THERMOPLASTIC-BASED COMPOSITES AS PROCESSED BY RTM

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Keywords: RTM, fast process, acrylic, thermoplastic-based composites

Abstract

Resin transfer molding (RTM) is commonly used to produce continuous fiber-based composites. However, its range of applications is still limited to high performance thermoset-based composites. In order to extend its development to industrial sectors such as automotive which require cost-effective and sustainable solutions, new RTM-compatible reactive thermoplastic systems have to be developed.

In this framework, the objective of our work is to propose an RTM-compatible acrylic-based reactive formulation which polymerizes rapidly leading to a thermoplastic matrix suitable for composite manufacturing.

1. Introduction

Nowadays, polymer matrix composites are widely used for aerospace, automotive, railway and sport industries. For similar structural properties, these materials coul be very attractive since they could be 30 to 40% lighter than metallic counterparts. In the current context of environmental development issues, thermoplastic-based composites, (in our case acrylic matrix based one), can be considered as they can be easily recycled as opposed to thermoset-based ones. Furthermore, they could exhibit good mechanical properties, i.e. stiffness and impact resistance, enabling them to be relevant for many applications.

Manufacturing structural composites requires to produce parts without defects having complex geometries. For this purpose Resin Transfer Molding (RTM) has been selected to process such composites. Indeed, it corresponds to a low temperature closed-mold process allowing for manufacturing complex continuous fiber-based-reinforced parts. However, it requires precursors with a very low viscosity ($\eta < 1$ Pa.s) to ensure a good impregnation of the dry preform. To be cost effective, fast reactive systems have also to be selected.

Thermoplastic polymers which own a very high viscosity in molten state cannot be directly used. Our strategy is to design an acrylic-based reactive formulation exhibiting a very low initial viscosity, i.e. about 100 mPa.s and which can subsequently polymerizes via a free radical mechanism once the mold is filled and the preform fully impregnated.

Therefore, our main objective is to optimize curing conditions (especially thermal initiator ratios and temperature) of RTM-compatible acrylic-based reactive formulations to lead to suitable composite parts with high conversion rate, low residual monomer content and relevant process cycles. Indeed, an uncomplete polymerization or a too high curing exothermicity can lead to defects and difficulties during de-molding step and may impact final properties (residual stress, porosities, etc.).

2. Experimental section

Materials

MMA (99% inihibited with 30ppm MEHQ) and PMMA (Mw: 100, 000 $g.mol^{-1}$) were purchased from Sigma Aldrich. Elium® acrylic system for RTM was provided by Arkema. A peroxide noted P was used as a free radical initiator.

Resin formulation

Different formulations were studied by mixing Elium® resin with several ratios of peroxide P. The reactive mixture was mechanically stirred during few minutes and then polymerized at 80°C.

Differential Scanning Calorimetry

A TA Q20, operating from -160 to 300°C and equipped with a liquid nitrogen cooling system, was used to determine the glass transition temperature, Tg. The DSC traces were recorded of 10 mg specimens sealed in hermetic pans during a heating rate of $10K.min^{-1}$ under a nitrogen atmosphere.

Kinetic

Kinetic study was monitored by near infrared spectroscopy NIR (Bruker Equinox 55). Samples were placed in a glass tube of 3mm diameter at 80°C. Measurements were conducted in transmission with 16 scans and a resolution of $4cm^{-1}$. The conversion, x, can be deduced from methacrylate C=C double bond integration at $6128cm^{-1}$.

Rheology

Complex viscosity changes were recorded using a stress-controlled Physica MCR 301 Anton Paar rheometer. Measurements were performed at 80°C with a 50mm 1° steel cone-plate at a frequency of 1Hz and a deformation amplitude of 10%.

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3. Results and discussions

Polymerization kinetics and thermal properties

As shown on Fig. 1, time to reach full conversion of the reactive system can be tuned by varying peroxide ratios. Indeed, peroxide content increase leads to a higher release of radicals in the reactive system. For 3phr (parts per hundred of resin) of P, full polymerization can be reached in less than 4 minutes, hence satisfying processing requirements, i.e. high polymerization rate.
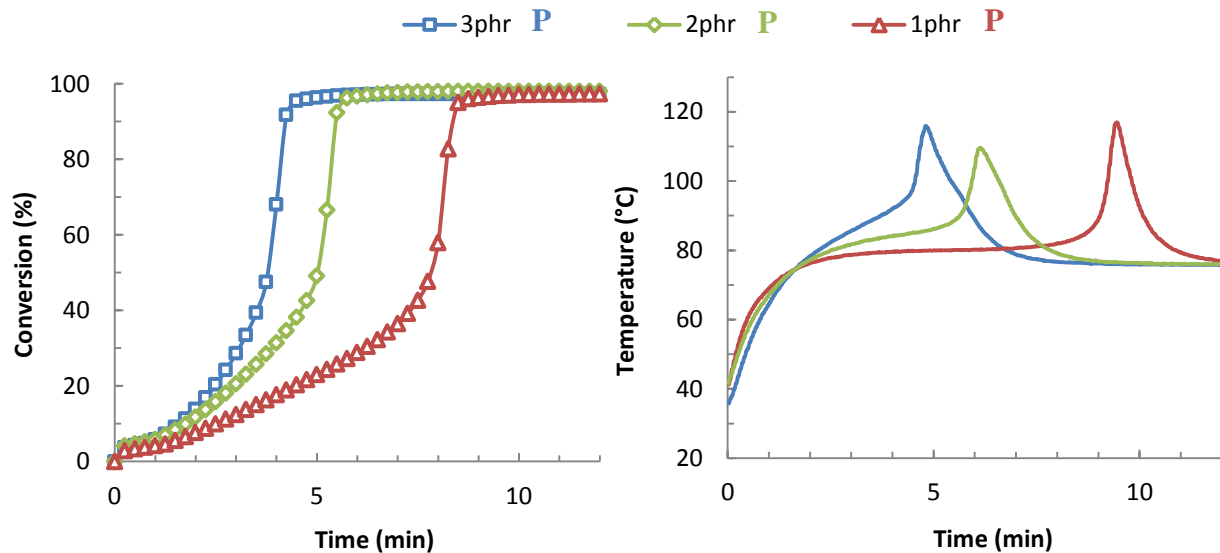

Figure 1. Conversion changes (left) and evidenced exothermicity (right) as function of polymerization time for various P peroxide contents.

When conversion level reaches about 40-50%, reaction rate increases due to a so-called Trommsdorff' effect[1]. In fact, it's an autoacceleration of the overall rate well known in free radical polymerization. It is due to the localized increases in viscosity of the polymerizing system that slow termination reactions. The rate of terminaison becomes limited by diffusion and propagation is favored. This effet is strongly dependent of temperature[2] and peroxide ratios[3] used.

Exothermicity measurements reveal that temperature rise above 110°C (for these experimental conditions) when Trommsdorff' effect occurs. As evidenced later on, it is well known that curing temperature must be higher than the matrix final Tg to reach a maximal conversion rate[4]. Indeed, Tg increases with conversion and when vitrification occurs, the polymerization rate dramatically decreases. In our case, a polymerization temperature of 80°C appears to be high enough to reach full polymerization even if maximum Tg is 110°C. In fact, polymerization exothermicity seems to promote complete polymerization.

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Relationships between glass transition temperature, Tg, and conversion x

When the glass temperature, Tg, reaches polymerization temperature, the matrix vitrifies. In fact, after vitrification, the reaction is controlled by the diffusion of reactive species. Usually employed to describe thermoset reactive mixtures, the Di Benedetto' equation modified by Pascault and Williams[5] is used to describe Tg changes vs. conversion, x.

$$\frac{(T_g - T_{g0})}{(T_{g\infty} - T_{g0})} = \frac{\lambda x}{[1 - (1 - \lambda)x]} \tag{1}$$

$$\lambda = \frac{\Delta C_{p\infty}}{\Delta C_{p0}} \tag{2}$$

Where, T_{g0}, $T_{g\infty}$, ΔC_{p0} and $\Delta C_{p\infty}$ are respectively the glass transition temperatures of the initial monomer mixture (x=0) and of the fully cured system (x=1) and associated heat capacities.
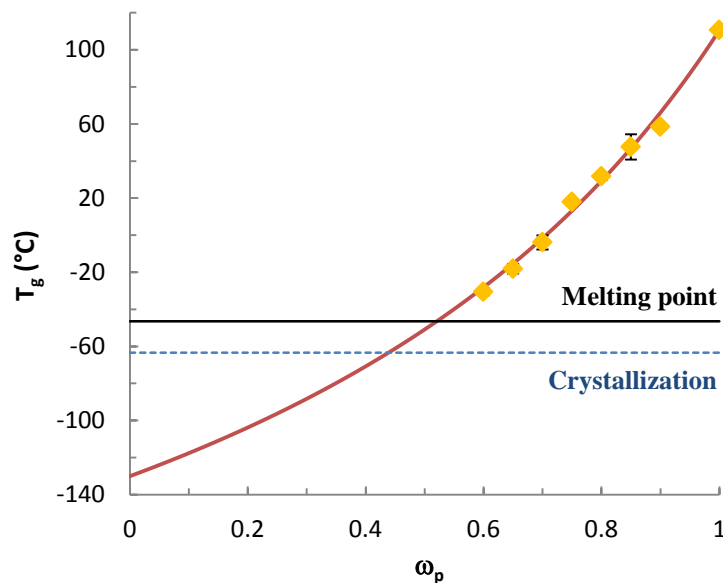

Figure 2. Glass transition temperature as a function of polymer concentration, ω_p of PMMA. Experimental points (in yellow) are fitted with Di Benedetto's equation (in red).

Since MMA crytallizes at low temperature, direct ΔC_{p0} measurement is not possible. Therefore, Tg evolution in respect to conversion x can be determined by measuring Tg of several MMA/PMMA mixtures at different ratios. Experimental points are represented on Fig. 2. Using MMA glass transition temperature (~ -130°C[6]), λ calculation becomes possible and leads to a value of 0.49 by fitting Tg experimental values with Di Benedetto's equation. It can be noted that experimental and simulated date are in good agreement validating the Di Benedetto' approach. Considering previous exothermicity effects reported previously, for a polymerization temperature of 80°C, the relative conversion is about 0.94. However, considering exothermicity leading to a temperature of 110°C, full MMA conversion can be reached. Thus, Di Benedetto's fit confirms kinetic results discussed previously and demonstrates that a completed polymerization is reached at 80°C.

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Viscosity versus conversion

During the mold filling stage, resin must entirely fill the mold cavity and must fully impregnate fiber tows. As shown on Fig.3, resin needs some time for impregnating fibers both at the macro scale (inter-tow spaces) and at the micro scale (intra-tow spaces). Macroflow is usually governed by resin viscosity while microflow is mainly driven by capillary forces.
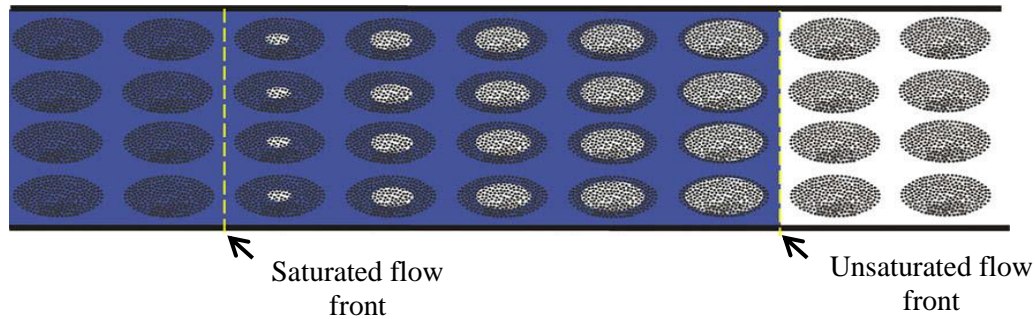

Figure 3. Fiber tows impregnation during mold filling.[8]

As a consequence, impregnation step strongly depends on viscosity changes upon polymerization and needs to be managed to ensure a complete mold filling before to reach the non-injection point NIP ($\eta < 1Pa.s$)[7].

Complex viscosity increases with time and its evolution profile is very similar to the one of the conversion as shown previously (Fig. 1). The viscosity which is initially lower than 0.1Pa.s, rises very rapidly during the first minutes[9], [10] then stabilizes before increasing again when the Trommsdorff's effect occurs.
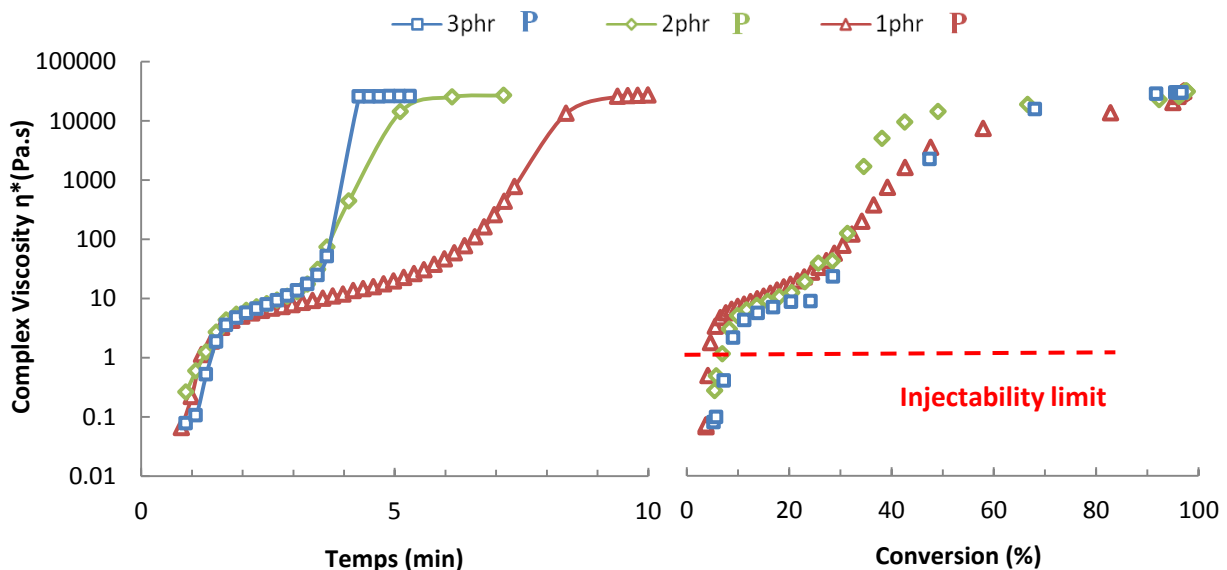

Figure 4. Complex viscosity (left) and conversion (right) changes versus time at 80°C (temperature of the rheometer oven).

By plotting complex viscosity versus conversion, it can be seen that the injectability limit is reached after nearly 2min which corresponds to 10% of conversion. In the present thermal conditions, it corresponds to the resin injection window. As mentioned earlier, depending on the processing conditions, this injection window may vary.

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4. Conclusions

An acrylic-based reactive system has been investigated as a potential candidate to the manufacturing of the thermoplastic-based composites by RTM. By a suitable choice of initiator content and taking advantage of the polymerization exothermicity, its completed radical polymerization can be achieved in less than 5 minutes at 80°C. This curing rate is compatible with fast process industrial requirements. Its initial viscosity is very low (0.1<Pa.s) and stays below the injection limit during 2 minutes before large increasing. Thus, by a fine tuning of chemiorheological properties, satisfying fiber impregnation can be achievedand and so low defects parts can be processed.

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