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**Publication date**
2022

**Document Version**
Final published version

**Published in**
Proceedings of the 20th European Conference on Composite Materials: Composites Meet Sustainability

**Citation (APA)**
Staal, J., Smit, E., Caglar, B., & Michaud, V. (2022). Processing of Fibre Reinforced Polymers by Controlled Radical Induced Cationic Frontal Polymerisation. In A. P. Vassilopoulos, & V. Michaud (Eds.), *Proceedings of the 20th European Conference on Composite Materials: Composites Meet Sustainability: Vol 2 – Manufacturing* (pp. 600-607). EPFL Lausanne, Composite Construction Laboratory.

# PROCESSING OF FIBRE REINFORCED POLYMERS BY CONTROLLED RADICAL INDUCED CATIONIC FRONTAL POLYMERISATION

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**Abstract:** *Radical Induced Cationic Frontal Polymerisation (RICFP) has recently been proposed as a promising strategy for processing of epoxide carbon fibre reinforced polymers. Control of the local heat balance is crucial towards the production of industrial-quality composites, which is typically achieved via controlling the heat generation. In this work we present a comprehensive overview of RICFP processing of cycloaliphatic epoxide composites with enhance heat insulation. The thermal initiating compound was identified as the main component to control heat generation, which correlated well with the front velocity. A processing window was defined as function of the fibre and initiator contents and composites with to 45.8%* $V_f$ *were successfully produced. Optimisation of resulting mechanical properties was made possible by optimisation of the heat balance, with matrix glass transition temperatures of up to 187°C achieved for the used cycloaliphatic system. Post-curing was found beneficial to overcome suggested inhomogeneous curing due to the dual-scale nature of fabrics.*

**Keywords:** Frontal polymerization, Fiber reinforced polymer, Composite processing

## 1. Introduction

Frontal polymerisation has emerged as a promising technique for out-of-autoclave processing of fibre reinforced polymers (FRPs), offering significant potential enhancements in processing time, cost and environmental impact[1]. Thermal frontal polymerisation is driven by thermal gradients formed by the distinct separation, i.e. a front, between the hot polymer and cold monomer resin. After an initial, e.g. thermal or UV-irradiation, trigger, an autocatalytic reaction mechanism allows the front to progress through the resin solution as long as a threshold temperature is exceeded. The approached steady-state temperature, assuming an FRP with constant thickness and fibre volume fraction ($V_f$), is a direct result of the local heat balance. As schematically illustrated in Figure 1, the local heat balance for a polymerisation front progressing through a fibrous preform is between the enthalpy of polymerisation, counterbalanced by thermal diffusion to the neighbouring resin layer, heat losses to the mould and heat uptake by the fibrous reinforcement.

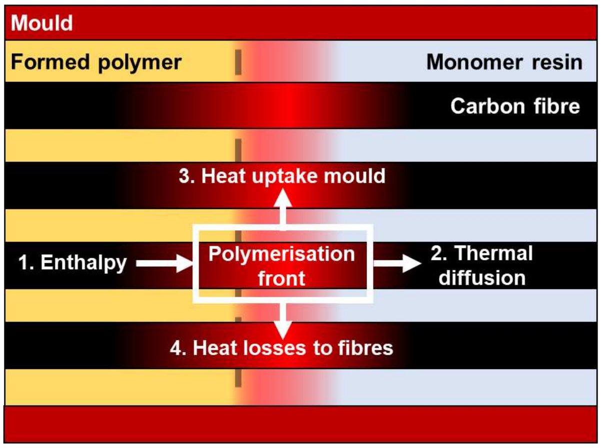

*Figure 1 Schematic representation of local heat balance in frontal polymerisation. 1. Generated enthalpy of polymerisation, 2. Thermal diffusion to boundary layer, 3. Heat uptake by the mould material and 4. carbon fibres*

First discovered by Chechilo and Enikolopyan[2,3] in the early 1970s, systems undergoing free-radical polymerisation are traditionally used for frontal polymerisation due to their beneficial high reactivities in combination with limited exothermicities. Promising systems based on dicyclopentadiene, following a frontal ring opening metathesis polymerisation (FROMP) mechanism, have recently been proposed. Robertson et al.[1] were able to produce carbon FRP panels with fibre $V_f$s of up to 51% and resulting properties comparable to oven-cured FRPs. While strong advances have subsequently been recorded e.g. further functionalisation[4,5], additive manufacturing[6,7] and simulation[8,9] of FROMP systems, their potential for use in industrial FRP processing is currently limited by the pot life of several hours in the presence of alkyl phosphite inhibitors[10].

Mariani et al.[11] were the first to propose so-called radical induced cationic frontal polymerisation (RICFP) to induce frontal polymerisation in epoxide systems. Based on radical induced cationic polymerisation proposed by Crivello[12], the autocatalytic mechanism in RICFP comprises the thermal initiation by the elevated front temperature of a free-radical thermal initiator, followed by an excitation of a cationic photoinitiator that creates new active polymer chains. This dual-initiator configuration allows RICFP systems to be uniquely stable, e.g. resins remained stable for over a month while being kept in a dark environment at 50°C[13], while fronts can be initiated both thermally and by UV-irradiation.

A number of studies have been dedicated to FRP processing by means of RICFP. While first articles mainly assessed the compatibility of RICFP systems with different fibre types[14–16], recent advances have paved a way for RICFP as a technique to produce industrial-quality FRPs. Using a system consisting of bisphenol A diglycidyl ether (BADGE), the highly reactive diaryliodonium (perfluoro-tert-butoxy) antimonate[17] and benzopinacol as monomer, photoinitiator and thermal initiator, respectively, Dung Tran et al.[18] were able to produce woven carbon FRPs with $V_f$s of around 35%. The resulting mechanical properties were comparable to those of anhydride-cured FRPs while glass transition temperatures exceeded 160°C. Gachet et al.[19] synthesised novel sulfonium-based initiators and were able to successfully cure carbon FRPs with 50 w% (40% $V_f$) carbon content with high front velocities of over 13 cm/min.

The influence of filler materials on the front characteristics was observed experimentally by Dung Tran et al.[18], who quantified the maximum volume fraction of different filler types that allowed for the formation of a front. The insulating nature of glass microspheres resulted in a nearly double allowed maximum filler content compared to the more conductive short carbon fibres and aluminium particles. This was explained by the increased spreading of the reaction zone, as also observed in numerical studies [9,20,21], which can significantly enhance front velocities at the cost of front temperature. Moreover, the dispersion of fillers was found of large influence on the reported slope of the front velocity as a function of the filler content[18]. The role of external heat losses on the other hand has merely been investigated. Knaack et al.[22] found a minimum thickness required to overcome external heat losses and hence the threshold temperature for successful front progression. Goli et al.[23] demonstrated that these heat losses acted as boundary effects, lowering the front temperature and potentially the degree of cure in the thin layers adjacent to the mould of which the thickness increases with the heat flow rate.

The control of the local heat balance is therefore crucial towards the production of high-performance composites. While significant effort is paid to the development of novel RICFP systems with increased reactivities[17,24,25] and thereby heating rates, the heat loss terms are generally left out of consideration. In this work we demonstrate the potential of reducing heat losses by the design of well-insulated system for RICFP processing. Minimising heat losses can increase the maximum possible fibre volume fractions that exceed those previously achieved using RICFP systems. Tailoring the local heat balance via the heat generation term is moreover demonstrated via adjustment of initiator concentrations. This can be used to optimise the mechanical performance of resulting FRPs, while the inhomogeneous curing due to the fabrics' dual-scale pore distribution can be overcome by post-curing.

## 2. Experimental

### 2.1 Materials

Omnilane OC1005 (IGM Resins, the Netherlands) resin, consisting of 3,4-epoxycyclohexyl-3',4'-epoxycyclohexane carboxylate (ECC) monomer was used in combination with photoinitiator p-(octyloxyphenyl)phenyl iodonium hexafluoro antimonate (IOC-8, ABCR, Germany) and benzopinacol (Acros Organics, Belgium) as thermal initiating compound. Isopropyl thioxanthone (Genomer ITX, Rahn, Switzerland) was used as photosensitiser to shift the initiation wavelength spectrum. 2x2 twill weave carbon textiles were acquired from Swiss Composites (Switzerland) and had an areal weight of 285 g/m$^2$, an ends/picks count of 3.5/3.5 cm$^{-1}$ and 6K fibres per yarn. Moulds were produced from a PVC foam, glass fabric and breather fabric (Swiss Composites, Switzerland). High-temperature Diatex Polyimide HM 25 µm were obtained from Global Tools (Switzerland). An EXFO Omnicure S2000 Standard UV-light source was used for front initiation.

### 2.2 Methods

Resins were purified under vacuum after which the thermal initiator, photosensitiser and photoinitiator were dissolved by mixing at high shear rate. Degassing under vacuum was done at room temperature for about 30 minutes.

Polymerisation enthalpy of resins was characterised by Differential Scanning Calorimetry (DSC) using a TA Instruments DSC Q100. Resin samples of 2-3 mg were weighed in closed aluminium hermetic pans and measured at a heating rate of 5 °C/min over a range of -20 - 105°C, followed by an isothermal procedure of 30 minutes. The procedure was subsequently repeated as baseline. Maximum heat outputs corresponded to peak maxima after baseline correction.

Front velocities were characterised for systems with varying compositions containing about 12% $V_f$ carbon fibres. For this scan, only compositions capable of forming a front in a neat resin system were selected while low carbon fibre $V_f$s were chosen to ensure frontal polymerisation to occur for all selected compositions. Carbon fibre tows were weighed and placed in an in-house made silicon mould with cavity dimensions of 45x12x7 mm that was subsequently filled with resin. A silicon mould half with an opening at one extreme of the cavity was placed on top. A schematic representation of the experimental setup is shown in Figure 2. Temperatures were recorded at an acquisition rate of 100 Hz via three thermocouples integrated in the top mould half, placed 15, 25 and 35 mm from the opening. Front velocities were determined by linear regression of the peak temperature times.

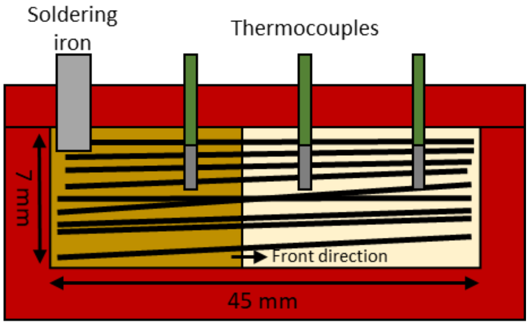

*Figure 2 Schematic representation of the experimental setup (longitudinal cut) for front velocity characterisation.*

Composites were produced by a hand layup method with fabrics and resin being alternately placed in a 5 mm mould cavity. A well-insulated system was designed to minimise heat losses to the ambient environment, which consisted of a Teflon-coated foam core that was subsequently enclosed by an envelope vacuum bag. The vacuum level was regulated to 0.5 bar and maintained for about 30 minutes to allow for further compaction of the impregnated fabric stack. Initiation was done by irradiation at an intensity of at least 500 mW/cm$^2$ from one of the resin-rich corners until the formation of a front was observed. The sample was kept under vacuum until cooled down to room temperature.

Dynamic Mechanical Analysis (DMA, TA Instruments DMA Q800) was carried out in three-point bending mode to characterize moduli and glass transition temperatures ($T_g$s) of composite samples. Samples were cut in strips of 55x10x5 mm and measured at 3°C/min over 2 heating cycles; a first cycles ranging from 15-250°C followed by a cycle of 15-300°C. Set amplitudes and frequencies were 10 µm and 1 Hz, respectively.

## 3. Results & Discussion

The heat generation term of a passing polymerisation front is defined by heat release of growing active cationic chains. Variation of the initiator concentrations has been reported[11,26] to allow for control of heat generation and thereby RICFP front characteristics. Nevertheless, no clear consensus on the role of individual initiating components has been reached and relations are generally established based on indirect observations, i.e. via front velocities or temperatures, while the resin enthalpy is generally overlooked. Figure 3a shows a comparative overview of the maximum heat output recorded by DSC and front velocities in 12% $V_f$ composites as function of the photoinitiator, photosensitiser and thermal initiator concentrations. Both the photo- and thermal initiators showed increased resin heat outputs with increasing concentration, which is supported by their Spearman correlation coefficients listed in Table 1. The recorded front velocities, shown in Figure 3b, moreover followed similar trends as observed in Figure 3a, which is in line with the observations made by Refs. [13,26], suggesting that the recorded heat output in DSC measurements is a good indicator to assess the behaviour of RICFP resins.

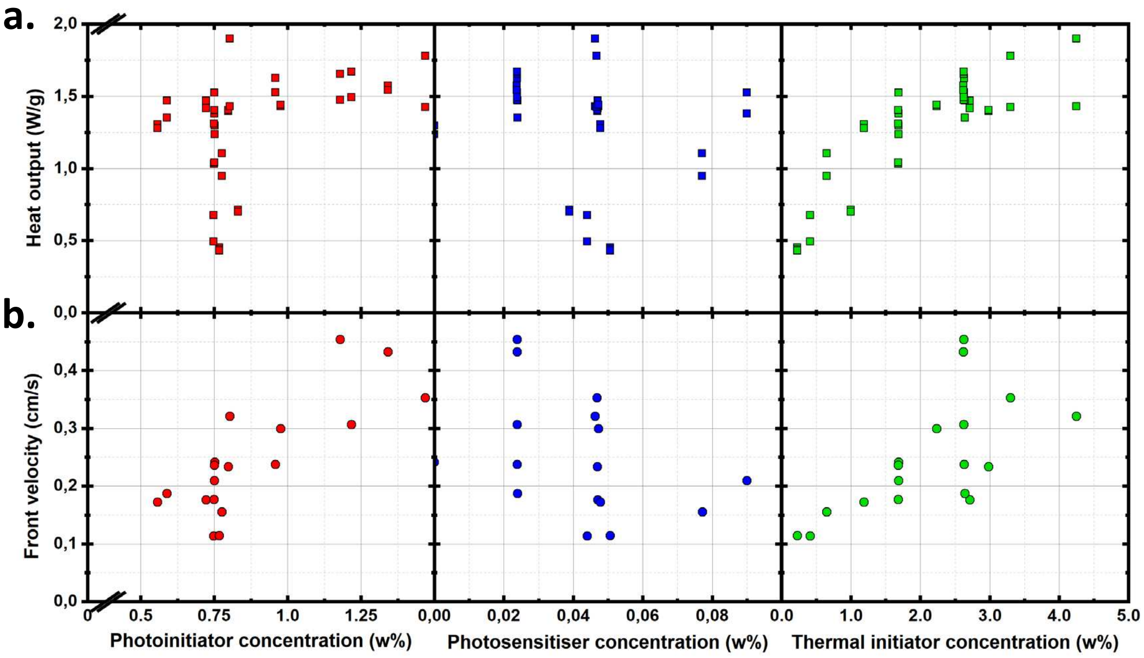

*Figure 3 Composition dependence of: a) Heat output recorded in DSC measurements and b) front velocities recorded by integrated thermocouples.*

The apparent slopes and larger Spearman coefficients moreover give rise to the hypothesis that, within the considered range of concentrations, the thermal initiator is of larger influence on both the heat output and front velocity. This would be in agreement with observations of Mariani et al.[11] who reported, despite the use of different initiator types in an ECC resin, a continuous increase of front velocity as a function of thermal initiator concentration while the photoinitiator concentrations resulted in a plateau of front velocity after a steep increase at low photoinitiator concentration. Hence, the significance of the photoinitiator concentration would be largely dependent on the chosen range of concentrations, while this would not be the case for the thermal initiator concentrations.

Table 1 also shows that the Spearman correlation coefficient for the photosensitiser concentration is slightly negative and significant, suggesting the increasing presence of a photosensitiser negatively impacts the enthalpy generated by the resin, while a significant correlation was absent for the front velocities. Although these observations gives rise to a hypothesis that a photosensitising compound slightly reduces heat output that does not affect the front propagation, which is in line with the work of Bomze et al.[13], further investigation is needed to elucidate the role of photosensitisers in RICFP and confirm this hypothesis.

*Table 1 Spearman correlation parameters of the composition dependence of heat outputs and front velocities*

| Resin component | Heat output [W/g] | | Front velocity [cm/s] | |
|---|---|---|---|---|
| | Coeff. | $p < 0.05$ | Coeff. | $p < 0.05$ |
| Photoinitiator | 0.529 | $4.6 \cdot 10^{-4}$ | 0.643 | 0.018 |
| Photosensitiser | -0.418 | $7.3 \cdot 10^{-3}$ | -0.258 | 0.394 |
| Thermal initiator | 0.759 | $1.4 \cdot 10^{-8}$ | 0.846 | $2.7 \cdot 10^{-4}$ |

Carbon FRPs were subsequently produced with a varying initiator concentration, while the molar ratio between photo- and thermal initiating compounds was fixed at 1:2.3. Three different scenarios could take place upon initiation in the resin-rich zone: a self-sustaining front forms that polymerises the complete fabric stack, the formation of a front that can only propagate through the fabric stack when followed by the light source and the inability to form a front. As shown in Figure 4, it was possible to induce self-sustaining fronts in fabric stacks with $V_f$s up to 45.8% with a thermal initiator concentration of 1 w%, which exceeds the previously published maxima reported for RICFP systems[18,19]. While partially a result from the use of the highly exothermic ECC monomer, e.g. compared to BADGE resin of Dung Tran et al.[18], this improvement is mainly attributed to the mould design, which aimed to minimise heat uptake and heat transfer to approach a quasi-adiabatic system.

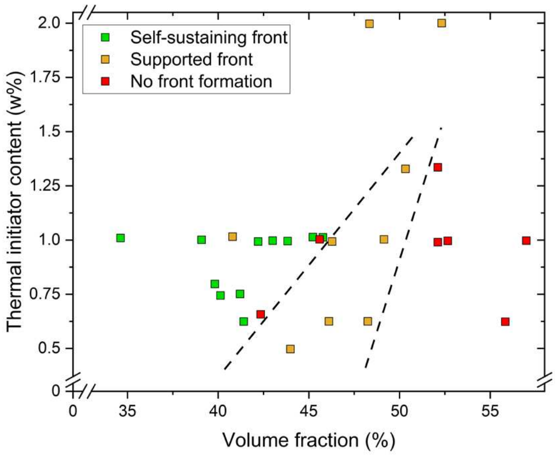

*Figure 4 Ability of front formation in an carbon FRP system with varying $V_f$ and thermal initiator concentrations*

Figure 4 shows a clear cut-off between the different scenarios, i.e. for systems containing 1 w% of thermal initiator, samples with $V_f$s above 46% required additional heat input by UV-irradiation to re-initiate the front while this also did not suffice for $V_f$s above ±50%. These cut-offs can be directly related to the local heat balance since the increasing fibre content results in increased heat losses up to the point that the front temperature drops below the threshold temperature for the autocatalytic mechanism. Figure 4 moreover shows that the cut-off $V_f$ increases with increasing thermal initiator concentration since it enhances the heat generation term in the local heat balance. Large initiator concentrations were found unable to induce a front despite the $V_f$ being lower than the observed cut-off. This could hypothetically be attributed to a rapid conversion as a result of these high concentrations, polymerising and heating the resin before heat transfer to the fibres could take place. This subsequently introduces a strong gradient between polymer and fibres, cooling down and potentially quenching the propagating front.

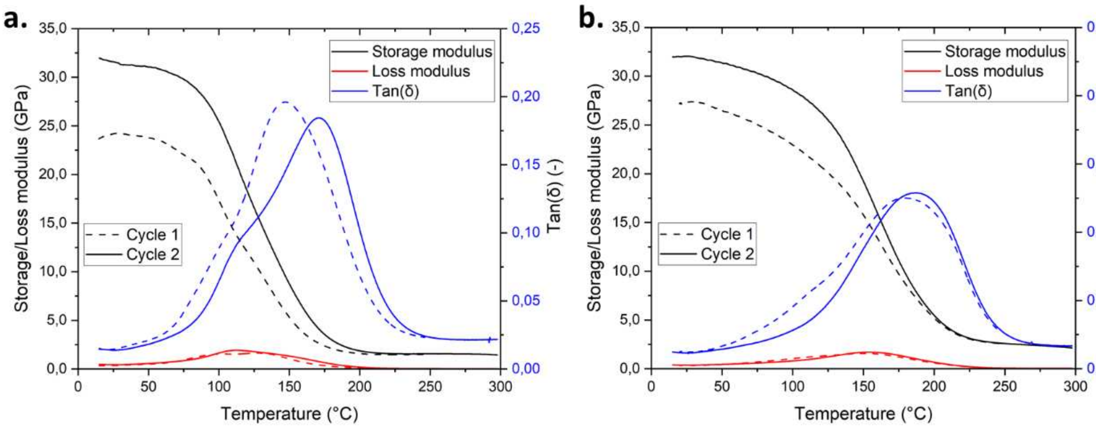

*Figure 5 Typical DMA curves of samples with 40% Vf and a) 0.624 and b) 1.001 w% thermal initiator*

Thermal management moreover impacts the mechanical behaviour of RICFP-produced FRPs. Assessment of the flexural modulus and the $T_g$ by DMA showed a shift of both parameters after one completed measurement cycle. This is attributed to post curing effects most likely taking place within yarns, where carbon fibres are closely packed and hence heat losses are more severe. Figure 5 shows two typical DMA curves of FRPs with $V_f$s around 40% and two different initiator concentrations. Counterintuitively, the moduli recorded in the first measurement cycle were higher at lower initiator concentration, which recovered to the roughly equal moduli after post curing. The $T_g$ was moreover 30°C higher than that when a higher concentration was used, reaching a $T_g$ of 187.4°C after the second measurement cycle. An explanation for this behaviour follows the hypothesis that a slower heat release, and thereby gradual heating of the resin-fibre region near the front, reduces local cooling or quenching of the front and hence improves the resulting FRP properties.

## 4. Conclusion

The current work aimed for the production of high-volume fraction carbon FRPs in a well-insulated system by RICFP induced in a cycloaliphatic epoxide resin system. While previous investigations mainly focussed on the maximisation of system reactivities, front temperatures and velocities, control of the local heat balance was found crucial towards the optimisation of the resulting FRP properties. A correlation between heat outputs recorded in DSC measurements and front velocities was observed. The concentrations of both the photo- and

doi:10.5075/epfl-298799_978-2-9701614-0-0

thermal initiating compounds were found of significant influence on both the heat generation and front propagation of the system. A processing window was identified that relates the formation of a self-sustaining or supported front to a required range of fibre $V_f$s and the initiator concentrations. This window was moreover related to the mechanical properties. Lower initiator concentrations, hence slower heat generation, was suggested beneficial for the resulting properties while a rapid post-treatment was found necessary to maximise the mechanical behaviour of FRPs. Confirmation of this suggestion is the subject of future work in combination with an extension of the processing window to gain a better insight in the role of the mould types and filler materials on the RICFP processing of FRPs.

## Acknowledgements

The authors acknowledge the support from the Swiss National Science Foundation (SNF n° 200021_182669).

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