LATENT ACID CATALYSTS FOR THERMOSET PROCESS CONTROL IN ADVANCED COMPOSITES

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Abstract

Bac2 has developed a storage stable, molding material, incorporating a latent acid catalyst for the compression molding of advanced composite bipolar plates, key components of fuel cell stacks. The latent acid catalyst technology is used to control the reactivity of phenolic resins and furan bio-resins, by-products from plant sources. The process control imparted using the hydroxylamine based latent catalyst has extended the opportunity to use phenolic and furan binders in wider composite and adhesives applications.

Introduction

Fuel cells are used to produce electrical power for stationary, portable and transport applications. To generate power at levels that are useful to feed external devices, individual fuel cells are connected in series to form a stack of cells to boost the total voltage available much in the same way batteries are assembled from a series combination of individual cells (see Figure 1). A key difference of a fuel cell from a typical battery is that the fuel is continually supplied by external means to the electrodes rather than having a finite store of fuel within the assembly. This means that a fuel cell can operate continually whilst the fuel is supplied compared to a typical battery which discharges as the internal fuel store is depleted.

Typically, fuel cells consume hydrogen as a fuel and oxygen from the air as an oxidant generating both water and electricity. Within the stack, each fuel cell is separated by a bipolar plate, which can be a compression molded composite plate with channels to direct the flow of the fuels.

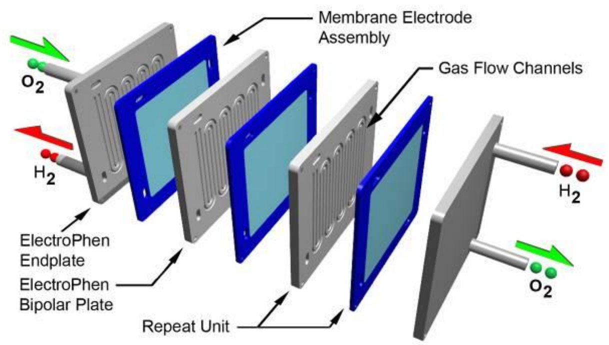


Figure 1. Exploded diagram of a fuel cell stack showing composite bipolar plates

The fuels and oxidant have to be channeled separately to the active electrode area for the chemical reaction to take place as well as acting as a conduit for the current generated by the cell. The bipolar plate is multifunctional as it must separate and channel the fuels through the stack, it has to be mechanically strong enough to withstand elevated temperatures and pressures, it must be resistant to corrosion due to the highly acidic electro-chemical processes occurring at the electrode and electrically conductive to carry the current generated by each individual cell with minimal resistive losses. Additionally, the highly conductive plates perform roles including heat transfer and water management of the water produced in the fuel cell reaction. Bipolar plates are critical to the exploitation of fuel cell stack technology and are key components making up about 80% of the total weight. It is well recognised within the fuel cell industry that the ability to economically produce bipolar plates for a mass market will be of major importance to the commercialization of fuel cells. For mass production of fuel cells, compression molded plates will be one of the main manufacturing methods using polymer and graphite based compounds.

Materials and Technology

Reactive Polymer Molding Compounds

Molding of a composite bipolar plate is not a trivial task. As the pre-mix material is highly filled with graphite, the flow properties are restricted and can cause many problems with incomplete filling of the mold cavity, non-flatness and low tolerance. Bac2 has developed a binder system and process to manufacture composite bipolar plates. Trademarked ElectroPhen®, the composite is made using a combination of graphite and a polymer binder. The process is based on a heat activated polymerisation involving and an acid catalyzed condensation reaction. Suitable polymers for use in molding bipolar plates are thermosets made from phenol-formaldehyde and bio-derived furan-formaldehyde resins, which show good heat and chemical stability in the polymer form. A well recognized problem when working with acid catalyzed phenol-formaldehyde and furan-formaldehyde resins, however, is controlling the reactivity of the catalyzed system which can be highly exothermic and dangerous. The reactivity of a catalyzed resin can be so rapid that the processing becomes difficult and expensive, or often impossible. Pre-mixing of resin and acid catalyst can only be carried out immediately before use with a requirement for additional process equipment and with the increased risk of batch errors and yield reduction.

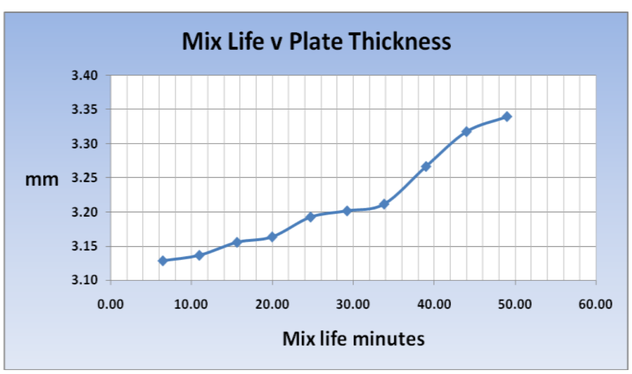
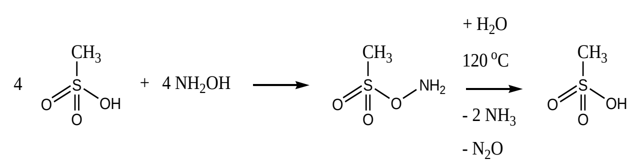


Figure 2. Mix life effects on the flow properties of an acidified resole composite mix as shown by increase in molded plate thickness

With a graphite/composite pre-mix, consisting of a phenolic resin and a strong acid, on first mixing the reaction will begin immediately and within minutes the moulding properties are affected. Typically a reactive pre-mix will lose flow properties and produce moldings' which are increasingly heavier and thicker over the duration of the mix life as illustrated in Figure 2. The conductivity of the molded plate at the same time is reduced. Clearly this level of variation is unacceptable for a production process.

Hydroxylamine Based Latent Catalyst

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. The problem was eventually overcome a latent acid system was developed which gives a very stable storage life of the bipolar plate composite pre-mix formulation. Based on an International Patent Application **[1]**, the novel feature of the latent catalysts (prefixed CSR) is the use of hydroxylamine as the base in association with a strong acid to give a stable adduct.



Stable Adduct

Figure 3 Sulphonic acid and hydroxylamine form a stable adduct latent acid, which decomposes at 120°C to release the acid.

Unlike all other bases, hydroxylamine is thermally unstable and decomposes around 120°C producing gaseous decomposition products **[2], [3]** and water vapor leaving the acid completely free to begin the catalysis. At room temperature the CSR catalyst is very stable and allows a molding compound containing the resin, catalyst and filler to be mixed, packaged, shipped and stored ready for use for up to 12 months. Without the hydroxylamine the pre-mix has to be used within 30 minutes. When moulding bipolar plate pre-mixes, cycles times of 2-3 minutes are typical at temperatures between 130 and 160°C depending on plate size.

Furan Bio-Resins

Following the success of using hydroxylamine based latent catalysts with phenolic resoles, a bipolar plate formulation based on a bio-polymer resin was developed.

A bio-polymer is a product of a polymerizable resin derived from renewable and sustainable biological resources. Furan Resins are bio-resins based on furfuryl alcohol, a product derived from a variety of large scale plant sources such as cotton seed hulls and sugarcane bagasse.

Property	Phenolic	Furan-Phenolic	Value
Density	1.81	1.79	g/cm^3
In-plane Conductivity	114	130	S/cm
Through-plane conductivity	41	40	S/cm
Surface resistance	0.240	0.254	mΩ
Flexural Strength	30	32	MPa
Thermal Conductivity	43	44	W/mk

Table 1. Properties of molded composite bipolar plate produced from storage stable phenolic and furan pre-mixes

Furan polymers are thermoset resins and have been used for many years primarily in the foundry industry as sand binders. The polymerization of Furan resins is catalyzed by a strong acid and is highly exothermic and very difficult to control, limiting the adoption of this polymer in composite industries where oil derived thermosetting resins such as polyester and epoxy are well established. Furan polymers are attractive for bipolar plate use due to their excellent chemical resistance and high temperature stability. The hydroxylamine based catalyst was used successfully in controlling the furan polymerization enabling a carbon composite moulding compound to be formulated exhibiting up to 3 month's shelf life at room temperature. Properties of the Furan and Phenolic based bipolar plates are compared in Table 1.

Phenolic and Furan BMC and SMC

Bulk and sheet moulding compounds today are predominantly polyester based due to the cost and ease of processing of the resins. Despite their superior fire properties, phenolic BMC and SMC products are not common whilst Furan is almost unknown. The work done at Bac2 using the hydroxylamine based latent acid technology has shown that a storage stable, processable molding material can be made from both phenolic and furan resins. Glass filled BMC material has been made at Bac2 with a storage life of over 3 months. See Tables 2 and 3.

Composition	***%***
Resin	30
Catalyst	1
Glass fibre (chopped)	20
Clay	48
Release Agent	1

Table 2. Composition of a phenolic bulk moulding compound stabilized with CSR latent catalyst

Storage and Processing	
Storage life	3 months at room temperature
Press Temperature	120 – 160^{o}C
Press Time	2-3 minutes
Post cure	No

Table 3. Storage and processing conditions for a phenolic bulk moulding compound stabilized with CSR latent catalyst

Mechanical and fire properties are excellent for the newly developed phenolic moulded parts. The main challenge is to demonstrate to the composite industry that Phenolic and renewable Furan options for storage stable BMC, SMC and other composite forms are available and can produce mechanically strong, fire safe products for many applications.

Latent Catalysts for Conductive Adhesives

The CSR latent catalyst has opened up an additional opportunity with the development of a screen printable conductive adhesive for composite parts. Figures 5 and 6 show screen printed adhesive on ceramic and graphite composite substrates.

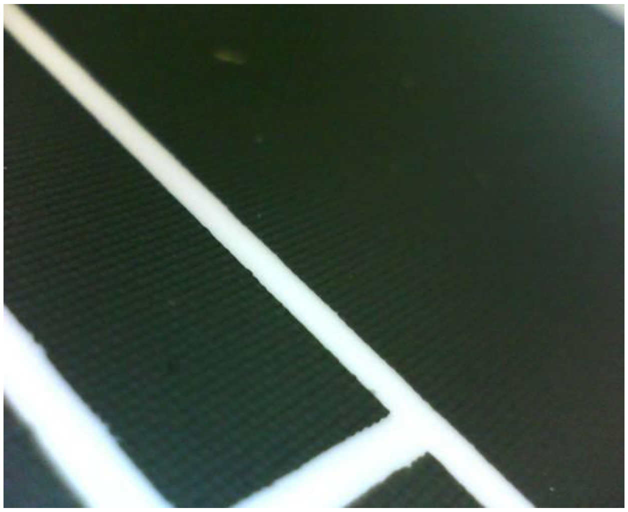


Figure 5. Screen printed conductive adhesive on a ceramic substrate

An adhesive with the potential to be screen printed for accurate and reproducible application has been formulated with a viscosity and flow suited to screen printing techniques. The screen printed layer is touch-dry shortly after being applied. Despite this, the adhesion layer can be activated when heated. This allows the adhesive to be applied to the part, then to be stored and used at a later date.

Figure 6. Screen Printed storage stable adhesive layer on a graphite composite bipolar plate

Conclusion

In summary, the hydroxylamine based latent catalyst has enabled Bac2 to produce advanced composite bipolar plates using a storage stable compression molding compound based on phenolic and furan resin chemistry. The opportunity now exists to develop phenolic and furan BMC, SMC and other composite forms in the wider composite industry to obtain the mechanical and fire properties these polymers can impart.

References

1) International Patent Application No **PCT/GB2010/050298**.

2) Hydroxylamine by K. Jones in Comprehensive Inorganic Chemistry, Vol. 2. J.C. Bailar, **1973**, pp 265-276.

3) Adiabatic Calorimetric Studies of Hydroxylamine Compounds, PhD Thesis, August **2002**.