CHARACTERIZATION OF A NEW THERMOPLASTIC REACTIVE ACRYLIC-BASED ADHESIVE FOR MULTILAYER COMPOSITE LAMINATES

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Abstract

This study focus on the characterization of acrylic reactive systems which polymerize to yield thermoplastic adhesive for multilayer composite laminates. Several investigations were made on a wide range of initiating systems and temperature to define polymerisation experimental conditions adapted to final applications. NIR measurements, DSC and oscillatory rheological analysis were done to follow evolution of conversion degree, complex viscosity and cure exothermicity with time. Influence of glass fiber on polymerisation kinetics was also examined. Results show great influence of glass fiber presence on kinetics and underline the importance of mould and materials thermal conductivity. Composite laminates were eventually processed, observed and compared with epoxy reference systems.

1. Introduction

Structural bonding have been in constant progress since several decades thanks to the improvement of adhesives mechanical performances and since it provides better stress distribution and weight loss compared to bolted joint. Today this solution is widely used in various industrial sectors as aeronautic or automotive to manufacture multilayer composite laminates [1]. When the adhesive hardening is obtained by chemical reaction, several types of chemistry can be involved and numerous families of adhesives are available. In the most frequent cases, it is constituted of a crosslinked polymer matrix resulting from polymerisation of multifunctional monomers. However, new environmental issues and especially a growing need for recyclability motivate efforts to develop solutions involving thermoplastic (TP) matrices and in this area, very few progress concerning TP structural adhesives or composite laminates has been done so far.

More specifically, acrylic family covers a wide range of reactive systems and hardening mechanisms [2]. Free-radical polymerisation of acrylic monomers is not a recent discovery : it has been commonly discussed since the 70's for methyl methacrylate (MMA) focusing on kinetics of initiation, propagation and termination steps to model reaction progress [3, 4]. As polymerisation goes through, an important autoacceleration effect occurs consuming suddenly almost all remaining monomers and releasing an high amount of heat due to multiple double bond opening. It is known as Trommsdorff or "gel" effect [5–7]. Later denomination refer to vitrification of the polymer/monomer mixture, occurring when temperature of the highly viscous polymeric blend falls under its glass transition (T_g) after exothermy dissipation.

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Experimentally, such phenomenon can be identified by an important temperature increase into the mold.

Today's challenge is to use this well-known phenomenon and adapt it to composite processing. Our work focused on the study of a reactive system which can yield a TP adhesive by free-radical polymerization and then can be used to bond layers in composite laminates. To achieve a better understanding, various experimental means were used to follow reactive mixture properties during polymerization such as conversion degree, viscosity or cure exothermicity. From one system to another, initiator nature and content, catalyst content and temperature were varied. Effect of fiber glass on kinetics and conversion profiles were also investigated. Finally, real-sized parts were processed and observed to compare current differences between acrylic-TP and thermosetting (TS) epoxy reference laminates. As our system is quite new, just a few studies have been reported until now on composite application [8, 9]. But for several years, cement bone for dental application were developed with very similar acrylic reactive blends. Associated literature, often addressing specific experimental issues, has proven to be very valuable during our research work and will frequently be mentioned in this paper. [10–12].

2. Experimental section

2.1. Materials

Acrylic matrices were obtained by free radical polymerisation of Elium resins supplied by Arkema. Reaction was triggered using two thermal initiators P1 and D1. A commercial catalyst, referred as C2, was also used for rheokinetic studies. In the following work, several reactive formulations were considered aiming maximum end of reaction time around 10 minutes. Table 1 sums up blend proportions.

Table 1: Studied reactive formulations

Sample name	P1 content (phr)	D1 content (phr)	C2 content (phr)	T polymerisation (C)
2P1-3C2-80	2.0	-	3.0	80
2P1-80	2.0	-	-	80
2P1-3C2-90	2.0	-	3.0	90
2P1-1C2-90	2.0	-	1.0	90
2P1-90	2.0	-	-	90
1P1-2D1-3C2-90	1.0	2.0	3.0	90
1P1-2D1-90	1.0	2.0	-	90
3D1-3C2-105	-	3.0	3.0	105

2.2. Experiments

2.2.1. NIR measurements

Near-infrared (NIR) spectra were recorded using an Equinox 55 Spectrometer (Bruker) equipped with a heating cell to monitor changes in absorption in the wavelength range of 8000 to 5000 cm^1 on 16 scans. Peak at 6170 cm^{-1} was attributed to double bound C=C of acrylic monomers [11, 13, 14]. Once radical polymerisation is initiated, their content progressively falls down to yield polymeric chains (figure 1).

End of reaction is declared when C=C peak vanishes (as in figure 1) or when its area stabilizes. The latter can occur when condition are not optimized so the system becomes glassy before consumption of

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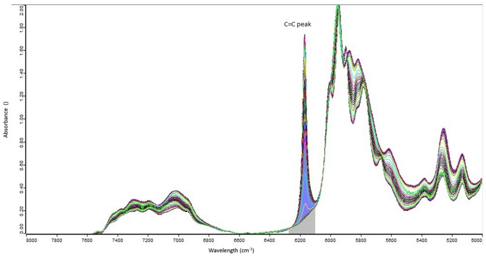

Figure 1: Diminution of acrylic monomers C=C peak during polymerisation recorded by NIR

all monomers. Conversion $\alpha_{(t)}$ is calculated through time as an expression of initial area A_0 and area $A_{(t)}$ at time t :

$$\alpha_{(t)} = \frac{1 - A_{(t)}}{A_0} \tag{1}$$

Study was conducted both on raw matrices and in presence of glass fiber. Composite samples were prepared by introducing several fiber tows into NIR analysis tubes. Content varied between 65% and 70% in mass percentage.

2.2.2. Thermal analysis

Differential scanning calorimetry (DSC) experiments were performed on a DSC Q23 (TA Instruments) under nitrogen flow of 50 mL/min. Heating procedure was an isotherm at polymerisation temperature. As the scanning starts at ambient room, a jump was use to go to set-point temperature. Heat flow was recorded and polymerisation enthalpy calculated for each reactive blend. Conversion $\alpha_{(t)}$ in time was also estimated according to eq. 2 :

$$\alpha = \frac{\Delta H_{(t)}}{\Delta H_{\text{inf}}} \tag{2}$$

where $\Delta H_{(t)}$ is the heat released from polymerisation start until time t and ΔH_{inf} the 100% conversion corresponding enthalpy for our acrylic reactive system.

2.2.3. Rheology

Rheology measurements were done on a stress-controlled Physica Anton Paar MCR301 rheometer with cone-plate geometry (50mm, 1°). Evolution of complex viscosity during polymerisation was obtained through oscillatory shear analysis. Parameters were fixed to 10% strain and 1Hz, sampling was set to 6 value per minute. Temperature went from ambient room to set-point when recording started.

3. Results and discussion

Results obtained through DSC analysis are represented in figure 2. Heat flow profiles are similar for all blends. They match reported data on equivalent systems [15]. However, more reactive is the formulation, more sudden is the exothermic release, especially with P1. Looking on conversion with time curves in this case, Trommsdorff effect is accompanied by a very marked slope breaking and a final conversion of 100%. For less reactive formulations (and particularly when combining both initiators), the latter

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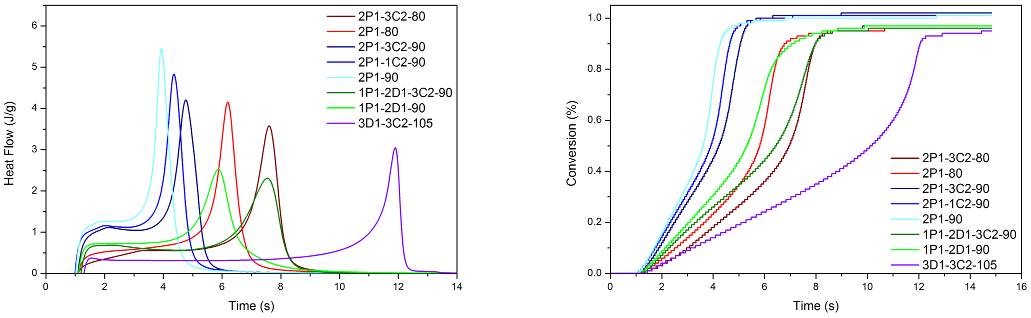
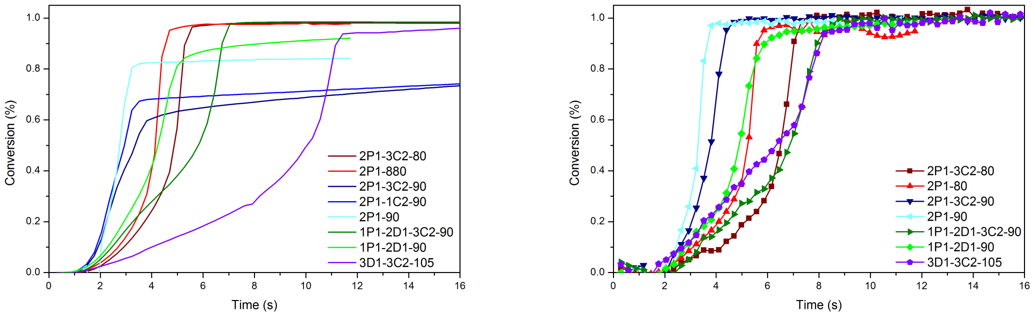


(a) (b)

Figure 2: Evolution of heat flow (a) and conversion (b) with time, DSC measurements

last a little bit more and polymerisation keeps evolving after. Same observations can be made on NIR-conversion profiles (figure 3). For such systems, when the reactive mixture passes its glass transition, it is well known that monomeric species and free radical can be trapped within the matrix [5, 16, 17]. Polymerisation is still occurring though, but mainly through diffusional mechanisms.



(a) (b)

Figure 3: Evolution of conversion with time for resin (a) and fiber-filled samples (b), NIR measurements

Focusing on NIR results on neat resin (figure 3), another phenomenon appears : most reactive blends do not reach a full conversion state. A high amount of residual monomer is still observable on NIR spectra slowly decreasing with time. Two causes could explain that. First one could be that, despite high monomer remaining content, these mixtures have already reached a glassy state and conversion only keeps evolving thanks to diffusional effect. But it is very unlikely considering vitrification curve for PMMA/MMA systems [18]. A second explanation could come from initiator properties with temperature leading to an early consumption of free radicals which terminate before end of reaction. Acrylic monomer content keeps decreasing because of diffusion and evaporation from the matrix, favoured by high temperature. This hypothesis is the most probable explanation and seems to be confirmed by studies on P1 currently in progress. Switching to fiber-filled specimens, this effect disappears. All formulations reach near 100% conversion. This could be explained by the loss of reactivity observed with P1 blends when adding glass fibers (table 2). Changes in characteristic times are quite significant. On the other hand, presence of glass fiber seems to improve D1 reactivity.

About initiator and catalyst content, adding C2 results in the same tendency as observed with glass fiber-filled samples : increasing quantity in P1 blends slows down the reaction whereas it quickens it for D1 mixtures. In the case of the two peroxides, changes in kinetics follow behaviour of P1 alone. Though thermal effects could explain glass fibers influence on kinetics, studies are currently in progress to chemically explain the opposite effects of adding C2-catalyst whether to P1 or D1 system.

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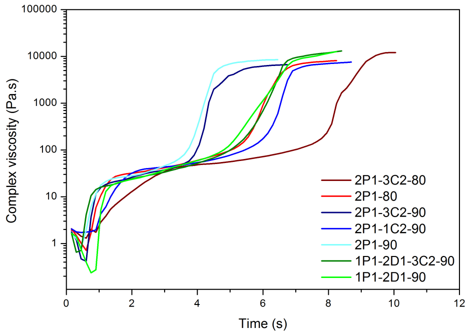

Figure 4: Complex viscosity evolution in time during polymerisation

Rheological study, which results are represented on figure 4, confirms the reactivity ranking established from both NIR and DSC measurements. Complex viscosity profiles show interesting fact : it seems that an important viscosity increase of near two order of magnitude occurs during first steps of polymerisation, when conversion degree is expected to be around 10%. This result is consistent with Malkin's work which predicted such behaviour for chemorheology of free radical polymerisation [19, 20]. Though it is not of primary concern for adhesive applications when wetting is done ahead, this could be a critical issue for RTM processing. The second transition is associated to Trommsdorff effect when matrix switch into glassy state.

For each systems, polymerisation time and final conversion have been determined by different methods (table 2). Confident accuracy is expected in α_{max} value for neat resin NIR analysis with less than 1% deviation. Uncertainties are more important for NIR measurements on fiber-filled samples due to glass fiber effect on spectra intensity and for DSC enthalpy (around 2%). ΔH_{inf} corresponds to the mean value of the three higher enthalpies experimentally determined. Specific times where graphically appreciated for NIR ($t\alpha_{max}$) and rheology ($t_{\eta G}$) measurements, they correspond to the moment when final plateau begins after inflexion point. DSC peak time t_P, coupled with maximum heat flow release, is a much more accurate parameter.

Table 2: Polymerisation times and conversion states obtained through various measurements

Analysis	Neat resin sample					Fiber-filled sample	
	NIR		DSC		Rheology	NIR	
	α_{max} (%)	$t\alpha_{max}$ (min)	α_{max}	t_P (min)	$t_{\eta G}$ (min)	α_{max} (%)	$t\alpha_{max}$ (min)
2P1-3C2-80	98	5.6	96	7.4	8.3	100	7.3
2P1-80	97	4.7	94	6.0	6.2	95	5.6
2P1-3C2-90	~75	3.8	101	4.6	4.4	100	4.7
2P1-1C2-90	~75	3.5	99	4.2	-	-	-
2P1-90	~80	3.2	99	3.8	4.2	99	3.8
1P1-2D1-3C2-90	99	7.0	95	7.4	6.2	100	8.2
1P1-2D1-90	92	5.3	96	5.7	5.9	96	6.2
3D1-3C2-90	100	11.4	94	11.7	-	99	8.2

As can be observed on table 2: important variations in characteristic times can be observed between methods. It can also be appreciated on the conversion plots of figure 5 where DSC and NIR are confronted : reaction appears always faster in the second case. Two interrelated causes can explain such

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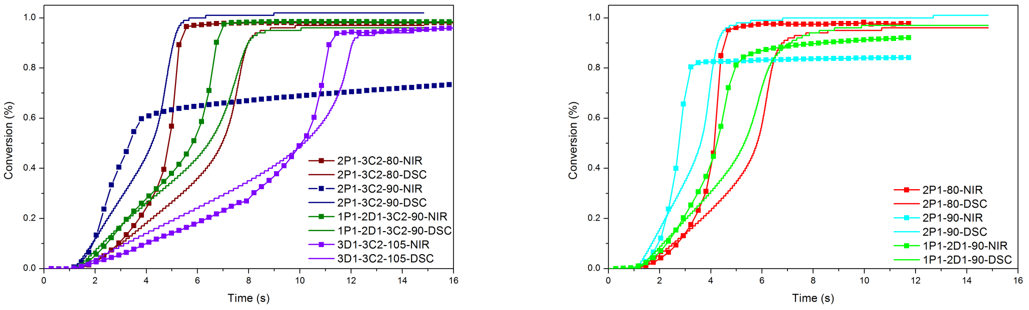
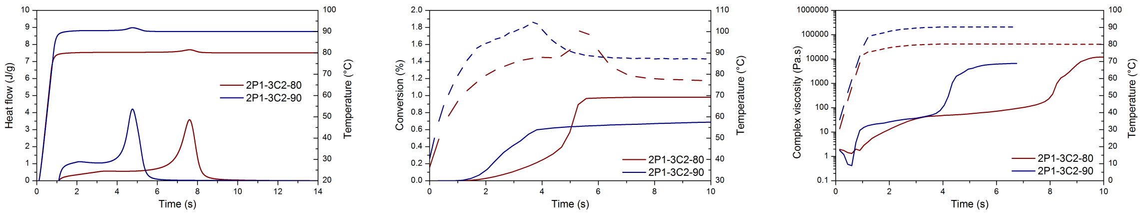
deviations : sample mass and heat transfer capacity. For DSC analysis, 10mg of reactive blend are put in alumina cell of high conductivity which lays onto a metallic support. Small quantity of resulting heat is consequently well evacuated. Oppositely, NIR measurements are done in glass tubes of 300 mL capacity. Heat accumulates leading to very important exothermies that could explain differences in conversion profiles and atypical cases. For a better accuracy, measurements of temperature during polymerisation were done for each method and are reported on figure 6. It confirms earlier hypothesis and shows that DSC and rheology analyses took place in near-isothermal conditions whereas NIR was near-adiabatic.



(a) (b)

Figure 5: Conversion profile : DSC vs NIR measurements



(a) (b) (c)

Figure 6: Temperature evolution during polymerisation for various methods : (a) NIR, (b) DSC and (c) rheology

Last statement meets Vallo's observations working on acrylic dental resins [12]. She showed that low residual monomer content in such materials comes especially from thermal effect and so mold characteristics. Focusing on our work, the two initiator mixtures seems also to illustrate heat storage impact. In formulations without C2, 100% conversion state is not reached and residual monomer is observed in NIR and expected in DSC. In fact, blends behave as if D1 molecules were not activated yet. For NIR 1P1-2D1-3C2-90 sample, it seems accumulated heat during polymerisation was enough to trigger D1 molecules explaining differences in final conversion and DSC profiles.

4. Observation of adhesive bonded laminates obtained by compression molding

Following part shows examples of multi-material laminate composites obtained using the acrylic resin as adhesive. An industrial TS-epoxy system which is currently commercialized for identical applications was used as reference for SEM and optical observations. Pictures in figure 7 detail such structures in which the adhesive bonds a top-coating to a wooden substrate. Acrylic specimen were processed either with P1 or D1 initiators and with C2 catalyst as the latter has proven to enhance final adhesion.

One of the present issues is the interfacial adhesion between acrylic adhesive and top-coating, giving random adherence results from very high to near-zero. Focusing on SEM observations, we identified decohesion alongside the acrylic composite/top-coating interface on poor adhesion specimens (figure 8).

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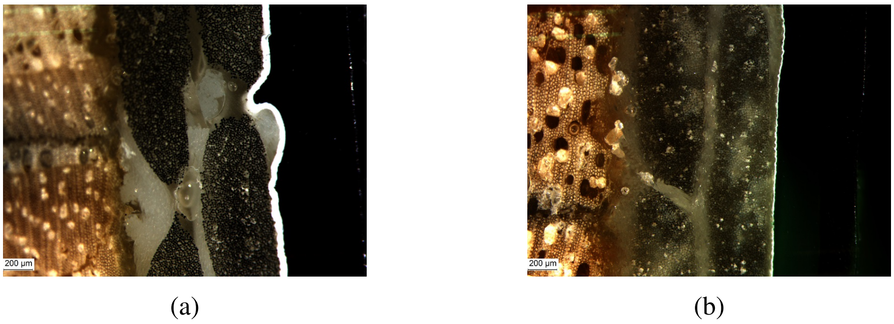
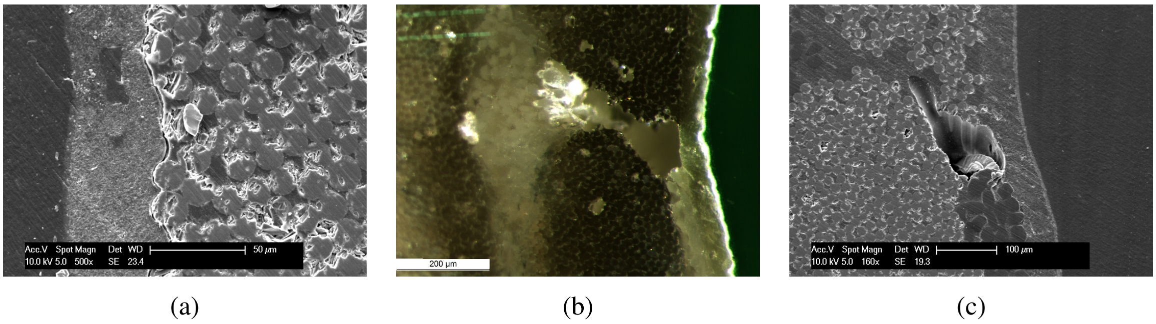


(a) (b)

Figure 7: Interface profile differences between acrylic (a) and epoxy laminates (b)

We could not be sure if such areas were already existing after processing or if it was induced by sample preparation. Anyway it reveals very low interfacial affinity.



(a) (b) (c)

Figure 8: Focusing on acrylic laminate decohesion near top coating/composite interface (a). Comparison with optic (b) and SEM (c) on TS-epoxy reference

Adhesion mechanisms ruling final adherence of such system yet remain to be identified so not much can be added. However, a major statement currently on study is the difference in properties between epoxy oligomers and acrylic monomers. These latter are highly volatile and have great diffusional capacity. Optical observation shows with certainty, through sinuous interfacial demarcation, interactions between acrylic resin and top-coating whereas its superior layer is supposed to be resin-proof.

5. Conclusion

Properties of acrylic reactive blends, further used as thermoplastic adhesive for multilayer composite applications, were studied during their free-radical polymerisation. Conversion profiles, polymerisation exothermicity and rheological properties were measured for various reactive formulations. Effect of initiator nature, catalyst content and presence of glass fiber on kinetics were assessed, though some behaviours still lack of explanation. Results also show huge influence of thermal effects during polymerisation, which can be optimized taking into account surrounding materials conductivity. Example of laminate composites processed with such reactive system were presented, showing adherence defects that yet remain to be elucidated.

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