OPPORTUNITIES IN WASTE MINIMIZATION: EPOXY COMPOSITES FOR POWER APPLICATIONS CASE STUDY

R. Sekula

ABB Corporate Research, Krakow, Poland
robert.sekula@pl.abb.com

Keywords: epoxy insulation, reactive molding, curing simulations, epoxy pyrolysis

Abstract

In the paper the methods for decrease amount of scrap generated during manufacturing of electrical devices with polymeric insulation have been presented. This is based on application of advanced numerical simulations in optimization of reactive molding process, including mold filling and epoxy curing phenomena. Using fully three-dimensional simulations number of potential problems (e.g. voids, porosity, cracking, etc.) can be identified and avoided during real production what results in lower scrap rate and energy savings. In addition to that, the utilization / recycling opportunities for that kind of the products have been presented focusing on thermal degradation by pyrolysis, as well as potential utilization of scrap epoxy in cement rotary kiln.

1 Introduction

Epoxy resins are broadly used as insulation materials in various electrical products due to their superior electrical and mechanical properties. The insulation being used in manufacturing process of products like: voltage and current transformers, combi sensors, embedded poles, dry transformers, bushings, etc. must be characterized by its mechanical stability at very high and very low temperatures, high mechanical resistance, excellent electrical insulation (dielectric strength) and thermal properties, good resistance to most chemicals, solvents, lubricants and fuels. To achieve such outstanding properties, as well as to reduce the material price, mineral fillers are incorporated into epoxy formulations creating a well performing epoxy composite. Also processing aspects of such materials are important, since proper manufacturing process (in our case reactive molding) must be performed avoiding any undesired properties as air bubbles, voids, premature gelation, wrong direction of gelation front, etc.

Having in mind complex design and variety of the materials used in electrical apparatus, as well as production volume, it is important to apply novel concepts in design, process optimization and final disposal to minimize generation of scrap thermosetting materials. Such pro-environmental thinking can be used in different stages of product life cycle, and the examples of the used tools and proposed technologies are presented below in relevance to ABB’s products based on epoxy composites. This refers to design optimization of epoxy components, optimization of reactive molding process parameters, and recycling of scrap epoxy products.

2 Design and process optimization of epoxy products

2.1 Reactive molding process

In manufacturing of various electrical products (Figure 1) that require good electrical insulation reactive molding technology is dominant, and two processes are used:

- Vacuum casting
- Automated Pressure Gelation (APG)

Figure 1. Sample products with epoxy composite electrical insulation

Vacuum process is mainly used for large parts for high voltage applications. Usually, these products are cast in small numbers and have long casting cycles (large distribution transformers coils, instrument transformers, high voltage bushings and spacers for gas insulated switchgears).

Automated Pressure Gelation (Figure 2) process is used for products manufactured in high numbers. This process can be characterized by short molding cycles (minutes versus hours for vacuum casting) and high accuracy.

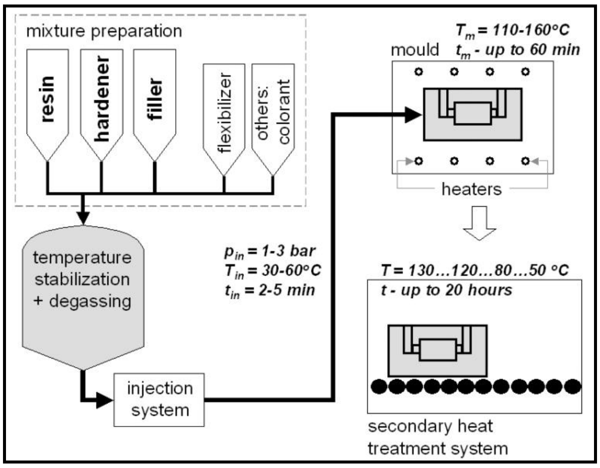

Figure 2. Automated Pressure Gelation process

In APG process two or more liquid reactants with additional components are mixed. After homogenizing and degassing the mixture is introduced by injection system into the heated mould. In an earlier stage the internal parts (cores, windings, conductors, etc.) of the component being cast are inserted into the mold. Polymerization of the resinous material generates additional heat and with increasing curing ratio, the component becomes harder obtaining a desired shape and required properties. Afterwards, de-molding is done and secondary heat treatment, aiming curing completion is carried out - very often in tunnel furnace.

Application of appropriate materials, process parameters (mold temperature, filling time, filling velocity, initial temperature of internal parts, gelation time), as well as design and geometric parameters are key factors for better quality epoxy products. Due to its complexity and various parameters to be set up, reactive molding processes can – especially at the production ramp-up phase – encounter problems such as air voids, incomplete filling, premature gelation, wrong curing propagation, high temperature gradients, local overheating, cracks, high residual stresses, deformations etc. To address these potential problems prior experiments and even before mold making, a fully three-dimensional simulation approach was developed [1] resulting with low scrap rates and reduced energy consumption. The simulation tool can simulate mold filling, curing, and post-curing stages.

2.2 Simulation approach

A proposed simulation methodology involves commercial CFD software FLUENT , however to calculate the behaviour of thermosetting mixture two additional models were implemented (in the form of so called user-defined subroutines) in the software: Kamal's model for reaction kinetics and Macosko's model to describe the viscosity changes. FLUENT calculations have been performed until degree of curing exceeds gelation point (α_g).

According to Kamal’s model [2] a degree of curing α at time *t* is defined as:

$$\alpha(t) = \frac{H(t)}{H_\Sigma} \tag{1}$$

In general it is assumed that curing rate depends on current temperature and curing value:

$$\frac{d\alpha}{dt} = f(T,\alpha) \tag{2}$$

The example equation that describes a curing rate can be expressed as follows:

$$\frac{d\alpha}{dt} = \left(k_1 + k_2\alpha^m\right)\left(1-\alpha\right)^n \qquad k_i = A_i e^{\frac{-E_i}{RT}} \tag{3}$$

where:

m, n – constants,
$k_i = A_i e^{\frac{-E_i}{RT}}$ – reaction rate constants (i = 1,2),
A_i – pre-expotential factors,
E_i – activation energies,
R – universal gas constant
T – absolute temperature.

Curing reaction of epoxy resin has exothermic nature and it is characterized by large temperature increase. Additional energy that is generated during the process has to be calculated. It is assumed that energy release is proportional to curing rate:

$$\frac{dH}{dt} = H_{\Sigma} \frac{d\alpha}{dt} \tag{4}$$

During development of the presented simulation tool, additional task was dedicated to take chemical shrinkage into account in structure analysis [3]. In general total strain increment can be expressed as sum of mechanical and thermal component:

$$\Delta\varepsilon_{xx}^{Total} = \Delta\varepsilon_{xx}^{Mech} + \Delta\varepsilon_{xx}^{Th} \tag{5}$$

Thermal component could be defined by user defined subroutine. It could be set to cover chemical as well as thermal effects and it is possible to calculate those effects based on density changes:

$$\Delta\varepsilon_{xx}^{Th} = \sqrt[3]{\frac{\rho}{\rho'}} - 1 \tag{6}$$

To utilize this equation it was necessary to have density dependency on temperature and curing degree. This dependency was derived based on the experimental measurements that were done by epoxy manufacturer.

For structural simulations ABAQUS code was used. The results obtained in CFD calculations (temperature and degree of curing) had to be transferred into ABAQUS mesh (Figure 3). Since no adequate direct data transfer codes are available on the market, external data transfer procedure has been developed and successfully implemented to perform the solution mapping between FLUENT and ABAQUS models.

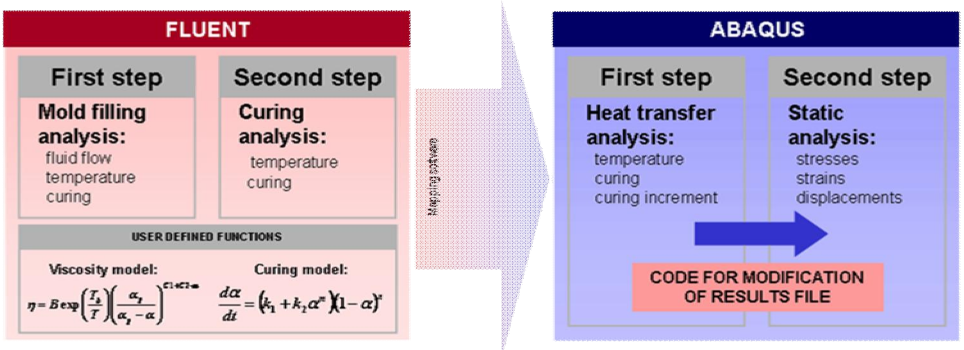

Figure 3. Simulation procedure for reactive molding process

Structural calculations are performed in sequentially coupled manner. In the first step only heat transfer analysis is done (including reaction kinetics) and then in the second step stress analysis (based on results obtained in the first step) are completed.

2.3 Selected simulation results

Developed simulation tool is a very powerful in respect to simulation results and visualization capabilities (Figures 4, 5, 6). Using the simulation methodology it is possible to predict number of potential already above mentioned problems associated with the mold filling and curing process: incomplete mold filling, premature gelation, wrong curing front propagation, local overheating, areas under high mechanical stresses. In real casting process a trial-and-error approach has to be used, which is time consuming and costly.

Using virtual optimization of the component design improvement and selection of the best process parameters can be done resulting in less failed products and lower energy consumption in the process.

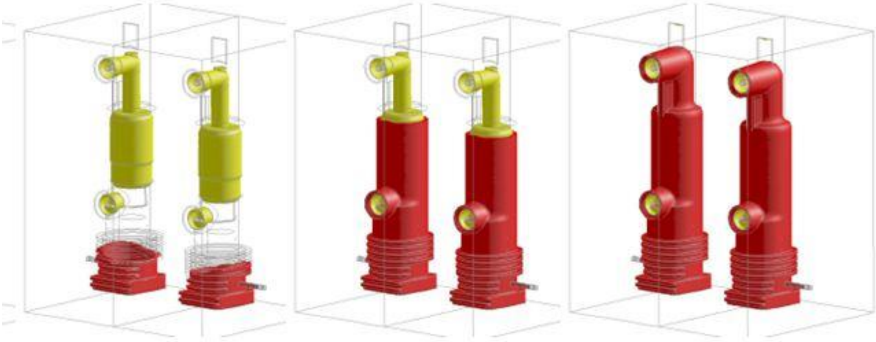

Figure 4. Mold filling pattern

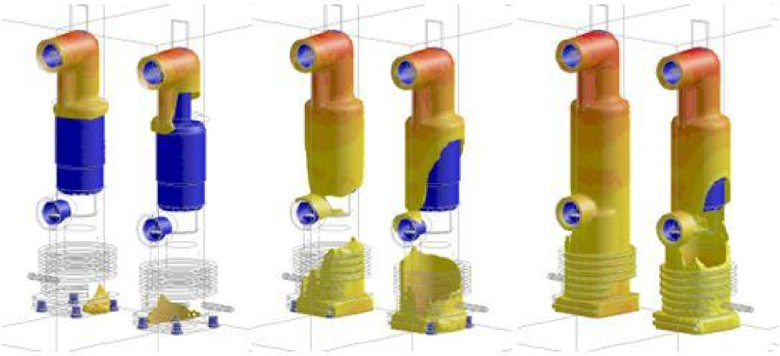

Figure 5. Curing propagation

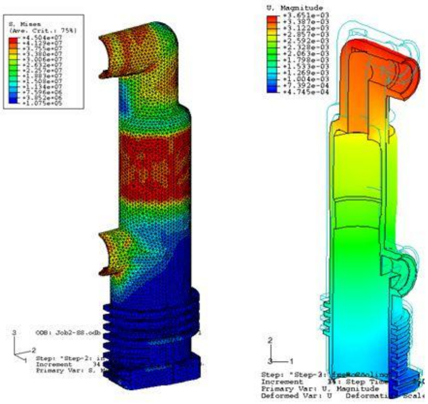

Figure 6. Stress and strain build-up

3 Waste management for scrap epoxy composites

3.1 Current disposal / recycling options

According to existing environmental regulations cured thermosets are not classified as hazardous and can be stored on landfills. In fact more than 90 percent of such waste is disposed of in this way [4]. However, increasing quantities of scrap materials and a limited amount of space for their disposal has created a need for more sophisticated, sustainable technologies for the reuse of these materials. Also, in some developed countries, landfill storage of the combustible wastes is not allowed, therefore they should be treated in the way allowing energy recovery.

The following methods can be used for disposal / recycling of scrap thermosets:

- Mechanical treatment
    - Landfill
    - Cryogenic treatment
- Construction industry (building/road)
- Thermal treatment
    - Combustion (incineration)
    - Gasification
    - Pyrolysis
- Chemical degradation
    - Dissolution in chemicals
- Novel methods
    - Cement process

A simple way to re-utilize cured epoxy based waste is to add it to concrete or asphalt construction materials. However, since only small amounts of waste material are generated relative to the construction material required and because it is dispersed geographical over a wide area, the economic value of such option is low. Moreover, epoxy based material is widely used to insulate electrical equipment, which means that various internal parts (cores, windings) made of metals must be removed before it can be reused. Some companies apply cryogenic techniques to recycle the embedded parts, but the quality of such parts is poor.

Energy recovery from thermosets is an attractive alternative to recycling. Generally the energy content of thermosets is high (lower heat value *LHV* from 10 to 20 MJ/kg, depending on filler content), making this type of material an attractive fuel for heating and power generation. The drawback is that thermoset combustion would result in the production of large amounts of inorganic matter, in the form of filler, which would have to be disposed of economically and with minimum impact on the environment.

Having in mind the above mentioned obstacles, the investigations have been focused on thermal recycling in form of a pyrolysis.

3.2. Pyrolysis of thermosetting products

Pyrolysis is considered as an attractive method for the re-utilization of thermosets. It is a thermal degradation process carried out in an oxygen-free environment that results in three products:

- pyrolytical gas
- liquid products
- solids (char, mineral fillers, metals)

In test experiments that have been performed in the laboratory, a pyrolytic reactor (Figure 7) electrically heated and equipped in a pyrolytic gas cleaning and combustion system was designed and constructed.

As a feed for reactor, scrap epoxy components were used. The gas produced by the pyrolytic thermal degradation of thermosets must be purified prior to combustion in the combustion chamber. Purification was achieved using a demister and a cyclone, which condenses the impurities from the gas to produce liquid products.

In total, three different sets of experiments were performed in order to find optimal process parameters. Optimally the organic material should be properly decomposed (i.e., the goal is to reduce the carbon content of solid residues to a minimum), while retaining good quality metallic parts for recycling.

Figure 7. Pilot pyrolysis installation

The minimum time taken in the laboratory to pyrolytically degrade one load of material (scrap epoxy components) was three hours while the maximum time recorded was five hours. The low temperature pyrolysis was conducted at 450°C, whereas the high temperature processes were performed at either 750°C or 850°C [5].

The results of these experiments showed that pyrolysis can be used to thermally degrade resin wastes and reclaim metallic components for recycling (Figure 8). The gas and oil produced by pyrolysis can be reused as fuel, recovering the energy trapped within the old discarded products.

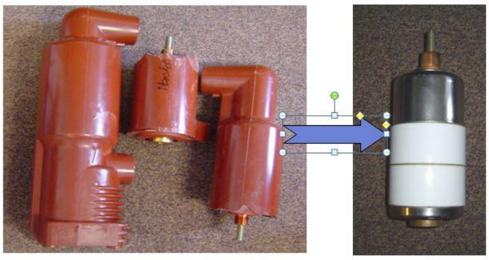

Figure 7. Recycled components from scrap epoxy

3.3 Utilization in cement kiln

As it was mentioned earlier, epoxy is characterized by high energy content, therefore it can be used as an additional source of heat in a clinker burning process. Moreover, the inorganic filler (SiO_2 or Al_2O_3 in most formulations) could be incorporated into the clinker itself what enhances the attraction of such manner. In the proposed technology, ground cured epoxy powder would be injected into the flame (preferably in a mixture with pulverized coal) inside the cement rotary kiln (Figure 9).

Detailed description of the presented disposal option and achieved results can be found in [6].

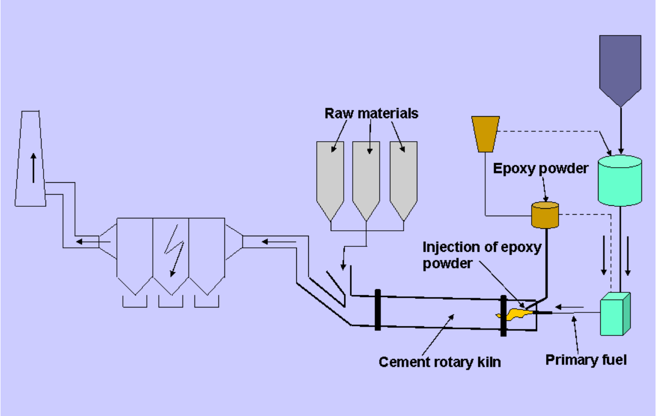

Figure 9. Concept of scrap epoxy utilization in cement kiln

4 Summary

The presented results confirmed that in a case of electrical insulation made of epoxy composites there exist number of directions resulting in minimization of waste generation. Already during design phase followed by process optimization – by application of advanced numerical tools – it is possible to achieve good quality products and to reduce scrap rate. Also, thermal treatment methods can be used to recycle valuable components embedded in composite. It should be underline, that detailed economic analyses should be performed case by case to see not only environmental benefits but also financial ones.

References

[1] Sekula R., Kaczmarek K., et.al., 3-D Modeling Reactive Molding Processes: From Tool Development To Industrial Application, Advances in Polymer Technology, **vol.22(1)**, pp. 1-14 (2003).

[2] Kamal M.R., Sourour S., Kinetics and thermal characterization of thermoset cure, *Polymer Engineering and Science*, **Vol. 13(1)** (1973).

[3] Sekula R., Nowak T., Claus O., Sequential Fluid Dynamics and Structural Mechanics Simulations of a Reactive Molding Process, *International Journal of Materials and Product Technology*, **Vol.40(3-4)**, pp. 250-263 (2011).

[4] Plastics Recovery in Perspective, report of *Plastics Waste Management Institute* in Brussels (1993).

[5] Sekula R., Leszczyznski S., Utilization of scrap thermosets using pyrolysis, *Energy Sources*, **Vol.31(1)**, pp.76-85 (2008).

[6] Sekula R., Wnek M., Slupek S., Potential utilization method for scrap ceramic insulators, *Journal of Solid Waste Technology and Management*, **Vol.26(2)** (1999).