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MATHEMATICAL MODELING OF FRONTAL POLYMERIZATION

JOHN A. POJMAN^{1,2,*}

Abstract. Frontal polymerization is way to convert liquid resin into a solid material with a self-propagating reaction. The reaction spreads like a flame from the heat of the reaction that diffuses into neighboring regions, starting more reaction. The frontal velocity has been accurately modeled for free-radical polymerization systems. The dynamics of fronts have been studied theoretically and experimentally. If the viscosity of the initial medium is low, then fronts can become unstable due to buoyancy-driven convection. A fascinating aspect of frontal polymerization is that fronts often do not propagate as a plane waves but exhibit complex modes such as “spin modes” and chaos. The kinetics of the polymerization significantly affects the onset of these modes. Multifunctional acrylates exhibit more complex dynamics than monoacrylates. Using multifunctional acrylates and inorganic fillers, 3P LLC created “cure-on demand” systems that do not require mixing before use, have a long shelf life and can be hardened in seconds to minutes. We consider two commercial products using frontal polymerization. The first is a wood filler that can be applied to a damaged section of wood and hardened in a few seconds by the application of heat to the surface. The second product is QuickCure Clay (QCC). QCC has an unlimited working time during which it can be sculpted. QCC is then cured by heating part of the object to 100 °C, setting off the propagating curing front. The modeling of frontal polymerization helped guide the development of these products.

Mathematics Subject Classification. 80A30.

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1. CURE-ON-DEMAND POLYMERIZATION AND FRONTAL POLYMERIZATION

The goal of “cure-on demand” chemistry is to create systems that are one-pot formulations, *i.e.*, do not require mixing before use, that will react rapidly when you want them to react. Photopolymerization can be used for curing thin layers but not for thick samples, especially those containing carbon fiber or other opaque materials. Another way to achieve cure-on demand polymerization is with “frontal polymerization.” Frontal polymerization is a method of converting monomer(s) to polymer *via* a localized reaction zone that propagates from the coupling of thermal diffusion with the Arrhenius kinetics of an exothermic polymerization. Frontal polymerization (FP) was first explored in the 1970s in Chernogolovka, Russia [4, 11–14, 19], with more work in the 1980s [6, 20, 61, 64, 65]. Pojman independently “rediscovered” frontal polymerization in the 1990s while researching methacrylate polymerizations [43, 44, 47, 48]. Since then, research on FP has expanded significantly to include cure-on-demand materials [29, 62], synthesis of gels [1, 38, 54] and gradient materials [3, 15], epoxide

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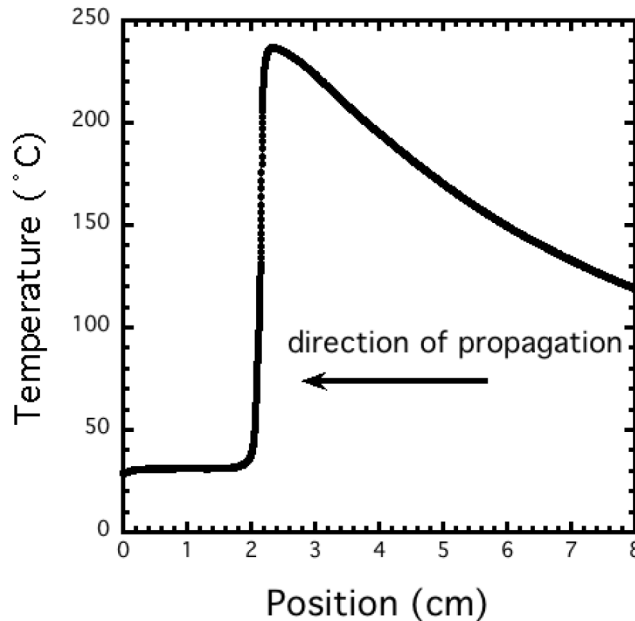


FIGURE 1. Temperature profile of a propagating polymerization front.

polymerizations [9, 33, 55, 56], composite materials [2, 16, 17, 30] and self-stiffening materials [52] and deep eutectic solvents [21, 37].

1.1. Features of frontal polymerization

The essential features of frontal polymerization that make it ideal for cure-on-demand applications are: (1) no significant reaction at room temperature; (2) rapid reaction at the temperature reached by the heat released by the reaction. These features allow formulations with a long shelf life to be cured rapidly as a propagating front. Figure 1 shows a typical temperature profile of a frontal polymerization reaction.

A promising application is the autoclaveless curing of composites using Frontal Ring Opening Metathesis Polymerization (FROMP) [53]. Robertson *et al.* showed that if an airplane could be cured by frontal polymerization with dicyclopentadiene instead of using epoxy-based composites cured in an autoclave, the energy required would be lower by a factor of 10^9 [53].

1.2. Free-radical frontal polymerization

Free-radical chemistry is the most amenable to frontal polymerization because the reactions can be rapid, very exothermic and with a high energy of activation, controlled by the type of initiator and is the basis for QuickCure Clay. A free-radical polymerization with a thermal initiator can be approximately represented by a three-step mechanism. First, an unstable compound, usually a peroxide or nitrile, decomposes to produce radicals:



where f is the efficiency, which depends on the initiator type and the solvent. A radical can then add to a monomer to initiate a growing polymer chain:





The propagation step (1.3) continues until a chain terminates by reacting with another chain (or with an initiator radical):



The major heat release in the polymerization reaction occurs in the propagation step. However, the propagation step does not have a sufficiently high activation energy to permit a front. Frontal polymerization autocatalysis is controlled by the energy of activation of the initiator decomposition. The steady-state assumption in the polymerization model gives an approximate relationship between the effective activation energy of the entire polymerization process and activation energy of the initiator decomposition reaction:

$$E_{eff} = E_p + (E_i/2) - (E_t/2) \quad (1.5)$$

where E_p is the activation energy of the propagation step, E_i is for the initiator decomposition and E_t is that for the termination step.

The second term in the right-hand side of equation (1.5) depends on the initiator. Because it has the largest magnitude, this value mostly determines the effective activation energy. Because of this, the initiator plays a significant role in determining if a front will exist, and if so, temperature profile in the front and how fast the front will propagate.

2. FACTORS AFFECTING VELOCITY

2.1. Velocity dependence on initiator concentration

Cechilo *et al.* studied methyl methacrylate polymerization with benzoyl peroxide as the initiator. By placing several thermocouples, they could infer the front velocity and found a 0.36 power dependence for the velocity on the benzoyl peroxide concentration [11]. More detailed studies for several initiators showed 0.223 for *t*-butyl peroxide, 0.324 for BPO and 0.339 for cyclohexylperoxide carbonate [14]. Pojman *et al.* reported a detailed study of tri(ethylene glycol) dimethacrylate (TGDMA) frontal polymerization [39].

Khanukaev *et al.* considered the theory of front propagation in terms of conversion and velocity as a function of initial temperature [41, 42]. Because of the high front temperature, all the initiator can decompose before all the monomer has reacted. The result is initiator “burn out”, which decreases conversion and velocity. High initial temperatures exacerbate this effect. Using their theory, they correctly predicted the conversion for one experiment with methyl methacrylate (46%) and a velocity of 0.12 cm/min.

The most careful study of velocity as a function of experimental parameters was performed by Goldfeder *et al.* [25]. They considered the frontal polymerization of butyl acrylate containing fumed silica (to suppress convection) in a custom-built reactor that allowed temperature control at 50 atm pressure (to suppress bubbles). They developed analytical solutions for the front velocity as a function of initiator concentration and initial temperature.

2.2. Front velocity as a function of temperature

The front velocity is a function of the initial temperature and the ΔT of the reaction, where ΔT is determined by the $|\Delta H|^* M_0 / C_p$. The value of ΔT is also affected by the presence of any inert material. Goldfeder *et al.* derived an expression for the front velocity in terms of the parameters for a free-radical polymerization [25]. The velocity is a function of κ , the thermal diffusivity ($0.0014 \text{ cm}^2 \text{ s}^{-1}$, T_b , k_d^0 = the pre-exponential factor for the initiator decomposition ($4 \times 10^{12} 1/\text{s}$, $E_1 = E_d$ = the energy activation for the dissociation constant for the

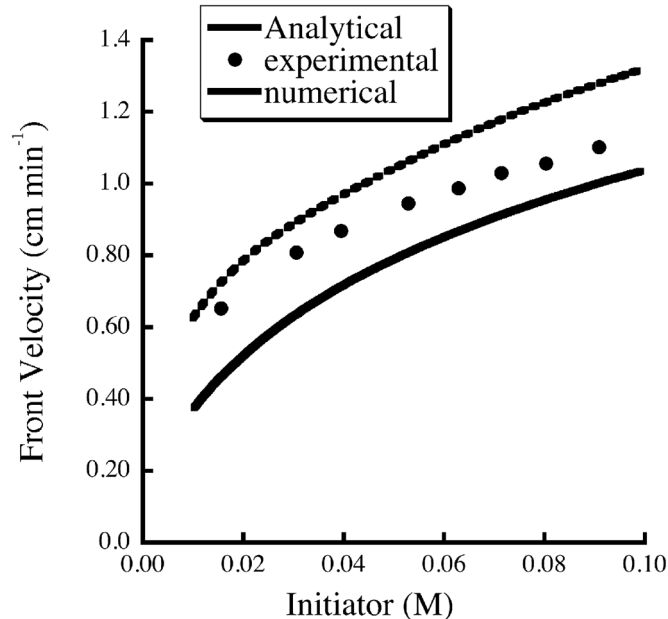


FIGURE 2. Comparison of the velocity dependence on the AIBN concentration for the frontal polymerization of butyl acrylate at 278 K, determined experimentally, numerically and analytically. Adapted from Goldfeder *et al.* [25].

initiator = 27 kcal/mol, R_g is the ideal gas constant.

$$u^2 = \frac{\kappa R_g T_b^2}{2E_1(T_b - T_0)} k_d^0 e^{-E_d/R_g T_b}. \quad (2.1)$$

The model worked well for butyl acrylate. Figure 2 shows the results for the experiment and analytical solution as well as numerical simulations with the complete model. This model does not work with multifunctional monomers because the kinetic parameters are a function of the extent of reaction.

3. INTERFERENCES WITH FRONTAL POLYMERIZATION

3.1. Buoyancy-driven convection

Because of the large thermal and concentration gradients, polymerization fronts are highly susceptible to buoyancy-induced convection unless the viscosity is increased by the addition of fillers. Garbey *et al.* performed the linear stability analysis for the liquid/liquid and liquid/solid cases [22–24]. The bifurcation parameter was a ‘frontal Rayleigh number’:

$$Ra = g\beta q \kappa / \nu c^3 \quad (3.1)$$

where g is the gravitational acceleration, β the thermal expansion coefficient, q the temperature increase at the front, κ the thermal diffusivity, ν the kinematic viscosity and c the front velocity.

Let us first consider the liquid/solid case. Neglecting heat loss, the descending front is always stable because it corresponds to heating a fluid from above. The front is always flat. If the front is ascending, convection may occur depending on the parameters of the system. Bowden *et al.* experimentally confirmed that the first mode is an antisymmetric one, followed by an axisymmetric one [10]. Figure 3 shows a flat descending front as well

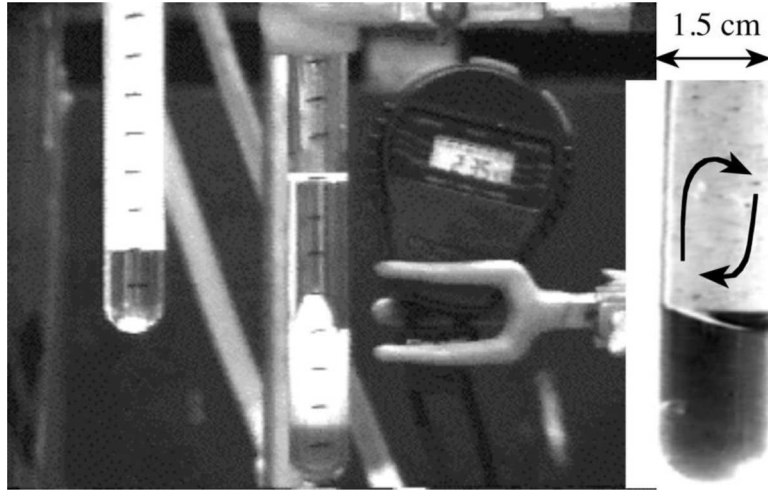


FIGURE 3. *Left*: The front on the left is descending and the one on the right ascending with an axisymmetric mode of convection. *Right*: An antisymmetric mode of an ascending front. The system is the acrylamide/bis-acrylamide polymerization in DMSO with persulfate initiator. Adapted from Bowden *et al.* [10].

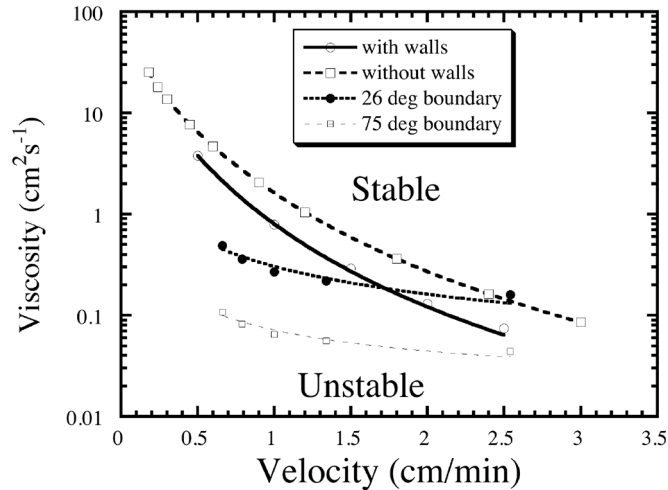


FIGURE 4. The stability diagram for the system in Figure 5. Adapted from Bowden *et al.* [10].

as axisymmetric and antisymmetric modes of ascending fronts. Figure 4 shows the stability diagram in the viscosity-front velocity plane. Most importantly, they confirmed that the stability of the fluid was a function not only of the viscosity but also of the front velocity. This means that the front dynamics affects the fluids dynamics. McCaughey *et al.* tested the analysis of Garbey *et al.* and found the same bifurcation sequence of antisymmetric to axisymmetric convection in ascending fronts [36] as seen with the liquid/solid case.

If the reactor is not vertical, there is no longer a question of stability – there is always convection. Bazile *et al.* studied descending fronts of acrylamide/bisacrylamide polymerization in DMSO as a function of tube orientation [5]. The fronts remained nearly perpendicular to the vertical (Fig. 5), but the velocity projected along the axis of the tube increased with $1/\cos$ of the angle.

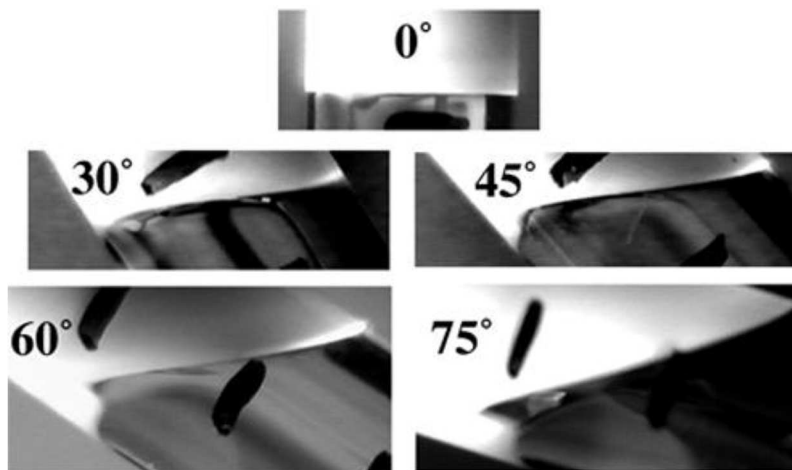


FIGURE 5. The dependence of the front shape for descending fronts of acrylamide polymerization in DMSO with persulfate initiator. Adapted from Bazile Jr. *et al.* [5].

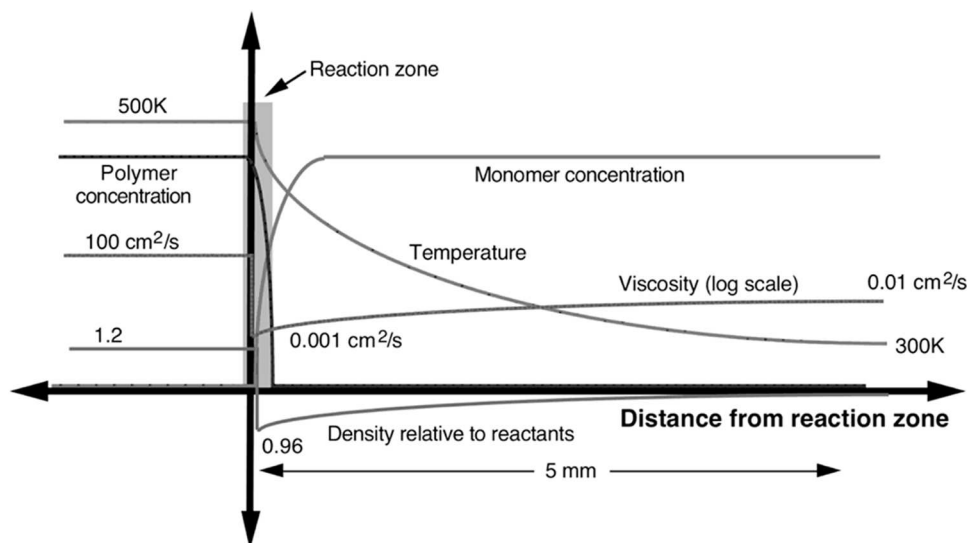


FIGURE 6. Schematic diagram showing changes in properties across a propagating polymerization front that produces a thermoplastic. (Courtesy of Paul Ronney.)

Liquid/liquid systems are more complicated than the previous case because a descending front can exhibit the Rayleigh-Taylor instability. The product is hotter than the reactant but is denser (Fig. 6), and because the product is a liquid, fingering can occur. Bidali *et al.* described the phenomenon as the “rainstorm effect” [8]. Such front collapse is shown in Figure 7. The Rayleigh-Taylor instability can be prevented using high pressure [11], adding a filler [25], using a dispersion in salt water [49] or performing the fronts in weightlessness [49].

3.2. Thermal instabilities

Fronts do not have to propagate as planar fronts. Analogously to oscillating reactions, a front can exhibit periodic behavior, either as pulsations or ‘spin modes’ in which a hot spot propagates around the reactor as the

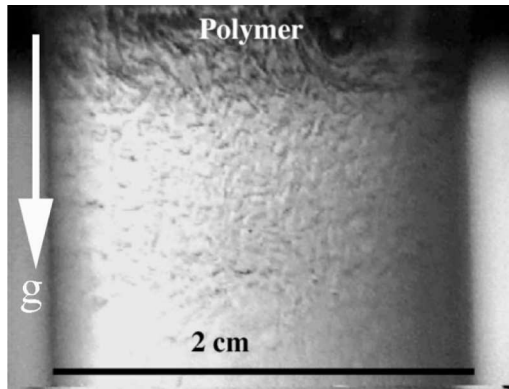


FIGURE 7. Rayleigh-Taylor instability with a descending front of butyl acrylate polymerization.

front propagates, leaving a helical pattern. This mode was first observed in Self-propagating High temperature Synthesis (SHS) [31].

The linear stability analysis of the longitudinally propagating fronts in the cylindrical adiabatic reactors with one reaction predicted that the expected frontal mode for the given reactive medium and diameter of the reactor is governed by the Zeldovich number:

$$Z = \frac{T_m - T_0}{T_m} \frac{E_{\text{eff}}}{RT_m}. \quad (3.2)$$

For FP, lowering the initial temperature (T_0), increasing the front temperature (T_m), and increasing the energy of activation (E_{eff}) all increase the Zeldovich number. The planar mode is stable if $Z < Z_{cr} = 8.4$. By varying the Zeldovich number beyond the stability threshold, subsequent bifurcations leading to higher spin mode instabilities can be observed. Secondly, for a cylindrical geometry the number of spin heads or hot spots is also a function of the tube diameter. We point out that polymerization is not a one-step reaction, so that the above form of the Zeldovich number does not directly apply. However, estimates of the effective Zeldovich number can be obtained from the overall energy of activation with the steady-state assumption for free-radical polymerization.

The most commonly observed case with frontal polymerization in cylinders is the spin mode in which a ‘hot spot’ propagates around the front. A helical pattern is often observed in the sample. The first case was with the frontal polymerization of ϵ -caprolactam [6, 7], and the next case was discovered by Pojman *et al.* in the methacrylic acid system in which the initial temperature was lowered [45].

The single-head spin mode was studied in detail by Ilyashenko and Pojman [40]. They were able to estimate the Zeldovich number. The value at room temperature was about 7, less than the critical value for spin modes. In fact, fronts at room temperature were planar and spin modes only appeared by lowering the initial temperature. However, spin modes could be observed by increasing the heat loss from the reactor by immersing the tube in water or oil.

3.2.1. Effect of complex kinetics

Solovyov *et al.* performed two-dimensional numerical simulations using a standard three-step free-radical mechanism [59]. They calculated the Zeldovich number from the overall activation energy using the steady-state theory and determined the critical values for bifurcations to periodic modes and found that the complex kinetics stabilized the front.

Shult and Volpert performed the linear stability analysis for the same model and confirmed this result [57]. Spade and Volpert studied the linear stability for nonadiabatic systems [60]. Gross and Volpert performed a



FIGURE 8. A single-head spin mode propagating around a front of 1,6 hexanediol diacrylate (40%) in diethyl phthalate with Luperox 231 as the initiator [35]. Tube diameter was 1.5 cm.

nonlinear stability for the one-dimensional case [27]. Commissiong *et al.* extended the nonlinear analysis to two dimensions [18]. They confirmed that, unlike in SHS [58], uniform pulsations are difficult to observe in frontal polymerization. In fact, no such one-dimensional pulsating modes have been observed.

An interesting problem arises in the study of fronts with multifunctional acrylates. At room temperature, acrylate like 1, 6 hexanediol diacrylate (HDDA) and triethylene glycol dimethacrylate (TGDMA) exhibit spin modes. In fact, if an inert diluent, such as dimethyl sulfoxide (DMSO) is added, the spin modes are more apparent even though the front temperature is reduced. Masere and Pojman found spin modes in the frontal polymerization of a diacrylate at ambient conditions [34]. This observation implicates the role of polymer crosslinking in front dynamics. In that same work, Masere and Pojman showed that pH indicators could be added to act as dyes that were bleached by the free radicals, making the observation of the spin pattern readily apparent (Fig. 8).

Tryson and Schultz studied the energy of activation of photopolymerized multifunctional acrylates and found it increased with increasing conversion because of crosslinking [63]. Gray found that the energy of activation of HDDA increased exponentially during the reaction [26]. Applying the steady-state theory of polymerization to Gray's results, Masere *et al.* calculated the effective energy of activation for thermally-initiated polymerization (photoinitiation has no energy of activation) by including the energy of activation of a typical peroxide [35]. They calculated that the E_a of HDDA polymerization increased from 80 kJ/mole at 0% conversion, the same as methacrylic acid, to a 140 kJ/mole at 80% conversion. This can explain how spin modes appear at room temperature with multifunctional acrylates but not monoacrylates. The Zeldovich number of methacrylic acid polymerization at room temperature is below the stability threshold. Using the activation energy at the highest conversion that can be obtained with HDDA, Masere *et al.* estimated a Zeldovich number of 12.

Masere *et al.* studied fronts with a peroxide initiator at room temperature and used two bifurcation parameters [35]. They added an inert diluent, diethyl phthalate, to change the front temperature and observed a variety of modes. More interestingly, they also varied the ratio of a monoacrylate, benzyl acrylate, to HDDA, keeping

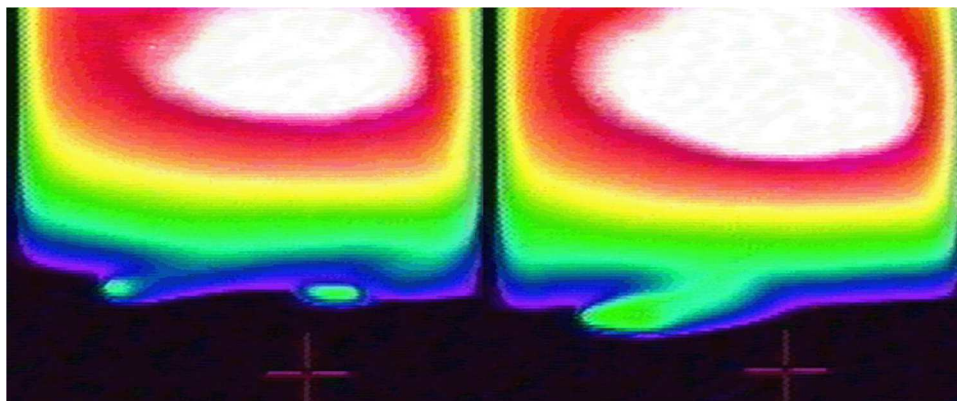


FIGURE 9. Complex modes of propagation observed with an IR camera in a 1.5 cm tube with trimethylol propane triacrylate in DMSO with Luperox 231.



FIGURE 10. Rapid repair of a hole in wood using QuickCure WoodFiller.

the front temperature constant. Changing the extent of crosslinking changed the effective energy of activation, which revealed a wide array of interesting spin modes. Using trimethylol propane triacrylate in DMSO, they observed complex modes (Fig. 9).

The three-dimensional nature of the helical pattern was studied by Manz *et al.* using Magnetic Resonance Imaging (MRI) [32]. Pojman *et al.* observed zigzag modes in square reactors [46] and bistability in conical reactors [28].

4. APPLICATIONS OF FRONTAL POLYMERIZATION

4.1. Applications to wood repair

In 2000, I had the idea of making material for the rapid repair of wood and floors. The first problem was repairing wood and floors. Conventional products work by solvent evaporation or chemical reaction. Solvent evaporation is a fancy way of describing water evaporating or evaporation of an organic solvent. For wood repair, these work well and are inexpensive, but they require significant amount of time before the repaired section can be painted or stained. This is because significant when the damaged area is deep because it the drying time can increase as the square of the hole depth; a hole that is twice as deep can require four times as long to dry.

QuickCure WoodFiller is a mixture of acrylates, a peroxide and fillers. (Acrylates are similar to materials used in dental fillings.) The chemical reaction is a free-radical polymerization. It has a shelf life of years, meaning it



FIGURE 11. A sculpture of a lizard (anole) created by Shelby Prindaville with QuickCure Clay. The sculpture is 15 cm in height.

can be stored at room temperature without reacting. Figure 10 shows the hole before, during and after curing. A significant advantage of frontal polymerization is that a hole can be filled rapidly. If a solvent-based system were used, the filler would have to be added in layers with time allowed between for the evaporation. If a two-part system were used, the components would have to be mixed, applied and allowed to react.

4.2. Application to art

QuickCure Clay is similar to the wood filler except that it is stronger and retains its shape well during curing. Figure 11 shows how delicate sculptures can be created without the use of internal reinforcement. It is also composed of multifunctional acrylates and inorganic fillers that create the proper consistency for sculpting and strength after curing.

QuickCure Clay has many advantages compared to other sculpting materials but the most important are the long working time but fast time to cure by heating a small section that ignites a propagating front.

QuickCure Clay consists of multifunctional acrylates and fillers. The high viscosity of the formulation prevents buoyancy-driven convection. However, a unique feature of QCC is the patterns that arise on the surface during curing. These patterns are the result of complicated modes of front propagation. These nonplanar modes arise



FIGURE 12. A nonplanar front propagating in a cylinder of QuickCure Clay. Parallel bands can be seen in the cured section.

for polymerization fronts when the energy of activation is high as with multifunctional acrylates. Figure 12 shows the patterns left in cured QCC for a front propagating through a cylinder along the long axis.

5. CONCLUSIONS

Frontal polymerization with free-radical chemistry has been well studied experimentally and the instabilities that arise successfully modelled. Buoyancy-driven convection can interfere with frontal polymerization in low-viscosity systems. Nonplanar modes of propagation arise independent of the viscosity. Frontal polymerization has been applied to “cure-on-demand” applications such as wood repair and art. The mathematical modeling helped guide the development of these applications and will no doubt continue to guide future developments.

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