration of each of the following toxic gases is recorded and compared to relevant reference values in order to determine the CIT value (the magnitude of the reference values is based on the danger posed from the gas in question):
Carbon Monoxide
Carbon Dioxide
Hydrogen Bromide
Hydrogen Chloride
Hydrogen Cyanide
Hydrogen Fluoride
Sulphur Dioxide
Nitrous Oxides

Ds(4) is the specific optical density at 4 minutes test duration.
Ds (max) is the maximum specific optical density obtained within the 20 minute test period.

VOF4 is calculated as follows: *VOF4 = D1 + D2 + D3 + D4/2*
Where D1, D2, D3 and D4 are the values of the specific optical density recorded at the 1st, 2nd, 3rd and 4th minutes respectively.

The results in Table 4 show that the phenolic SMC easily meets the HL3 target, which requires the highest level of performance.

A video of the SMC production and the basic fire tests can be seen at http://www.bac2.co.uk/csr/smc.

CONCLUSIONS

Bac2 Ltd has developed novel latent acid catalysts for use in the production of resole based SMC with low fire smoke and toxicity values. Based on the use of hydroxylamine with a strong acid, the latent catalyst allows storage stable moulding compounds to be produced containing highly reactive phenolic resole based polymer binders. At room temperature the CSR catalysts can stabilise an active phenolic resole resin to give storage life from a few hours to many months depending on the blend ratio of CSR20 and CSR100 used. The catalysts enable phenolic SMC to be manufactured and formed into rolls which thicken to a pseudo "B Stage" and mature, without the need for additives, after a few days to a consistency allowing the easy cutting, stripping and moulding of a low FST phenolic parts. The rolls can be stored at ambient temperature for up to 3 months. The newly developed SMC easily meets the HL3 target in indicative tests in accordance with DD CEN/TS 45545-2 Annex C.

REFERENCES

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[2] Hydroxylamine by K. Jones in Comprehensive Inorganic Chemistry, Vol. 2. J.C. Bailar, 1973, pp 265-276.
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[4] BS EN ISO 9397:1997