An Optical Sensor for Polymer Injection Molding

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ABSTRACT

An optical sensor using fiber optics to access the mold cavity was used to monitor the mold filling and cooling phases of injection molding. The sensor consists of a sapphire window at the end of a sleeved ejector pin into which an optical fiber is inserted. For the application presented here, the molded product was a tensile specimen 16 cm in length by 3.175 mm (1/8") thick. The optical view with this sensor is through the thickness of the molded product. The measured optical signal was either from a fluorescent dye that was mixed with the resin or from light that was transmitted through the resin, reflected off the opposite wall of the mold and retraced its path through the resin to the optical sensor. Both modes of sensing have been used to monitor molding of polyethylene, polystyrene and polypropylene during the packing and cooling phases of the process. Shrinkage of the molded product to dimensions less than the mold cavity can also be monitored because, when the product separates from the wall of the mold, the geometry of a Fabry-Perot interferometer is created. Interference fringes map the product shrinkage. Sensor behavior is described quantitatively by a processing model that includes a solution to the thermal diffusion equation, crystallization and glass formation kinetics, light transport properties, and principles of interferometry.

INTRODUCTION

The primary objective of our sensor development program for injection molding monitoring is to detect significant events in the mold cycle such as mold filling, the onset of resin solidification, and product shrinkage, and to characterize the resin properties such as temperature and crystallinity. To do this, we have employed ultrasonics, pressure, and optical sensors. In this paper, we describe an optical sensor and its application to real-time monitoring of injection molding and we review and summarize previous work.¹⁻⁴ Our work with ultrasonics sensors will not be discussed here, but is described in a previous publication.⁵

EXPERIMENTAL PROCEDURE

Access to the mold cavity is accomplished by utilizing the ejector pin channel as shown in Figure 1. The sensor consists of a bundle of optical fibers which is inserted into a sleeved ejector pin with a sapphire window at its end.

The optical fibers view the resin through the sapphire window that is placed flush with the mold cavity surface. The bundle of optical fibers contains nineteen 100 μ m diameter fibers, six of which transmit light to the resin and thirteen of which collect the light signal. The molded product was a tensile specimen 16 cm in length by 3.175 mm (1/8") thick. The measured light is either light reflected from surfaces of the mold cavity and the product or it is fluorescent light from a fluorescent dye that has been mixed with the resin at dopant levels of concentration (less than 10⁻⁵ mass fraction of the dye in the resin). Both measurement methods have been employed to monitor injection molding of polyethylene, polystyrene and polypropylene.¹⁻⁴

Also shown in Figure 1 is a pressure sensor for monitoring the mold cavity pressure. This measurement is an essential complement to the optical data because pressure data are needed to develop models of optical sensor behavior. Pressure causes several significant effects: it increases the rate of crystallization; it increases the glass transition temperature; and, it produces compression heating.

Three resins were used in these studies, high density polyethylene (Phillips Marlex TR885) whose density crystallinity is 0.73 after molding, polystyrene from Fina Corp., PS 525P1, and Himont PD701 polypropylene from Montel Polyolefins.⁶

Fluorescence monitoring was employed during molding of polyethylene and polystyrene. Two temperature sensitive fluorescent dyes, whose molecular structures are shown in Figure 2, were used. Dimethylamino diphenyl hexatriene (DMA DPH), a molecular rotor dye was used for polyethylene. Bis-(pyrene) propane (BPP), an excimer producing dye, was used for polystyrene. Both dyes were obtained from Molecular Probes Inc.⁶ DMA DPH was chosen as the dopant in polyethylene because of its sensitivity to temperature, and BPP was chosen for polystyrene because, as a large molecule, its molecular dynamics are greatly impacted by the rubber to glass transition. The photochromic behavior of these two dyes has been described in the literature.^{1, 7, 8} DMA DPH is called a mobility dve because its fluorescence radiation is controlled by its intramolecular rotational motion, i.e. fluorescence is modulated by the mobility of the dimethyl amino end group. Excitation energy is either released as fluorescence radiation or as intramolecular rotational motion of the end group. As temperature increases, the mobility of the end group is enhanced resulting in reduced fluorescence. Fluorescence intensity If can be expressed as

$$I_{\rm f} = D^{\eta} /_{T} \tag{1}$$

where D is a constant, η is a molecular microviscosity in the neighborhood of the dye and T is temperature.

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For BBP, an excimer state is produced when the two pyrene rings are positioned in close molecular contact. Excimer fluorescence is observed in the wavelength range from 450 nm to 550 nm and will increase in intensity with increasing temperature because of increased intramolecular rotation mobility that enhances excimer formation. BPP data are usually expressed as the ratio I_{ex}/I_m where I_{ex} is the excimer fluorescence intensity and I_m is the monomer fluorescence intensity of pyrene at 400 nm. The light source was a xenon arc lamp whose output was filtered at 400 nm for excitation of DMA DPH and at 345 nm for excitation of BPP. The fluorescence signal was detected using a photomultiplier tube connected to a photon counter.

Monitoring without fluorescent dyes has been done with semicrystalline polymers, notably polypropylene. In this case, the detected light is that which reflects from any interface at which there is a discontinuity in the index of refraction and from the opposite wall of the mold. Some of the light collected by the sensor will have traversed twice through the product thickness. Growing crystallites attenuate the light yielding a light versus time profile that reflects the crystallization kinetics. For the data reported here, the light source was a helium neon laser with power out put of 5 mw and the detector was a silicon photodiode. Increased sensitivity may be obtained by using a photomultiplier detector.

PREVIOUS RESULTS

Real-time processing data for polyethylene and polystyrene are shown in Figures 3 through 6 where we have presented both the fluorescence and pressure data. Time t = 0 corresponds to the instant of mold filling by the resin at the position of the optical sensor. Immediately thereafter, the resin began to cool and subsequent solidification of the resin is reflected in the I_f and I_{ex}/I_m versus time responses. For DMA-DPH doped into polyethylene, we observed that fluorescence intensity increased for the first 18 s as the resin cooled, then, for several seconds, hesitated, after which the intensity resumed its monotonic increase until the resin approached ambient temperature at long times. The short plateau at 18 to 20 s was attributed to an increase in temperature of the resin due to the heat of crystallization.

In the case of the BPP doped into polystyrene, we observed that, below the glass transition temperature T_g , the production of excimer fluorescence was reduced to zero within the sensitivity of our measurement. This is seen in Figure 5 at t \approx 14 s where the slope of the curve becomes zero. (The intensity values of Figure 5 are not zero for T < T_g because of a background signal which has not been subtracted out.)

Sensitivity to resin solidification is different in each case. DMA DPH responds to polyethylene crystallization because heat of crystallization raises the local temperature in the neighborhood of the dye molecules. BPP responds to the onset of the glass phase because the collapse of free volume inhibits the formation of the excimer state.⁹

Standard uncertainty in the measurements of fluorescence intensity of Figure 3 is 0.002; for I_{ex}/I_m the uncertainty is 0.001 and for the pressure measurements of Figures 4 and 6 it is 0.05 MPa.

Light transmission without a fluorescent dye was the method used to monitor polypropylene molding. Figure 7 shows transmitted light versus time for two mold cycles: (a) the polypropylene product crystallizes causing attenuation of the transmitted light but, upon cooling, does not shrink enough to separate from the mold wall, and (b) transmitted light attenuation is followed by a step function increase in detected light at t = 36 s and by fringes that result from the separation and shrinkage of the product away from the mold wall. The measured light intensity is light that has traversed through the mold and resin, reflecting from any surface at which there is a discontinuity in the index of refraction as well as from the opposite mold wall. These data are normalized with respect to the initial intensity at t = 0 at which time the mold cavity was empty. The standard uncertainty in the normalized intensity data is 0.005. Polypropylene resin was injected into the mold at 220 °C while the mold temperature was held constant at 38 °C by circulating water, where the standard uncertainty in the temperature measurement is 2 °C. Referring to Figure 7(a), the time of mold fill was clearly indicated by the abrupt drop in intensity at t = 4 s. Crystallization proceeded immediately and its effects were observed as a monotonic decrease in intensity from 4 s to 30 s. The distinct minimum in the curve at t = 27 s to 33 s is due to light scattering characteristics of the spherulitic morphology of the crystalline phase. Cavity pressure measurements, shown in Figure 8, correspond to the filling and packing phase of the data of Figure 7(a) and have an uncertainty of 0.05 MPa.

The data of figure 7(b) follow closely to that of 7(a) until a step function increase in intensity at 36 s marks the separation of resin from mold. A distinctive feature of the data of Figure 7(b) is the onset of an oscillatory signal, i.e. light fringes that develop when the molded product shrinks away from the wall or sapphire window thereby creating the geometry of a Fabry-Perot interferometer. By counting fringes it is possible to calculate product shrinkage and the rate of shrinkage.

DISCUSSION

The data of Figures 3 through 8 illustrate the breadth of information that can be obtained with this sensor. It is a multifunctional sensor that can be used to detect mold filling, to follow crystallization kinetics, to identify glass

formation, and to measure product shrinkage. In most cases, it is possible to qualitatively interpret the data, but in order to eliminate uncertainty about the significance of the observations, we have developed a mathematical model of sensor behavior. The model furnishes valuable insights about the process regarding conduction of heat from the resin, crystallization and glass formation kinetics, and effects due to pressure.

The model is composed of several modules, each applicable to a particular physical phenomenon that is expressed during the molding cycle.²⁻⁴ The modules are easily changed to accommodate changes in the resin or dye being used. Modeling starts with a solution to the thermal diffusion equation modified to include the effects of compression heating, the thermal resistance at the resin/mold interface, and, if needed, the heat of crystallization. The solution produces spatial and temporal arrays of temperature and crystallinity in the resin that are subsequently available for use in another module to calculate fluorescence intensity or light transmission. Finally, shrinkage and rate of shrinkage are calculated by another module of the model. A schematic of the model development is sketched in Figure 9.

Model for a semicrystalline polymer, polyethylene. The model that we have developed to describe monitoring of high density polyethylene (PE) is representative of the model description for semicrystalline polymers in general.

To simulate cooling in the mold, a one dimensional heat flow equation was solved. That is

$$\mathbf{r}C_{p}\frac{\P T}{\P t} = \nabla \cdot (\mathbf{k}\nabla T) = \dot{q}$$
⁽²⁾

where C_p is specific heat, κ is thermal conductivity and \dot{q} is the rate of heats generated by crystallization and by compression (adiabatic) heating and cooling, i.e.

 $\dot{q} = \dot{q}_c + \dot{q}_a$. $\dot{q}_c = \rho H_f \dot{\chi}$, where H_f is the heat of fusion and $\dot{\chi}$

is the time rate of change of crystallinity. $\dot{\chi}$ can be calculated from the Avrami equation,

$$\boldsymbol{c} = 1 - e^{-Kt^3} \tag{3}$$

where K is the Avrami rate constant.², 10, 11

 \dot{q}_a is created in the process by the application and release of

the packing pressure. In an adiabatic process, $\dot{q}_a = T\alpha \dot{P}$ where α is the volume thermal expansion coefficient.

The Avrami equation describes crystalline growth after crystal nucleation has occurred. We must specify the nucleation temperature in the model. Considerable supercooling of the PE melt is needed before nucleation occurs. At atmospheric pressure, we observed a nucleation temperature $T_n = 108$ °C. At elevated pressures, the melting temperature T_m and correspondingly T_n increase.¹² In our calculation, we assumed that T_n is a

linear function of pressure, $T_n = 381 \text{ K} + 0.6 \text{ (K/MPa)P}$, where P is expressed in MPa. An effect of the packing pressure is to increase the rate of crystal growth.

Boundary Conditions. The initial conditions for PE molding were a resin temperature of 200 °C and a steel mold temperature of 25 °C. The assumed boundary conditions were that the extreme outer edge of the mold (steel/air interface) is an insulating boundary and that, because of symmetry, the centerline of the resin at 1.587 mm (1/16 inch) is also an insulating boundary.

Another thermal boundary to be defined is the interface between resin and mold. Here we assume that the heat flux is continuous across this interface and that there exists a thermal resistance that impedes the transfer of heat from resin to mold. We describe the thermal resistance in terms of a thermal transfer coefficient h where h= $Q/\Delta T$. Q is the heat flux and ΔT is the temperature difference between resin and mold at the interface. Kamal and coworkers found that h was a function of time and could be expressed as an exponential decay.¹³ Thus,

$$h = h_o e^{-\overline{t}} + h_\infty \tag{4}$$

where $h_o=5h_{\infty}$ and $\tau=0.4$ s. For model calculations, h_{∞} was used as an adjustable parameter for fitting the calculations to experimental data, and was found to be $0.05~J/cm^2s^oC$.

Solution by Finite Differences. With the boundary and initial conditions cited above, equation (2) was solved by the method of finite differences for both the steel mold and the resin.¹⁴ The one dimensional path z was divided into 81 elements where elements 0 and 80 were at the resin/mold interfaces. The results are shown as temperature and crystallinity profiles in Figures 10 and 11. For calculated temperature/time profile, Figure 10, the data are shown for five equi-spaced positions in the resin from the skin (the resin/mold interface) to the inner core. The effects of compression heating and the heat of crystallization are readily seen. The skin temperature falls rapidly to the ambient temperature after a small increase due to heat of crystallization and the decrease in the value of h. The core temperature initially increases (compression heating) and then decreases to a plateau value of approximately 127 °C for 10 s. The plateau occurs because the heat of crystallinity that is generated by the crystallizing resin at positions closer to the skin impedes the transport of heat from the core. Upon crystallization of the core at 20 s, the core temperature drops relatively quickly to ambient temperature. The growth of the crystallinity is seen in Figure 11 where the calculation shows that the crystallization front proceeds from the skin to the core in approximately 20 s. We note that the calculations were carried out for a thermal transfer coefficient at the resin/mold interface of

 $h = 0.25e^{-t/.4} + .05 (J/cm^2 s^{\circ}C).$

The effect of varying h_{∞} is shown in Figure 12 where we have plotted average crystallinity versus time for a range of h_{∞} values. The lower the coefficient, the longer it takes to reach the final crystallinity of 73%. It is clear that h has a very marked effect on the elapsed time for crystallization.

(5)

Calculation of Fluorescence. Fluorescence intensity was calculated by summing the contributions from the 81 elements modified by the appropriate geometrical and attenuation factors. For the molecular rotor dye DMA DPH, fluorescence intensity is modified by the rotational motion of the dimethyl amino group and is proportional to the ratio of viscosity to temperature as indicated in equation (1). η depends on temperature according to

 $\boldsymbol{h} = \boldsymbol{h}_o e^{\frac{\Delta H}{RT}} \tag{6}$

where ΔH is the activation energy for DMA DPH in polyethylene which we measured to be

2.09 x 10^4 J/mole (5 kcal/mole) with an estimated standard uncertainty of 5%.

Light attenuation due to scattering by microcrystals in high density polyethylene is taken into account by considering two effects: (a) Scattering of light by growing spherulites which scatter light because of the difference in index of refraction between spherulites and the surrounding amorphous material, and (b) Scattering caused by microcrystals within the spherulites. Scattering due to growing spherulites in polyethylene was studied by Stein and co-workers who observed that scattering increases as the spherulite grows, reaches a maximum and returns to zero at the completion of crystallization.^{15, 16} Scattering becomes small at the end of crystallization because, at this stage, the spherulites are entirely volume filling, i.e., there is little amorphous material to offer a differential index of refraction. On the other hand, scattering by the microcrystals within the spherulites increases with crystallinity, and remains finite at the end of crystallization because the microcrystals are separated by interfacing amorphous material.

The Stein scattering function α is given as

$$\boldsymbol{a} = A(\boldsymbol{f}_s - \boldsymbol{f}_s^2) \tag{7}$$

where A is a constant that depends on polarizability of the scattering medium. From measurements on polypropylene, we estimated A = 45 cm⁻¹, but we found that the model calculations are insensitive to changes in A over a factor of 3. ϕ_s is the volume fraction of the spherulites. Attenuation

of the transmitted light $I_{t}\xspace$ can be expressed as

$$-\frac{dI_t}{dx} = \mathbf{a}I_t \tag{8}$$

We note that ϕ_s is not equal to crystallinity χ because spherulites contain amorphous material. For these

calculations, spherulite crystallinity was set equal to the specimen crystallinity, 73%.

Attenuation of light by high density PE is the result of diffusion-like photon transmission that results from multiple scattering and reflection of photons.² In the diffusive regime, light transmission is described by the function 1/z which is a solution to the steady-state Laplace equation. In the model, the transmission function is expressed as $1/(\chi(z)z)$, i.e., we consider the product $\chi(z)z$ to be the characteristic scattering length where $\chi(z)$ is the crystallinity at z.

Consideration of the above factors yields the following expression for fluorescence intensity from high density polyethylene of thickness d containing a molecular rotor dye,

$$I_f = B \int_0^d \mathbf{b} e^{-\mathbf{b}z} \cdot \frac{\mathbf{h}}{T} \cdot \left[C e^{-\mathbf{a}z} + \frac{(1-C)}{\mathbf{c}z} \right] \cdot \frac{A_o}{A(z)} \cdot \frac{A_b}{(z_o+z)^2} dz \quad (9)$$

Here, B and C are constants. The first term under the integral is the probability that excitation light is absorbed by a medium with absorption constant β ; the second term, n/T, is the molecular rotor dve modulation term as noted above; the third term is the light scattering attenuation factor that describes attenuation as the sum of Stein spherulite scattering plus attenuation due to light diffusion; α is the Stein scattering function and χ is crystallinity; the fourth term expresses the effect of excitation light divergence where A_0 is the cross sectional area of the excitation beam at z = 0 and A(z) is the cross sectional area of the excitation beam at position z; the fifth term depicts the collection efficiency of a fiber bundle with cross sectional area A_b for which light collection falls off as $1/z^2$; and z_0 is the thickness of the sapphire optical window.

The calculation of I_f , carried out numerically over the same finite element mesh as used for the calculations of Figures 10 through 12, is shown in Figure 13. The calculated and observed curves for

t < 18 s have identical shapes but differ in magnitude by 12% at the knee. The concave upward shape for t < 18 s is caused by a combination of adiabatic cooling, heat of crystallization, temperature and pressure dependent crystallization kinetics, and the functional form of the thermal transport coefficient h. The fit of the calculated curve to the experimental observations was optimized by using h as a fitting parameter. The optimum fit was achieved for h as expressed by equation (5).

Polystyrene. The same general procedure as was used for polyethylene calculations was used for modeling real-time fluorescence observations of excimer forming BPP in polystyrene. That is, we solved the heat diffusion equation in one dimension by the method of finite differences, and using the temperature arrays thus obtained, the ratio of excimer to monomer fluorescence I_{ex}/I_m was calculated.

Important factors incorporated in the model were volume viscoelastic relaxation and compression (or adiabatic) heating. The effect of compression heating was calculated as noted above, but adiabatic cooling effects were neglected because the rate of pressure release, as seen in Figure 6, was relatively slow.

As mentioned above, I_{ex}/I_m obeys the WLF equation at temperatures immediately above $T_g.^1$ The basis of the WLF dependence is the I_{ex}/I_m versus temperature plot of Figure 14 where the glass transition is indicated by the knee in the curve at 105 °C. The WLF dependence of the BPP data for T>Tg supports the view that intramolecular excimer formation follows the macromolecular dynamics of the polymer molecule. Thus, the BPP molecule must completely cooperate with the polymer dynamics in order to carry out its own motion. Monnerie and coworkers have published similar results using other resin/dye systems.¹⁷ Below T_g , the ratio I_{ex}/I_m was found to be insensitive to temperature because the glass state inhibits the formation of the BPP excimer.

Real-time processing data for polystyrene, Figure 5, shows the observed value of Iex/Im approaching the long-time plateau in a slow relaxation. The plateau, reached at 14 s, indicates that the resin is in the glass state. If we examine the temperature/time profile of the resin as calculated from the thermal diffusion equation, we note in Figure 15 that the temperature of the entire molded resin is below the glass temperature (105 °C) at 7.7 s. The difference between these two times can be accounted for by viscoelastic volume relaxation which controlled volume contraction of polystyrene as it cooled and also controlled the production of excimer fluorescence. While the temperature descended rapidly, volume changes were controlled by the slower molecular dynamics of the polymer in the vicinity of the glass transition temperature. Considering that Iex/Im obeys the WLF equation, it is not surprising that our observations show the effects of viscoelastic volume relaxation.

In order to include relaxation effects in the model, we consider that production of excimer fluorescence is controlled by the intramolecular rotational relaxation time τ of the BPP molecule. Excimer fluorescence and the ratio I_{ex}/I_m are proportional to the rate constant k of excimer formation or to the reciprocal of $\tau.^{18}$ We calculate I_{ex}/I_m by averaging over the q+1 elements for which k_i and τ_i are the rate constant and relaxation time of the ith element. We have

$$\left(\frac{I_{ex}}{I_m}\right)_{calc} = \frac{F\sum_{i=0}^{q} \left(1 / t_i\right)}{q+1}$$
(10)

where F is a constant of proportionality.

The manner in which k_i and τ_i depend on temperature, pressure and volume at the ith element can be described by

the model of Kovacs and coworkers who express τ of a glass forming polymer as a function of temperature, pressure and structure shift factors, a_T , a_p , and a_8 ¹⁹⁻²¹

$$\boldsymbol{t} = \boldsymbol{t}_o \boldsymbol{a}_T \boldsymbol{a}_P \boldsymbol{a}_{\boldsymbol{d}} \tag{11}$$

Here, a_{δ} describes the shift in relaxation times for relaxation to equilibrium from a non-equilibrium state, where the non-equilibrium state has been created by a temperature and/or pressure jump. The shift factors are expressed as

$$a_T = e^{-\boldsymbol{q}_T(T - T_{ref})} \tag{12}$$

 $a_P = e^{q_P P} \tag{13}$ and

$$a_{\mathbf{d}} = e^{\left[(1-x)\mathbf{q}_{P}\mathbf{d}/\Delta \mathbf{a}\right]} \tag{14}$$

where T_{ref} is a reference temperature, θ_T is a constant

associated with the activation energy of the process, θ_P is the pressure coefficient, $\Delta \alpha$ is the change in the thermal expansion coefficient at the glass transition, x is a material constant (x = .2 for polystyrene) and δ is the normalized deviation from equilibrium defined by volumes V(t) and V(∞), i.e.,

$$\boldsymbol{d}(t) = \frac{V(t) - V(\infty)}{V(\infty)}$$
(15)

 $\delta(t)$ can be calculated from

$$\boldsymbol{d}(t) = \int_{o}^{t} (-\Delta \boldsymbol{a} \, \boldsymbol{T} + \Delta \boldsymbol{k} \, \boldsymbol{P}) \boldsymbol{R}(t) dt$$
(16)

where T and P are the change in pressure and temperature with time and $\Delta \kappa$ is the change in compressibility at the glass transition. R(t) is a relaxation function defined as

$$R(t) = e^{-\left[\int_{t}^{t} dt/t\right]^{g}}$$
(17)

where γ is a constant of the Williams-Watts stretch exponential.²² From equations (14) through (17), we note that a_{δ} is a function of τ so that the calculation of τ for any in equation (11) implies density to show the strength of τ

for use in equation (11) involved an iteration technique.

For the calculation, the following constants were used: $\Delta \alpha = 0.00034 \text{ K}^{-1}$, $\beta = 0.5$, $\tau_0 = .01 \text{ s}$, $T_{ref} = 220 \text{ °C}$, and $\Delta k = 2\text{E-4} - 6.9\text{E-8P MPa}^{-1}.^{20}$ The pressure P was obtained from the data of Figure 6. In carrying out the fit to the data, the constant F of equation (10) was adjusted so that calculated and measured values matched at t = 0; also, a constant was added to account for the background. The resultant calculation is shown in Figure 15. θ_T and θ_P , which were used as adjustable fitting parameters, were found to have values 0.018 K⁻¹ and 0.022 MPa⁻¹ for the short-dashed curve. Because θ_T and θ_P complement each other, increasing θ_T and decreasing θ_P by 20% did not affect the quality of the fit. These values of θ_T and θ_P are lower than those obtained by Tribone et. al.,²¹ but their data was confined to T < 150 °C whereas our data extends

to 220° C. The long-dashed curve was calculated for $\dot{P} = 0$, i.e., pressure remains atmospheric throughout the process; the curve shows that the applied pressure causes volume compression and a decrease in the rate constant for formation of the excimer state. The model calculation reveals that the initial rapid decrease in excimer intensity was due primarily to the nearly stepwise buildup of pressure at t = 0.25 s (see Figure 6); the decrease in temperature played a secondary role here.

In this case, the calculation is not nearly as sensitive to the value of h as is the calculation for polyethylene. This is because h is a thermal parameter whereas BPP excimer fluorescence is primarily dependent on the volume state of the resin and the availability of free volume cells which are large enough to accommodate BPP photochromic activity. Pressure rather than temperature has the greater influence on the free volume of the resin and this is reflected in the calculation. We found that h_{∞} values in the range (0.04 to .15) J/cm²s^oC yielded satisfactory agreement with the data.

Polypropylene. The light intensity measurements of Figure 7 arise from the reflection of light from any boundary at which there is a discontinuity in the index of refraction. The data clearly show four events: the instant of mold filling at the sensor site; the crystallization kinetics of polypropylene; the separation of resin from the mold wall upon shrinkage; and, the development of fringes arising from resin shrinkage.

For Figure 7(a), a final intensity plateau was observed for t > 33 s, indicating the end of crystallization. Our model shows that the minimum at t = 30 s coincided with crystallization at the core of the resin product. From the shape of the curve near the minimum, we estimate that the duration of core crystallization was 6 s. From cavity pressure measurements, Figure 8, it is seen that core crystallization, for t > 26 s, proceeds at atmospheric pressure, and as a consequence, the rate of crystallization at the core is much slower than the rate of crystal growth near the skin.²³ It is this slow growth rate at the core in conjunction with the large size of core spherulites, greater than 20 μ m, that produce the clear manifestation of

Stein scattering. 15, 16

Also shown in Figure 7(a) is a calculated light transmission curve that was obtained from a model similar to that which was used for the fluorescence light calculation of Figure 13. The same scheme was followed, i.e. a solution to the thermal diffusion equation yielded temporal and spatial arrays of temperature and crystallinity that were then used to calculate light transmission through twice the thickness of the resin. As in the case for polyethylene, the scattering/transmission function for polypropylene contains two factors: scattering by the crystalline spherulites (Stein scattering) and scattering by the microcrystals within the spherulites. The transmitted light $I_{t}\xspace$ is given by

$$I_t = I_o e^{-\int_o^d [2\mathbf{a}(x) + 2\mathbf{b}(x)]dx}$$
(18)

where I_0 is the incident light intensity, and the factor 2 indicates that light has traversed twice the thickness. α is the Stein scattering parameter of equation (7) and $\beta = C \chi$ is a Beer's law attenuation factor proportional to crystallinity that describes attenuation due to microcrystals in the spherulites. C is a constant of proportionality. In contrast to 73% crystalline polyethylene, light transmission through 50% crystalline polypropylene is not diffusive, but obeys Beer's law. The calculated results are very sensitive to nucleation temperature and dependence of supercooling on pressure. Under rapid cooling and at atmospheric pressure, the nucleation temperature for polypropylene was 110 °C but increased to 121 °C for P=28 MPa. Thus. the nucleation temperature for crystallization at the skin was 121 °C and for the core it was 110 °C.24

Similar to the procedure used for polyethylene, the thermal barrier at the resin/mold interface was determined for polypropylene by using the thermal transport coefficient h as a fitting parameter for the calculated curve of Figure 7(a). We obtained h_{∞} =0.045 J/cm²s^oC, a value close to the polyethylene result of 0.05 J/cm²s^oC.

Shrinkage Model. In some cases, the volume contraction is large enough to cause separation between product and the mold wall as sketched in Figure 16 and expressed by the fringes of the light transmission data of Figure 7(b). The optical consequences of separation between mold and resin are reflections from air/sapphire, air/polymer and air/mold interfaces instead of the resin/mold and resin/window interfaces as diagrammed in Figure 16. Because the index of refraction differences are greater for the separated interfaces than for sapphire/resin or mold/resin, the reflected intensity is greater. The effect of resin/mold separation is seen in Figure 7(b) at t = 36 s where a large jump in intensity occurred.

Fringes occur in the data of Figure 7(b) immediately after separation because the separated resin and sapphire window (or resin and mold wall) are parallel surfaces that create the geometry of a Fabry-Perot interferometer. Light is reflected from both nearby surfaces, and the reflected beams interfere with each other. Since reflection from the surfaces is small, the effect of multiple reflections can be neglected. The inset of Figure 7(b) contains the data for t >36 s on an expanded scale. Three fringe patterns are seen: one of small amplitude between t = 36 s and t = 38 s, a slightly distorted pattern between 38 and 41 s, and a single mode pattern of larger amplitude for t > 41 s. We attribute this fringe pattern to the sequential separation of the mold and resin, first from one side of the mold at t= 36 s followed by separation from the other side at 38 s.

Figure 17 shows fringe data for polystyrene, polyethylene and polypropylene. We observe that the fringe amplitude fluctuates and there is clear evidence of beats in the oscillations. This was a common observation, although it was not present with every mold cycle. Beating phenomena occur when both product surfaces are separated but are moving at slightly different velocities, thus establishing a modulated interference pattern. If the two velocities are significantly different, greater than 50% different, then the fringe pattern is distorted with secondary and double peaks as seen in Figure 3 for 38 s < t < 41 s. The various fringe patterns that we have observed for all three resins of this study can be interpreted in terms of the relative times of the separation at each side and the velocities of the product surfaces as they move away from the window and wall.

The detected fringes can be interpreted by using two beam and multiple beam interference theory.²⁵ In general, reflections from all interfaces at which there is a difference in the index of refraction must be considered. Fringes will develop because of the relative movement of the resin surface with respect to the fixed position of the mold wall and window. Figure 18 shows a coordinate system for the most general case, i.e. for light transmitting through the resin, reflecting off the back wall, retracing its path through the resin to the detector, and reflecting from all intermediate interfaces. This is the situation for our experiments. The model calculation consists of adding the amplitudes of light waves for each reflection taking into account the appropriate phase of the light wave, the optical path length, the attenuation of light by the resin, the coefficients of reflection, and the phase change which occurs upon reflection.

The total intensity of the five reflected light beams shown in Figure 5 is

$$I_{tot} = \left[\sum_{i=0}^{4} A_i \cos(\frac{2p}{l}(ct - z_i) + q_i p)\right]^2$$
(19)

where z_i is the optical path length of the ith light beam, A_i is the amplitude of the electric field vector of the ith reflection, λ is the wavelength of light and q_i is 0 or 1 depending upon the phase change at the reflecting interface. The values of A_i will be determined by the reflection/transmission coefficients at the interfaces and by the attenuation due to the crystalline polypropylene. Reflection r at the interface between material with index of refraction n_1 and that with index n_2 is

$$r = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2} \,. \tag{20}$$

For polypropylene, polystyrene and polyethylene, n = 1.498, 1.559 and 1.532 respectively,²⁶⁻²⁸ and for sapphire n = 1.760. Although these are room temperature values of n, they will yield close agreement with our reflection observations because the change in n between 25 °C and the temperature at which resin/mold separation occurs, 60 °C to 80 °C (3,4), is less than 0.5%. The reflection coefficient at

the steel mold wall was measured and found to be 0.36 ± 0.05 for steel/air and 0.16 \pm 0.03 for steel/polymer interface. The large uncertainty in these values arises from the difficulty measuring reflections at surfaces which are not optically polished. The attenuation coefficient for transmission through 3.175 mm (1/8 inch) of resin material was measured to be 0.32 ± 0.01 for 50% crystalline polypropylene, and 0.33 ± 0.01 for 73% crystalline polyethylene.

Application of equation (19) to the sensor measurement is greatly simplified because of low coherence in the incident light. The coherence of light exiting the laser is severely compromised while transmitting through the multimode optical fibers of the sensor. The model calculation (see below) supports our assumption that coherence exists only for reflections from near surfaces with optical path differences (z_2-z_1) and (z_4-z_3) , i.e. only the cross terms I_{12} and I₃₄ of equation (19) are considered significant, and all other cross terms are neglected. In addition, the cross term amplitudes, A1A2 and A3A4, are reduced by an order of magnitude from those calculated from the reflection coefficients. The model calculation will demonstrate that the lack of coherence works to our advantage. If we include all cross terms, then a very complicated interference pattern results.³

Retaining only $I_{12} \mbox{ and } I_{34}$ of the cross terms, equation (19) reduces to

$$I_{tot} = \sum_{i=0}^{4} A^{2} + 2(A_{1}A_{2} + A_{3}A_{4})$$

$$\cdot \cos\left[\frac{2p}{l}(L_{o} - (z_{3} - z_{2}))\right]$$

$$\cdot \cos\left[\frac{2p}{l}(z_{3} + z_{2} - 2S_{o} - L_{o})\right] \qquad (21)$$

where S_o is the thickness of the sapphire window and L_o is the thickness of the mold cavity. The argument of the first cosine contains the shrinkage, L_0 -(z_3 - z_2). The argument of the second cosine term is constant if the two surfaces move with the same speed in opposite directions, because z_2 will increase by as much as z_3 decreases. Under these circumstances, the period of equation (21) is twice that of the period for the simple interferometer with only two separating surfaces. This means that the displacement associated with two adjacent minima in the fringe pattern is λ for equation (21) rather than $\lambda/2$. The change in period is the result of two interferometers operating in tandem when both surfaces of the resin are separated from the mold. As long as fringes generated by the two interferometers maintain a constant phase relationship, then a simple fringe pattern with λ displacement between fringe minima results. If, however, the velocities $v_2 = dz_2/dt$ and $v_3 = dz_3/dt$ are slightly different in magnitude, then the second cosine term of equation (21) imposes a beat modulation on the fringe

pattern. This is the source of the beating phenomena that we observed. If the difference in magnitude between v_2 and v_3 becomes larger than 50%, then secondary minima appear, a situation that we have observed occasionally such as in Figure 7 (b) for t between 38 s and 41 s. Because of the symmetry of the mold dimensions, one would assume that the shrinkage is symmetric and that both surfaces move at the same rate. Our observations indicate that this was only approximately true. When we observed a beating pattern, the velocities of the two surfaces usually differed by no more than 15% when the data were analyzed using equation (21). On the other hand, if only one side of the resulting fringe pattern will be associated with $\lambda/2$ displacements and no beating pattern will be observed.

For polystyrene, we often observed fringe patterns modulated into beat packets as seen in Figure 17. To analyze the polystyrene data, the reflection coefficients were calculated using n = 1.5588 and we assumed that light attenuation by polystyrene was zero. During several dozen injection cycles for polystyrene, we did not observe multistep separation response as we did for polypropylene. Thus, we assumed that both sides separated simultaneously. Application of equation (21) yields the calculated results shown in Figure 19 where the calculations were carried out assuming $v_3 = v_o e^{-t/t}$ where $v_o = -1.0 \ \mu m/s$, $\tau = 15 \ s$, and assuming that $v_2 = -1.025v_3$ and $v_2 = -1.1v_3$, i.e. the relative velocities of the two surfaces differ by 2.5% and 10%. The 2.5% relative difference is in close agreement with the observed data of Figure 7 (b). The calculation for 10% difference (Figure 19) shows how the beat pattern changes at higher relative velocities.

In order to calculate shrinkage, a determination must be made that one or both surfaces have separated from the mold. If only one surface has separated, then $\lambda/2$ is used as the displacement for adjacent fringe minima, but for both surfaces separated, λ is used for the corresponding displacement. The intensity jump upon separation can be used to establish that one or both surfaces are separated as we determined for polypropylene. Also, if the fringe pattern is modulated into beats, then it can be assumed that both surfaces have separated. Using a computer program developed to count the minima of the observed intensities, we carried out measurements of shrinkage for polyethylene, polystyrene, and polypropylene. Figure 20 shows typical results and shows that the shrinkage of the amorphous polymer, polystyrene, is much smaller than that of the semicrystalline polymers, polyethylene and polypropylene. Comparison of the absolute shrinkage values is not appropriate because the total shrinkage will be a function of the processing conditions, particularly packing pressure and mold temperature. To date, we have not carried out a systematic study of shrinkage and its relationship to processing parameters.

An evaluation of the uncertainty of the shrinkage measurement is problematic for two reasons: (a) using monochromatic light, an accurate shrinkage measurement depends on confident acquisition of the first fringe, and (b) we must determine that one or both sides have separated in order to assign the appropriate displacement associated with each fringe event. If we assume that we have accurately acquired the first fringe and that we have determined that one or both sides have separated, then the uncertainty in the shrinkage measurement is conservatively stated as $\lambda/2$ or 0.317 um.³

CONCLUSION

The experiments that we have described here demonstrate the broad versatility of the NIST optical sensor for injection molding. We have used it to detect mold filling, resin solidification by crystallization or glass formation, crystallization kinetics, volume viscoelastic relaxation in glass forming resins, heat transfer characteristics, separation from the mold wall due to shrinkage, shrinkage and the rate of shrinkage. The observations were carried out in both the fluorescence and non-fluorescence mode. Using fluorescent dyes, it is possible to gain insight into resin molecular dynamics, as was done for BPP doped into polystyrene. Our understanding of sensor behavior is greatly enhanced by the process model. For example, the model yields valuable insight regarding the role of pressure in solidification process. In glass forming resins, applied pressure combined with decreasing temperature push the resin into the glass state in a quench-like process that is much faster than molecular dynamics will allow the volume contraction to proceed. For crystallizable resins, applied pressure causes the rate of crystallization to increase.

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FIGURE CAPTIONS

- 1. A sketch of the optical sensor situated in the mold.
- 2. (a) The fluorescent dye bis-pyrene propane is shown.(b) the structure of dimethyl amino diphenyl hexatriene is

shown. The arrows indicate mobility about the chemical bonds.

- 3. Real-time monitoring data of fluorescence intensity versus time are plotted for polyethylene doped with DMA DPH.
- 4. Cavity pressure corresponding to the polyethylene data of Figure 3 is shown.
- 5. Real-time observations of I_{ex}/I_m are plotted for polystyrene doped with BPP.
- 6. Cavity pressure corresponding to the polystyrene data of Figure 5 is shown.
- 7. (a) Transmitted light intensity versus time is plotted for polypropylene molding. (b) Transmitted light intensity versus time is plotted for polypropylene molding for the case of product separation from the mold wall.
- 8. Cavity pressure corresponding to the polystyrene data of Figure 7(a) is shown.
- 9. The scheme for the model development is shown.
- 10. Calculated temperatures versus time are plotted for polyethylene for five equi-spaced positions between skin and core.
- 11. Calculated crystallinity versus distance into the polyethylene product is plotted for a series of times after injection.
- 12. The calculated average crystallinity for high density polyethylene is shown for a range of thermal transport coefficient h_{∞} values from 0.015 to 10 J/cm²s^oC.
- 13. The fit of the calculated fluorescence to the observed data is shown. The best fit was obtained for $h_{\infty} = 0.05 \text{ J/cm}^2 \text{s}^{\circ}\text{C}$.
- 14. I_{ex}/I_m is plotted versus temperature for polystyrene at atmospheric pressure.
- 15. I_{ex}/I_m calculated using KAHR model relaxation parameters is plotted versus time and compared to the real-time data of Figure 5. Short-dashed curve: calculated for optimum fit; long dashed curve: calculated assuming that pressure is atmospheric.
- 16. Light transmission and reflection from interfaces in the mold are depicted.
- 17. Real-time observations of fringes from molding of polyethylene (PE), polypropylene (PP), and polystyrene (PS) are shown.
- 18. The electric vector amplitudes A_i and coordinates z_i .
- 19. Calculated fringe patterns for polystyrene showing beat phenomenon are plotted for front and back surface velocities that differ by 2.5% and 10%.
- 20. Measured shrinkage for polyethylene, polypropylene and polystyrene is plotted versus time after separation from the mold.









(b)

Figure 2.



Figure 3.



Figure 4.



Figure 5.



Figure 6.



Figure 7(a)













Figure 10.



Figure 11.



Figure 12.



12

Figure 13.



Figure 14.



Figure 15.





Figure 16.



Figure 17.







Figure 19.



Figure 20.