

Preparation Of Functionally Gradient Materials via Frontal Polymerization

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ABSTRACT: Ascending frontal polymerization in a body with a moving boundary was accomplished experimentally. This process was shown to be a steady-state process within a certain range of the parameters. Temperature profiles of the front were recorded. This new method gives an excellent opportunity to prepare functionally gradient materials because composition of a monomer feedstream can be varied in a programmable manner. Polymer samples with hyperbolic gradients of optical dye concentration were manufactured at ambient pressure and temperature. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 2398–2404, 2000

Key words: frontal polymerization; functionally gradient material (FGM); optical limiter; temperature profile; polyacrylate

INTRODUCTION

Functionally Gradient Materials

Homogeneous materials, with no spatial variation of properties, are traditionally employed for most applications. Such materials are reliable and can be analyzed by many common techniques. Some situations however require material with divergent properties. The concept of functionally gradient materials (FGM) was proposed to make such a material with gradient of one or several properties in one or more dimensions. This concept was first and successfully implemented in a new composite for the Japanese Space Program.¹ The composite had a heat-resistant ceramic on the high-temperature side and tough metal with high thermal conductivity on the low-temperature side, with a gradual compositional variation from ceramic to metal. This composite could withstand high temperatures more effectively than a ceramic or metal alone.

Since then the concept of FGM was employed for different types of materials including polymers and composites. Special techniques were developed to make a gradient of reinforcement filler in a polymeric composite. In the work of Jang and Lee² a gradient of carbon and glass fibers was created by changing the feeding ratio of the two chopped fibers in the course of composite manufacture. Centrifugal force was used in work of Lee et al.³ to make a gradient of more dense filler in a polymer matrix. The superior properties for FGM were reported in comparison with the uniform composites.

Several types of polymeric FGMs were prepared by a number of methods for different purposes. A polymer with a discrete variation of plasticizer content was cast for the study of crack propagation.⁴ A desirable fracture behavior could be tailored by choosing the proper gradient of plasticizer content. Xie et al.⁵ reported that gradient morphology ensures superior adhesive properties for films made from polymer blends. Interfacial tension between polymers was the driving force for formation of a gradient in the blend. Gradient interpenetrating polymer net-

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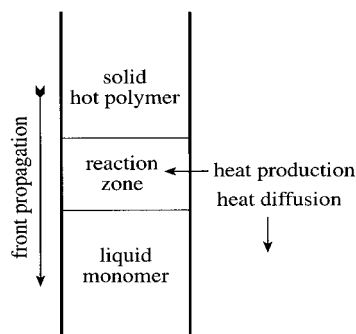


Figure 1 Scheme of frontal polymerization.

works were studied by Mueller and Heiber⁶ as a potential drug release system.

A great deal of work has been done on Gradient Refractive Index (GRIN) materials for fiber optical applications.^{7–10} These materials were prepared via isothermal frontal polymerization (interfacial gel polymerization), which is a slow process limited to producing gradients over about 1 cm.

Another type of gradient material with definite utility is an optical limiter based on a gradient of nonlinear optical dye dissolved in a polymer matrix. An optical limiter is a device that strongly attenuates intense optical beams but allows high transmittance of low-intensity light. Such a device would be very useful for protecting human eyes from intense laser pulses.¹¹ Perry et al.¹² discussed the types of organic materials that exhibit such nonlinear absorption. They have found that metallophthalocyanine (M-Pc) complexes containing heavy central atoms work well. These dyes are compatible with poly(methyl methacrylate) and dissolve in the monomer. This affords the great advantage of inexpensive materials.

Miles¹³ calculated that the maximum attenuation of a light pulse can be achieved if the absorbing species is distributed as a hyperbolic function of position. Perry et al.¹² demonstrated the value of a gradient by approximating the hyperbolic distribution with slabs containing different dye concentrations at set distances. One of the purposes of this work was to prepare polymer samples with a hyperbolic dye distribution.

Frontal Polymerization as a New Method for Preparation of FGM

Frontal polymerization is a self-sustaining process in which a localized reaction zone or front propagates through a monomer converting it to

the polymer (Fig. 1).^{14,15} High exothermicity of the polymerization reaction and Arrhenius dependence for the polymerization rate are the most important requirements for a monomer to support a front. It was shown that fronts can exist with free-radical polymerization of mono- and multifunctional acrylates,^{15–17} or epoxy curing.¹⁸ Frontal polymerization can be achieved in solution polymerization with reactive monomers such as acrylamide, methacrylic acid, and acrylic acid in solvents such as water and dimethyl sulfoxide (DMSO).¹⁹

Frontal polymerization reactions are relatively easy to perform. In the simplest case, a test tube is filled with the reactants. The front is ignited by applying heat to one end of the tube with a heater. The position of the front is obvious because of the difference in the optical properties of polymer and monomer. Under most cases, a plot of the front position versus time produces a straight line whose slope is the front velocity. The velocity can be affected by the initiator type and concentration but is on the order of one centimeter per minute.

The defining feature of thermal frontal polymerization is the sharp temperature gradient present in the front. A typical temperature profile for the descending front is shown in Figure 2. The temperature jumps about 180°C over as little as a few millimeters, which corresponds to polymerization in a few seconds at that point.

Buoyancy-driven convection, however, can be a serious problem for an ascending front. Preheated monomer right above the front will eventually float, and heat dissipation due to convection will overcome heat production in the reaction zone, which will cause the front to quench. On the other

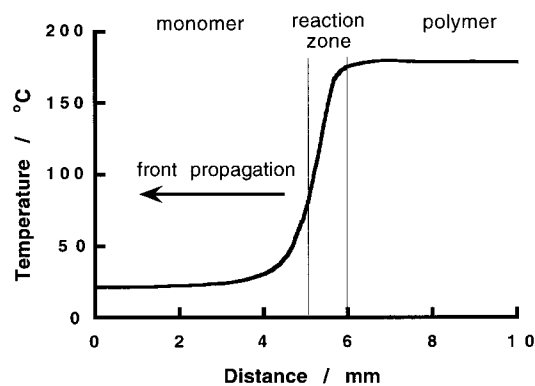


Figure 2 Temperature profile of the descending front in tri(ethylene glycol) dimethacrylate (TGDMA) and tricaprilmethylammonium persulfate as an initiator. Front velocity was 11.0 mm/min.

hand, if one could restrict convection in a narrow layer of liquid monomer it would be possible for the front to propagate. To solve this problem a continuous feeding of fresh monomer on the top of the moving front was proposed.^{20,21} This approach offers an excellent opportunity to create any type of gradient in a polymeric material by simply changing the composition of the monomer feedstream.

The influence of feed flow rate and initiator concentration on temperature profile of the ascending front were studied in the presented work. A hyperbolic dye gradient over a scale several centimeters was created by the proposed technique.

EXPERIMENTAL

Chemicals

Tri(ethylene glycol) dimethacrylate (TGDMA) was used as a monomer and tricaprilmethylammonium persulfate or Aliquat 336 persulfate²² was used as an initiator for free-radical polymerization. TGDMA was stored over molecular sieves, dried over CaH₂, and then filtered before use. Aluminum phthalocyanine chloride was used as a dye. The dye was dissolved in TGDMA to its saturation point –0.0034% by weight, and this solution was used as a coloring component. All chemicals are from Aldrich (Milwaukee, WI, USA).

Creation of Dye Gradient

Two peristaltic pumps (Dynamax RP-1 from Rainin Corp., Woburn, MA, USA) were used to supply the reactive media into the test tube in which the ascending front propagated (Fig. 3). The inner diameter of the test tube was 14 mm. One of pumps (pump 1) supplied a solution of TGDMA with the initiator and another pump (pump 2) supplied a solution of dye in TGDMA with the same amount of initiator. The sum of the flow rates from both pumps was kept constant in the course of sample formation, $F_1(t) + F_2(t) = F_{\text{sum}} = \text{const}$. Thus, the surface velocity v_s for motion of the free surface of monomer was also constant, $v_s = F_{\text{sum}}/A$, where A is the cross-sectional area of the test tube. The flow rate $F_2(t)$ for pump 2 was computer controlled in time corresponding to tailored gradient as follows:

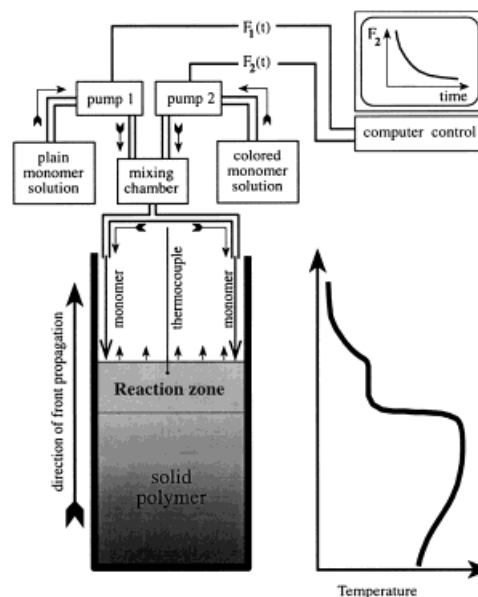


Figure 3 Scheme of FGM formation via frontal polymerization.

$$F_2(t) = F_{\text{sum}} G(v_s \cdot t) \quad (1)$$

$$G(x) = \begin{cases} C(x)/C_{\text{max}} & \text{if } C(x) \leq C_{\text{max}} \\ 1 & \text{if } C(x) > C_{\text{max}} \end{cases} \quad (2)$$

where $C(x)$ is the function expressing programmed spatial variation of dye concentration along the test tube axis. Spatial variable in function G was substituted by $v_s \cdot t$ in eq. (1). C_{max} is the dye concentration in a colored monomer solution. Flow rate $F_1(t)$ was also computer controlled as $F_1(t) = F_{\text{sum}} - F_2(t)$.

The test tube in which the front propagation was accomplished was exposed to ambient pressure and temperature. The front was ignited in the bottom of the tube by a soldering iron. The soldering iron was removed from the test tube as soon as front ignited to ensure that front propagation was a self-sustaining process.

Temperature Profile Measurement

Temperature versus time plots were recorded in the course of front propagation by means of thermocouple and then converted to temperature versus distance profiles using the surface velocity. The thermocouple was positioned in the center of the test tube. Monomer was supplied along the test tube wall. The thermocouple measured the vapor temperature until the monomer surface reached the thermocouple.

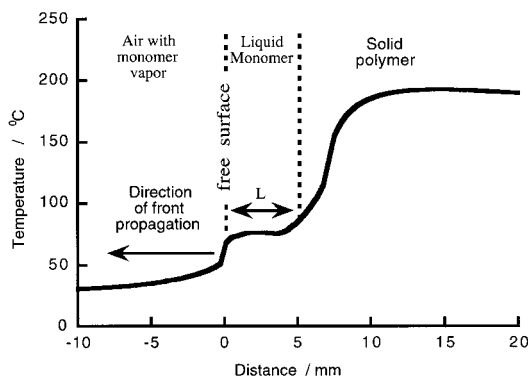


Figure 4 Temperature profile of the ascending front in a body with moving boundary. TGDMA with 2.5 vol % of tricaprilmethylammonium persulfate as initiator. Surface velocity 23.4 mm/min.

Characterization of Dye Gradient

Polymer samples with dye gradient were video recorded, and the gray level of the sample's image was analyzed using the National Institutes of Health's Image software to obtain the dye concentration profile. A region of sample without dye was considered as a reference for gray level corresponding to zero dye concentration. The area of sample with the maximum concentration of the dye was taken as a reference for gray level corresponding to the maximum of dye concentration.

RESULTS AND DISCUSSION

Temperature Profile for the Ascending Front in a Body with a Moving Boundary

A typical profile for an ascending front with continuous monomer addition is shown in Figure 4. Unlike for the temperature profile of the descending front, there is a plateau with constant temperature right after the free surface of monomer, which corresponds to a layer of the liquid monomer just above the front. Intensive convection makes the temperature constant throughout the layer.

The stability of an ascending front depends on the liquid layer thickness L . A front with an infinite layer of unreacted monomer above it will be less stable than one with a narrow layer because of buoyancy-driven convection. Unfortunately, no theory exists for this case. Rough estimates can be made, though, by analogy with the nonreactive case of a fluid layer of thickness L heated from below. The Rayleigh number for this case is:

$$Ra = \frac{g\beta qL^3}{v\kappa} \quad (3)$$

Here, κ is the coefficient of thermal diffusivity, q is the temperature change, v is the kinematic viscosity, g is the gravitational acceleration, and β is the coefficient of thermal expansion. Because of the cubic dependence, the front stability is very sensitive to L . Therefore L was used as characteristic value for the temperature profiles and influence of different factors on this value was investigated in this work.

Steady-State Front Propagation in Ascending Mode

Frontal polymerization is a complex dynamic process with many factors interacting with each other in a nonlinear fashion, so it is important to investigate if front propagation observed in experiments is a steady-state process. To accomplish this experimentally, the temperature profile of an ascending front was measured in two different points of the sample in the course of front propagation. The temperature profile of the front preserves its shape while the front propagates, as is shown in Figure 5, so it is a steady-state process. Visual observations of the front propagation have also confirmed that it was steady-state process because the observed liquid layer thickness did not change in time while the front propagated. All the temperature profiles reported in this paper are the steady-state profiles.

Effect of Surface Velocity and Initiator Concentration on Liquid Layer Thickness

It was found experimentally that a front would always adjust its velocity to the surface velocity or

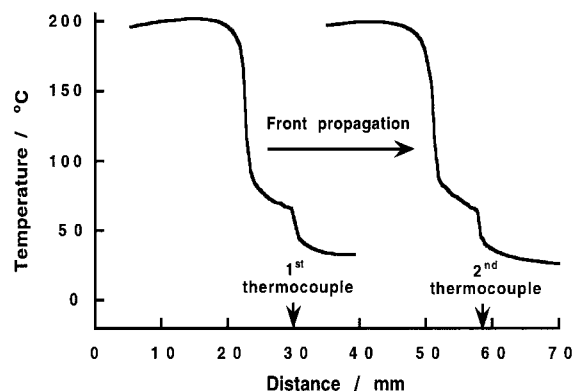


Figure 5 Temperature profiles of the ascending front measured at two different positions during the front propagation. TGDMA with 5 vol % of tricaprilmethylammonium persulfate initiator. Surface velocity 33 mm/min.

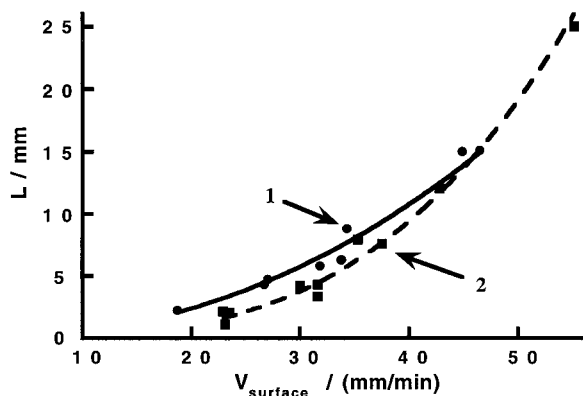


Figure 6 Liquid layer thickness L vs. surface velocity v_s for TGDMA with tricaprilmethylammonium persulfate initiator. 1st curve (circles—experimental points), monomer with 5% of initiator; 2nd curve (squares—experimental points), monomer with 10% of initiator.

would not propagate at all. By this reason, there existed a unique temperature profile for each value of the surface velocity. In our opinion, convection is the most probable feedback mechanism for such a dependence between the surface and front velocities. The value of L increased significantly with the surface velocity, as is shown in Figure 6. For example, the front could propagate with as much as 25 mm of liquid layer thickness atop of the growing sample for the monomer solution with 10% of initiator. Thus, surface velocity is one of the parameters of the method allowing to control L .

From the viewpoint of practical applications, L can be considered as a parameter characterizing the spatial resolution of the technique. It can be explained as follows: suppose that the gradient has to be formed over distance H . Obviously, L should be less than H , because the concentration of an additive will be constant in the liquid layer L due to intensive convection. Thus the smaller L is, the easier it is to create a gradient over a short distance.

Increasing the reactivity of the system with amount of initiator will also change the liquid layer thickness. Namely, the liquid layer thickness for the more reactive solution with 10% of initiator is smaller than for the less reactive solution with 5% of initiator for the same surface velocity (Fig. 6). Qualitatively it can be explained that for the same surface velocity, the front propagates faster and by this reason it will stay closer to the free surface of the monomer.

Dynamic Range for Ascending Front Propagation

Unlike for descending fronts, where no more than one front velocity can exist for a particular chemical composition, a range of surface velocities supporting fronts can exist for the ascending mode, which we call its dynamic range. This range of surface velocities was determined experimentally for different initiator concentrations (Fig. 7). For velocities slower than $(v_s)_{\min}$, the front could not propagate because of heat loss from the free surface. For velocities faster than $(v_s)_{\max}$, the front could not propagate because of the quenching effect of convection in the liquid layer. Obviously, the ascending front could propagate for any value of surface velocity in the range between $(v_s)_{\min}$ and $(v_s)_{\max}$. The dynamic range becomes more narrow with decreasing initiator concentration because the reactivity of the system decreases.

Dye Gradient Formation

Polymer samples with a hyperbolic gradient of dye concentration were prepared by the method developed as promising materials for optical limiters. The intensity of the sample's color depends on the dye concentration, so the plot of gray level corresponds to dye distribution in the sample (Figs. 8 and 9). The formula for the programmed gradient was $C(x) = a/x + c$, where x equals distance, c equals 0.03, and a equals 6.8 for the plot on Figure 8a; a equals 3.4 for the plot on Figure 8b, and a equals 1.7 for the plot on Figure 8c. All defects seen on Figure 9 are surface ones. A great number of the defects at the bottom side of the sample (left side) were caused by overheating.

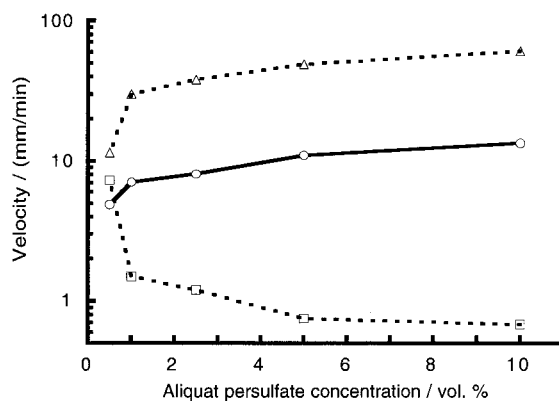


Figure 7 Dynamic range for the ascending front propagation. (—○—) front velocity of the descending front; (---△---) $(v_s)_{\max}$; (---□---) $(v_s)_{\min}$. Experimental error is not bigger than size of the symbols.

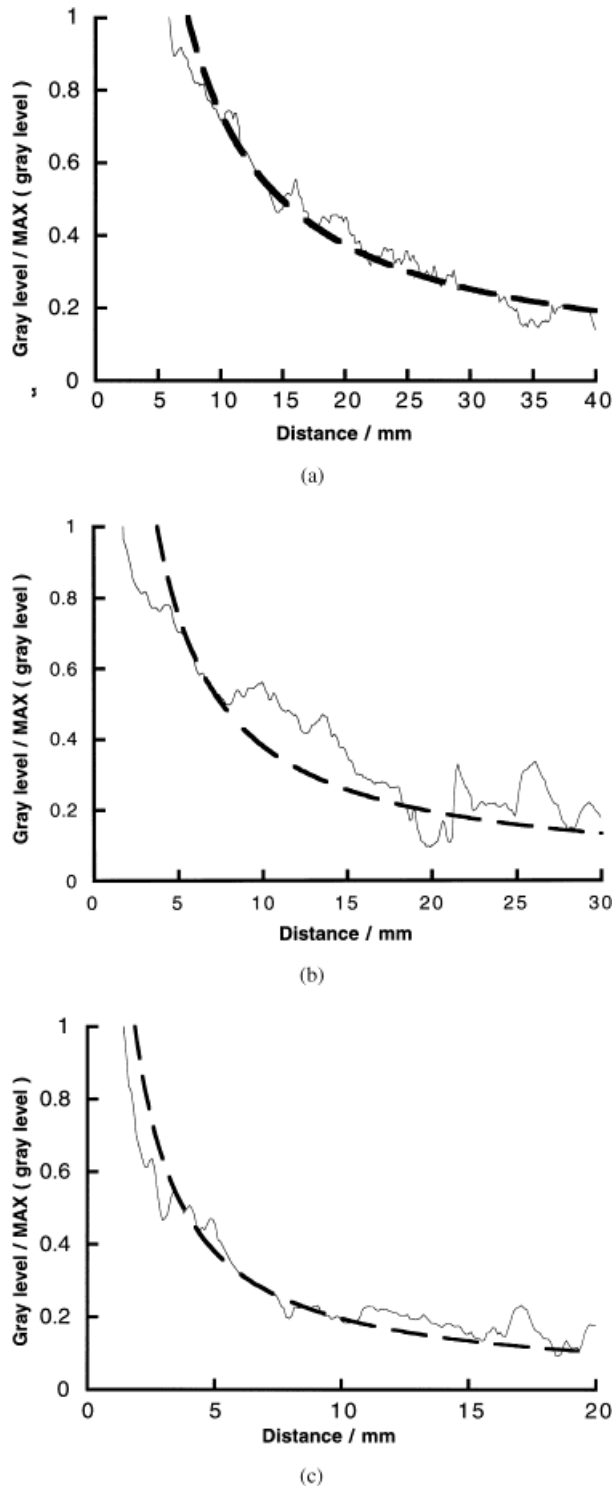


Figure 8 TGDMA with 5% of initiator. Gray level plots show hyperbolic dye distribution in the three different samples. Solid thin line is experimental measurements. Dashed thick line is preprogrammed dye distribution. Surface velocity for all three samples was 18.9 mm/min. $C(x) = a/x + 0.03$; (a) $a = 6.8$; (b) $a = 3.4$; (c) $a = 1.7$.

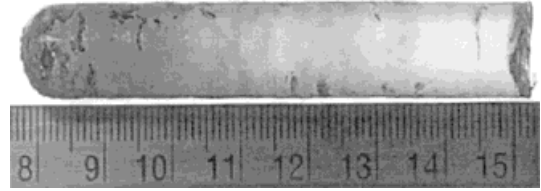


Figure 9 Polymer sample with hyperbolic dye gradient along the axis corresponding to plot on Fig. 8b. Numbers on ruler correspond to centimeter divisions.

ing of the polymer at the moment of front ignition. Surface defects are the main reason for the scattering of gray level measurements in Figure 8, but the created dye distribution matches the programmed distribution reasonably well.

The developed method was also used to create a polymer sample with a gradient of monomer composition. To accomplish this one of the pumps supplied solution of TGDMA with initiator and another pump supplied solution of benzyl acrylate with initiator. The procedure for creation of the compositional gradient was the same as for making gradient of dye except for benzyl acrylate with initiator was supplied instead of dye solution in TGDMA. Mechanical properties as well as cross-link density varied along with composition in the sample, although precise characterization was not performed. As a matter of fact different types of composition variations from many polymers can be created by this method.

CONCLUSIONS

1. A new method was developed to create different types of property gradients in polymers on the macroscale.
2. The use of frontal polymerization in the method allows to implement process continuously and utilize heat from polymerization reactions and so avoid energy-consuming external heaters.
3. Ascending front propagation in a body with a moving boundary is a steady-state process within the determined dynamic range.
4. A hyperbolic gradient of optical dye has been created in polymer samples over a distance of several centimeters.
5. Dye distribution matched satisfactory well-programmed distribution in the samples, although all samples had minor surface defects.

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