

## **IMPACT OF GLASS TRANSITION TEMPERATURE OF UNSATURATED POLYESTER RESIN ON THE FINAL DOUBLE BONDS CONVERSION**

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**Keywords:** Unsaturated polyester resin, glass transition temperature, Dynamic Mechanical Analysis, Differential Scanning Calorimetry.

### **Abstract**

*SMC (Sheet Molding Compound) is a fiber-reinforced unsaturated polyester (UP) composite molded by heating and compression. SMC is currently molded at 140-170°C under 60-100 bars in a massive and expensive steel mold. The aim of this paper is to develop new SMC compounds in order to modify the process by decreasing the molding temperature until 100°C. The main objective of this paper is to underline the relation between the molding temperature, the glass transition temperature and the final conversion of UP resin/styrene formulation. A blend of two different resins was used to adjust the crosslinking density of the UP resin in order to modify the Tg of the cured formulation.*

### **1. Introduction**

Sheet Molding Compounds (SMCs) are semi-finished products based on fiber-reinforced thermosets matrix which are molded by compression in order to produce composite parts [1]. The SMC composite applications are for example building materials, electrical parts, automotive parts, and railway sector ... [2]. The formulation of the composite is complex with many components such as: an unsaturated polyester (UP) resin, styrene, initiators, inhibitors, fillers, glass fibers, low shrink agents, release agents, thickening agents ...

Currently, SMC parts are molded at a temperature of 140-170°C and under a pressure of 60-100 bars. These molding conditions are adapted to process SMC formulations with minimal residual reactive double bonds and thus a minimal residual styrene in SMC final part (below 100 ppm). There are two main reasons explaining this fact. First, the molding temperature is higher than the boiling temperature of styrene which means that the residual non-reacted styrene is converted into gas and goes out the SMC final part [3]. Secondly, the diffusion of reactive species has to be easy and this is done by lowering the gap between the molding temperature and the SMC Tg to a value under 50°C.

Previous projects already aimed at developing new SMC formulations to lower the molding temperature and pressure for economical and ecological purposes [4–6]. However, decreasing the molding temperature below 150°C can lead to some issues with the residual styrene content. The unreacted styrene is trapped in the SMC part because the boiling temperature of the styrene is higher than 100°C and the difference between SMC's Tg and molding temperature increases. When the reaction medium becomes solid, the reaction is then stopped

and this phenomenon is known as vitrification. The relationship between the glass transition and the curing temperatures was detailed by several publications [7–9]. Sourour and Kamal [7] have made for example a study based on isothermal cure of an epoxy system. They have stressed the fact that there is an exponential variation of the residual conversion as a function of the T<sub>g</sub>. As soon as the glass transition equals or exceeds the curing temperature by a certain value, the reaction ends and the system is chemically frozen.

In this papers, the influence of glass transition temperature (UP resin, styrene) on the final conversion (double bonds of UP resin and styrene) have been determined.

## **2. Experimental**

### *2.1. Material*

The modling resin (named M in the manuscript) is an unsaturated polyester resin with a number-average molecular weight (M<sub>n</sub>) of 980 g/mol measured by Size Exclusion Chromatography (SEC) with polyester calibration in THF solvent (supplier's data). This resin contains a molar amount of 51% of unsaturations (determined by SEC and <sup>1</sup>H NMR). The flexible resin (named F in the manuscript) has a M<sub>n</sub> of 825 g/mol with polyester calibration (supplier's data). This resin contains a molar amount of 23% of unsaturations. Both UP resins were dissolved in 32.5 wt % of styrene (≥ 99%, Sigma Aldrich, W323306) and supplied by CCP Composites.

29 wt % of styrene were added into the UP resin in order to be representative of a SMC formulation. 1.5 wt % of peroxide was added to the solution and a magnetic stirring was performed during 2 minutes to provide an homogeneous mixture. This process involves the introduction of oxygen into the system. Therefore, the solution was placed 2 minutes in an ultrasonic bath to eliminate the dissolved O<sub>2</sub>.

The samples were cured in a laboratory SMC mold containing a rectangular loading chamber. The final sample part dimensions are 100 mm, 10 mm and 2 mm of thickening. The formulation was molded at 100°C during 8 minutes. For DMA measurements a postcuring at 150°C during 20 min was performed after the molding step.

### *2.2. Instrumentation*

#### *2.2.1. DMA measurements*

Dynamic Mechanical Analysis (Anton Paar MCR 302, DMA) measurements were carried out on cured sample with a torsion mode at 1 Hz, with a strain at 0.01 % and a temperature ramp from 25 to 250°C with a heating rate of 2°C/min. The dynamic mechanical spectra showed the storage modulus (G'), the loss modulus (G'') and loss tangent (tan δ). The T<sub>g</sub> were determined on the maximal tan δ value [10]. The samples were 20-30 mm long between clips, 10 mm wide and 2 mm thick.

#### *2.2.2. DSC measurements*

The polymerization kinetics of UP resin/styrene formulations were studied by Differential Scanning Calorimetry (TA Instrument Q200, DSC). The experiments were carried out on 15 ± 1 mg samples of UP resin placed into hermetic Tzero aluminum DSC capsules which can

withstand an internal pressure of 2 bars. The reaction was studied during an isothermal curing at 100°C followed by a scanning mode from 50 to 250°C with a heating rate of 10°C/min.

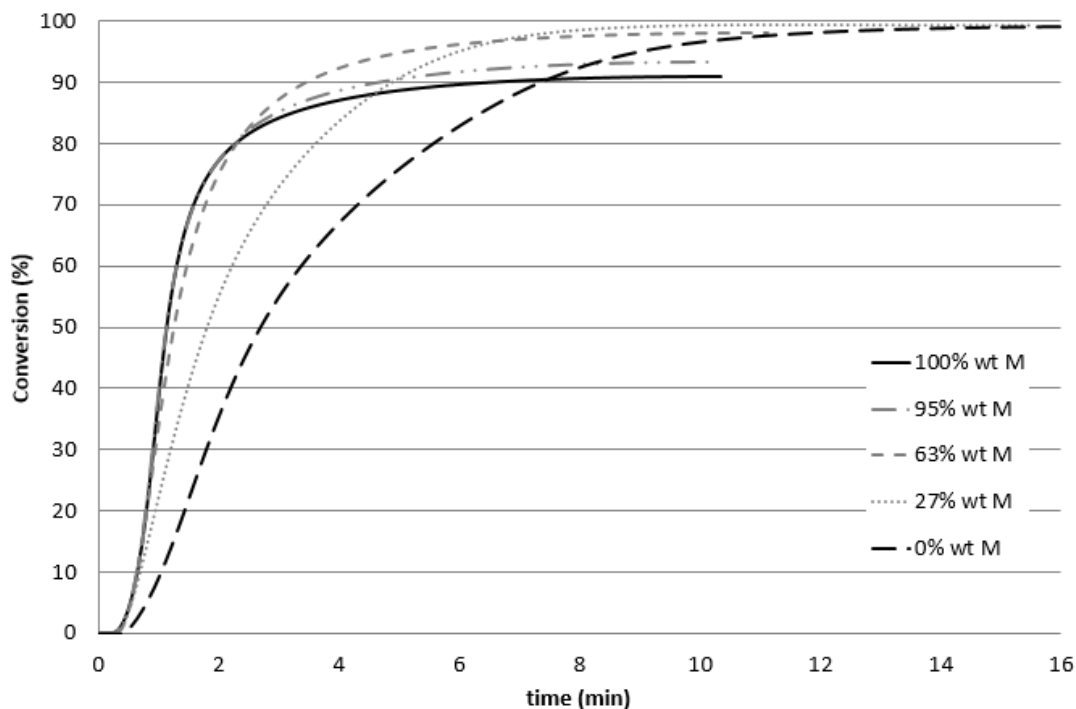
### **3. Results and discussion**

An isothermal curing at 100°C followed by a temperature ramp were made by DSC in order to study the UP resin's curing kinetics. The reaction enthalpy, which is proportional to the quantity of reacted double bonds, is measured during this experiment. An isothermal curing at 100°C represents the molding step and gives the reaction enthalpy ( $H_i$ ). The residual double bonds content into the sample was then determined thanks to a scanning mode from 50 to 210°C with a heating rate of 10°C/min. A numerical approach allows to determine the conversion as a function of time (equation (1)):

$$\alpha = 1 - \frac{H_i}{H_{total}} \quad (1)$$

Where  $\alpha$  is the conversion of double bonds (styrene and UP resin),  $H_i$  is the integration by part of reaction enthalpy during the isothermal curing calculated at a given time,  $H_{total}$  is the total reaction enthalpy of the UP resin (addition of enthalpies measured during the isothermal and temperature ramp curing). The reaction rate was determined by the slope of the curve ( $\text{mW} \cdot \text{min}^{-1}$ ).

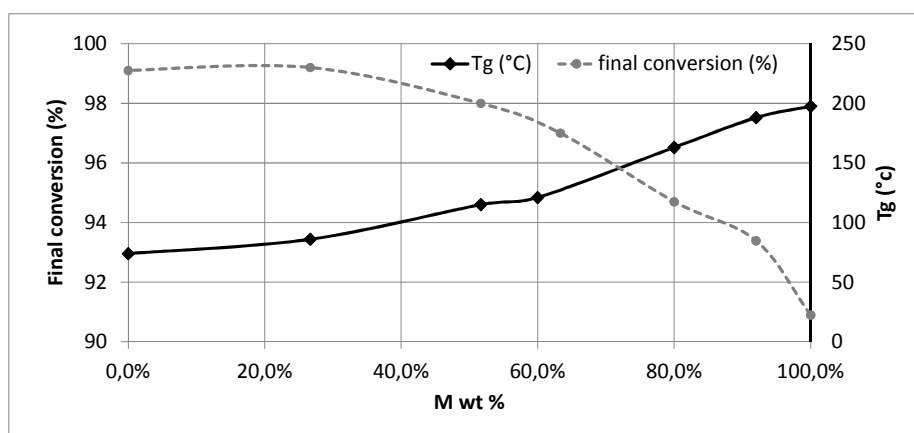
A blend of molding and flexible UP resins was used in order to modify the double bonds density of UP resin. The newly obtained resin has a  $M_n$  ranged between 980 and 825 g/mol and the polyester unsaturation monomer percentage is ranged between 51 and 23% relative to all monomer contained in the polyester chain. Figure 1 presents the double bonds conversion (%) as a function of time (min) for different molding resin (M) contents (% wt) for a curing at 100°C.



**Figure 1.** Double bonds conversion (%) as a function of time (minutes) for different molding resin (M) contents (% wt).

The molding resin (M) weight percentage is calculated as a function of the total UP resin (flexible and molding resins). The increase of the M resin quantity leads to an increase of the reaction rate (represented by the slope of the curve) and to a decrease of the final conversion. The increase of the M content leads to an increase of the polymerization rate, explained by an increase of the double bonds concentration. The final conversion decreases from 99 to 90% for a formulation containing respectively only pure flexible resin (F) or pure molding resin (M). In order to explain the increasing conversion, the cured resin's Tg was measured.

The glass transition temperature (Tg) was determined by DMA on the UP resin cured at 100°C in the laboratory mold. Figure 2 presents the correlation between the final conversion (measured by DSC) and the glass transition temperature (measured by DMA).



**Figure 2.** Tg (°C) and final conversion (%) as a function of M content (% wt).

Contrary to the previous conversion measurements, the comparison between both values is difficult because the resin's Tg was measured after a postcuring (necessary to prevent a curing

during the measure). However, the effect of the glass transition on the final conversion was undeniable as the conversion was maximal when the Tg decreases.

Figure 2 exhibits the great influence of diffusion of reactive species on the final conversion. Indeed, the final conversion of double bonds increases rapidly when the Tg decreases from 188°C to 110°C (temperature superior to the one used during the resin curing). The final double bonds conversion is weakly modified (from 98 to 99%) when the Tg of the cured UP resin is equal or below 100°C. Thereby, when the Tg is inferior to the curing temperature, the resin mobility is high and the final conversion remains constant (98-99%).

During an isothermal curing of UP resin, the results show a great influence of the glass transition temperature on the final conversion. When the curing temperature is inferior to Tg, the reaction is slower because the polymerization becomes diffusion-controlled in the later stages, particularly after vitrification (corresponding to the Tg rising to the curing temperature). Thus, a high residual double bonds in the resin part is generated when the chemical reaction is stopped or continues with a very low rate. The reduction of UP resin's Tg enables to delay the vitrification phenomenon, the reaction lasts longer and the residual double bonds content decreases.

#### **4. Conclusion**

An isothermal curing at 100°C performed by DSC was used to study the UP resin curing kinetics while the resin's Tg was measured by DMA after a curing in the laboratory mold. The aim of this paper is to show the influence of the glass transition temperature on the final conversion of medium double bonds.

Results showed a vitrification phenomena induced by the high cured UP resin Tg which limited the radicals diffusion in the reaction medium. The Tg of UP resin cured was reduced in order to increase this diffusion during an isothermal curing. To do so, a blend of molding (high in double bonds) and a flexible resin (poor in double bonds) was performed. The result on the final conversion is significant with an increase from 92% to 99%.

To go further in this study, the influence of the decreasing UP resin's Tg on the residual styrene and final mechanical properties will be investigated.

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