PROCESS MONITORING AT THE NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY: CELEBRATING 100 YEARS OF MEASUREMENT EXCELLENCE

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Abstract

Two events that coincide in the year 2001 are the NIST centennial year anniversary and the inauguration of the SPE Special Interest Group on Process Monitoring and Control. To celebrate these two events, this paper will highlight polymer process monitoring activities at NIST describing the full range of measurement and sensor developments for real-time monitoring of resin temperature, rheology, morphology, molecular orientation, and dielectric properties of polymers, filled polymers and polymer blends.

Introduction

A prerequisite for process understanding, process modeling and process control is process measurement. In order to control a process parameter, it must first be measured. Also, in order to ascertain that a controlled parameter is actually under control, it must be measured. The route to improved product quality and productivity is through measurement, particularly real-time monitoring of important process parameters. In most processes, temperature is the most important processing parameter because temperature plays a fundamental role in determining flow characteristics, degradation phenomenon, phase transitions, and morphology of the final product. Temperature alone, however, does not yield enough information to model the process and/or to predict product performance. Ideally, one would obtain a multiplicity of information from different on-line sensors to measure parameters such as pressure, molecular orientation, degree of mixing, morphology, viscosity and strain rate.

Each sensor has its assets and shortcomings. But, working in concert, a group of sensors can yield a critical mass of information that will be the basis for process model development. Such has been the objective of the NIST program on process monitoring. A large concentration of our effort has centered on the development of optical sensors using fluorescence, microscopy and light scattering. Ultrasonics and dielectric sensors have also been employed. In some applications we have used a sensor as a stand alone unit for which the lack of concurrent information from other sensors was readily apparent.

This paper will summarize ongoing sensor development, process monitoring, and process modeling and demonstrate the importance of the integration of different process sensors.

Experimental Procedure

Sketches of sensor designs are shown in Figure 1. They fall into two categories. Type A uses optical fibers in conjunction with a sensor head that contains lenses, windows or polarizing optics. It is designed to insert into a machine instrument port. The optical fibers transmit light between the light source, sensor head, and detector. Type B is a unit that is fixed in-line on an extrusion machine and uses direct illumination and collection of light without optical fiber interfaces. We have used type A sensors to monitor extrusion and injection molding. In conjunction with fluorescent dyes that were mixed with the resin, type A sensors have yielded real-time temperature, temperature profiles, light transmission, crystallization kinetics, viscoelastic relaxation, and molecular orientation data.[1-4] Type B sensors have been used to obtain velocity profiles, strain rate, morphology, light scattering from particulate, and phase transition data.[5, 6]

In Figure 1, the sensor bolt with confocal optics is a standard half-inch bolt that can be inserted into instrumentation ports on extrusion machines. It is used to obtain profiles of materials properties across the resin flow stream. By virtue of the confocal design, optical signal is detected only from the point of focus, and, by varying the distance of the focus from the end of the sensor bolt, a profile can be obtained.[2]

The anisotropy sensor employs polarization optics to interrogate the resin with polarized incident light and to analyze the polarization character of generated fluorescence. Fluorescence anisotropy is a measure of molecular orientation of the fluorescent dye which, under extensional stress, is known to orient with the resin matrix. Under these circumstances the fluorescence anisotropy orientation factors correspond to resin orientation. The sensor head is also equipped with optical fibers for collecting fluorescence and subsequently analyzing its spectral content to obtain a temperature measurement simultaneously.[7]

Two type B sensors, the slit die with optical windows and the sapphire capillary die, have been used extensively to observe resin flows with optical microscopy and light scattering. The emphasis is on measuring rheological conditions, morphology and morphological transitions in polymer blends. With these observations it is possible to correlate relative viscosity and interfacial adhesion with morphology and processing conditions. Recent experiments using the sapphire capillary die have elucidated the functionality of

processing aids that suppress the onset of shark shin in the extrudate.[8]

Fluorescent dyes have played a prominent role in our sensor development and process monitoring. They are mixed with the resin at dopant levels of concentration, less than 10^{-5} mass fraction of dye in the resin. The dyes fall into two categories: molecular rotor dyes and band broadening dyes. Bis-pyrene propane (BPP) and dimethyl amino diphenyl hexatriene (DMA-DPH) are examples of molecular rotors. Perylene, benzoxazolyl stilbene (BOS), and bis(di-tert-butylphenyl)-perylene dicarboximide (BTBP) are band broadening dyes. The fluorescence of molecular rotors is modulated in accordance with the degree of internal rotational motion of the molecular constituents. The behavior of band broadening dyes with respect to temperature or applied stress is quantum mechanical in origin. All of the dyes listed above can be used as temperature probes. BTBP and BOS have large geometrical asymmetry and are candidates for fluorescence anisotropy applications because they will readily orient with extensional stress. BPP has large photochromic volume activation associated with the sweeping motion of the pyrene rings that we have utilized to observe volume viscoelastic relaxation during injection molding of polystyrene.[1, 9] The molecular structures of two dyes, DMA-DPH and BTBP, are shown in Figure 2. These dyes were used in applications discussed below. The arrow on DMA-DPH structure indicates rotational mobility of the dimethyl amino end group.

Observations from one sensor alone will not yield enough information to understand or model a polymer process. At the very least a combination of accurate temperature T and pressure P data are needed. At low to moderate shear rates, T and P data in combination with an equation of state equation will completely define the system. However, in many cases, such as polymer blends and filled polymers, the equations of state are not known. Filling the knowledge gap requires additional monitoring that is determined by product specifications; for example, light scattering and microscopy to yield morphological information, dielectric measurements for electrical properties, and ultrasonics measurements for mechanical properties. Rheological properties require dedicated instruments to measure stress and strain rate.

Consider the case of fluorescence anisotropy measurements. Incident polarized light creates fluorescence that is analyzed for its polarization character. To carry out this measurement a frame of reference for defining polarization direction must be established. For polymer processing this is usually the machine and transverse directions. Anisotropy r is defined as

$$r = \frac{I_{vv} - I_{vh}}{I_{vv} + 2I_{vh}} \qquad (1)$$

where I_{vv} and I_{vh} are respectively vertically and horizontally polarized fluorescent light that are produced by vertically polarized excitation light. Published molecular models develop the relationship between equation (1) and the orientation of the absorption dipole moment of the dye.[10-12] In general,

$$r = f(\cos^2 q, \cos^2 f, \frac{t_f}{t_r}) \qquad (2)$$

where θ and φ are spherical coordinates and θ is the angle between the absorption dipole moment and the z or vertical direction, τ_f is fluorescence decay time and τ_r is the rotational relaxation time of the dye. If the ratio τ_f/τ_r is small, then the effect of the rotational motion of the dye can be neglected. However, the usual situation in molten polymers is that τ_f and τ_r are within an order of magnitude in value. Since τ_r is dependent on the viscosity (or temperature) in the molecular neighborhood of the dye, the anisotropy measurements need to be compensated for temperature changes. Concurrent anisotropy and temperature measurements are needed.

Currently, we are using an anisotropy sensor to monitor biaxial stretching of polypropylene films at temperatures near the crystalline melting point. The temperature of the process must be precisely controlled because at temperatures above the melting point, the film losses its integrity, but if the temperature is too far below the melting point, stretching is impossible. Measurement of the film temperature and control of that temperature are essential. The sensor sketched in Figure 1 is designed for simultaneous acquisition of temperature and anisotropy using the same dye. With this sensor, the specimen can be excited by either vertical or horizontal polarized light, so that biaxial orientations in the machine and transverse directions can be measured. The temperature measurement is obtained from the fluorescence spectrum by measuring the ratio of fluorescence intensities from BTBP at 544 nm and 577 nm.

Results and Discussion

Fluorescence Anisotropy. Figure 3 shows a fluorescence anisotropy area scan for polypropylene doped with BTBP that has been biaxially stretched having a stretch ratio of 4.5. The thickness of this material is approximately 0.3 mm. The scan is over an area of 40 mm by 50 mm of a plaque that is a precursor to a biaxially stretched film with 7.5 stretch ratio. This scan displays the condition of orientation in the middle of this process. Stretching stresses have been applied in alignment with the sides of the plaque. Dark colors at 45° are low anisotropy ($r \approx 0.2$) and lighter colors correspond to higher orientations and anisotropies ($r \approx 0.34$). These data were obtained at room temperature and did not utilize the fluorescence temperature capabilities that are being employed during real-time monitoring. The standard uncertainty of the anisotropy measurement is 0.005.

Injection Molding. We have done considerable work using an optical sensor for injection molding that accesses the mold cavity via the ejector pin channel (Figure 1). Fluorescence monitoring the molding of high density polyethylene doped

with DMA-DPH is shown in Figure 4. Zero time on this plot is time of mold fill at the position of the sensor. Polyethylene melt at 200 °C was injected under pressure into a mold whose temperature was maintained at 25 °C. Concurrent cavity pressure measurements are shown. Standard uncertainty of fluorescence intensity measurements is 1% and for pressure measurements it is 0.07 MPa. The increase in fluorescence intensity with time is due to the dye's response to decreasing temperature in the resin environment. For DMA-DPH, the rotational motion of the dimethyl amino end group becomes slower as temperature decreases allowing more energy to be dissipated as fluorescence radiation. A singular feature on this curve is the changes in slope that occur at 18 and 20 s. This is due to the heat of crystallization that is generated within the resin and delays the transfer of heat from resin to mold.

A quantitative interpretation of the data of Figure 4 required the development of a process model that takes into account effects due to applied pressure, the crystallization kinetics and the heat of crystallization. The model highlights the role that pressure plays in determining crystallization kinetics, compression heating and cooling, and crystal nucleation temperatures. The model calculations would be impossible without pressure data and thus, we see the advantage of using a combination of sensors to monitor the process.

The model is composed of several modules, each applicable to a particular physical phenomenon that is expressed during the molding cycle. 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 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. A schematic of the model development is sketched in Figure 5.

The calculated fluorescence intensity is obtained from an integration over the path of the excitation light beam weighted by effects due to light scattering, temperature of the dye, and geometrical factors associated with the divergence of the light beam and the collection aperture. Thus,

$$I_f = \int_0^d FLR(T) \cdot FLR(P) \cdot SCATT[c(z)] \cdot GEOM(z) dz \quad (2)$$

where I_f is fluorescence intensity, FLR(T) is the fluorescence intensity temperature dependence, FLR(P) is a pressure dependence factor, SCATT[χ(z)] is the light scattering effect caused by crystallization (χ = crystallinity) in the resin, and GEOM(z) is a function which describes the geometrical optics of light collection and divergence. Calculation of the integral was carried out using a one dimensional finite element summation, details of which have been published.

In summary, the NIST process monitoring program is based on multiple sensor development that recognizes the need for sensors that complement each other and provide a multi-dimensional information. From a broad database of information it is possible to achieve process understanding through the development of process models.

References

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Key words: process monitoring, fluorescence, injection molding, optical sensors

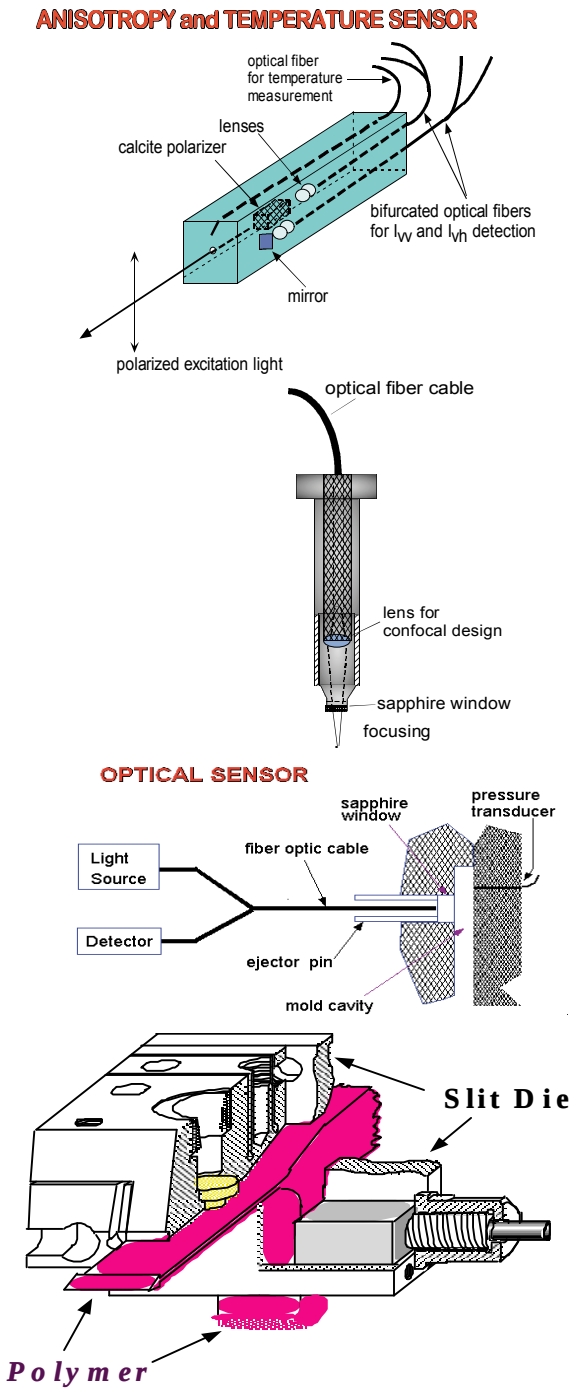
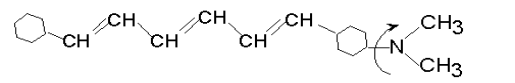
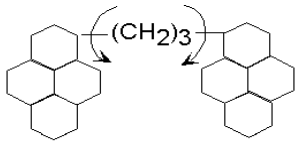


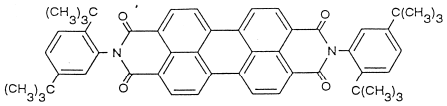
Figure 1. Four NIST designed sensors are shown. From top to bottom: anisotropy sensor with fluorescence temperature fiber optic; half-inch standard sensor bolt with confocal optics design; optical sensor for injection molding; and slit die with optical windows for microscopy and light scattering.



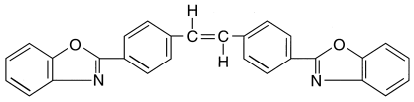
dimethyl amino-diphenyl hexatriene (DMA-DPH)



bis-pyrene propane (BPP)



bis(di-tert-butylphenyl)-perylene dicarboximide (BTBP)



benzoxazolyl stilbene

Figure 2. The molecular structures of fluorescent dyes

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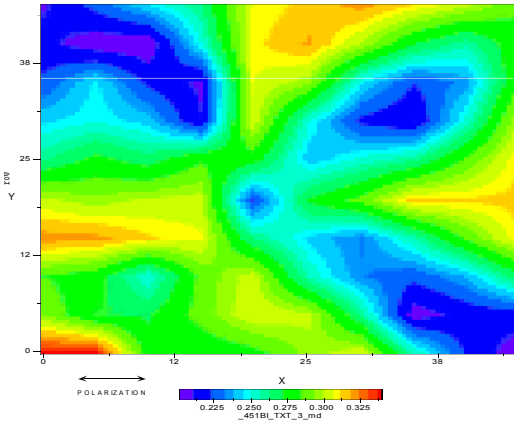
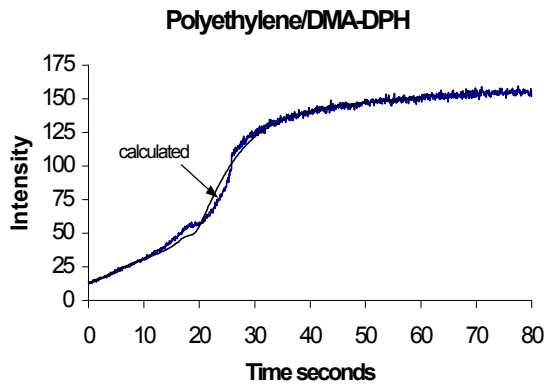
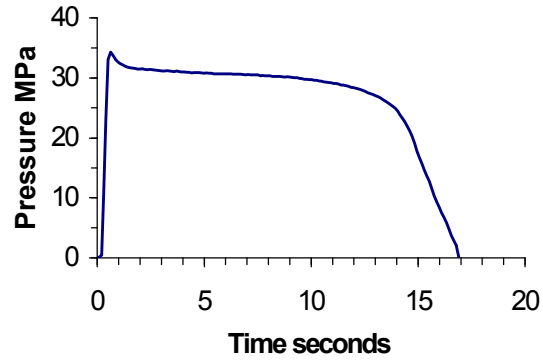


Figure 3. Anisotropy area scan for biaxially oriented polypropylene doped with BTBP.



(a)



(b)

Figure 4. Fluorescence monitoring of injection molding of polyethylene doped with DMA-DPH. (a) Calculated and measured fluorescence intensity versus time for the cooling phase; (b) cavity pressure versus time. Time axis on (a) and (b) plots is identical.

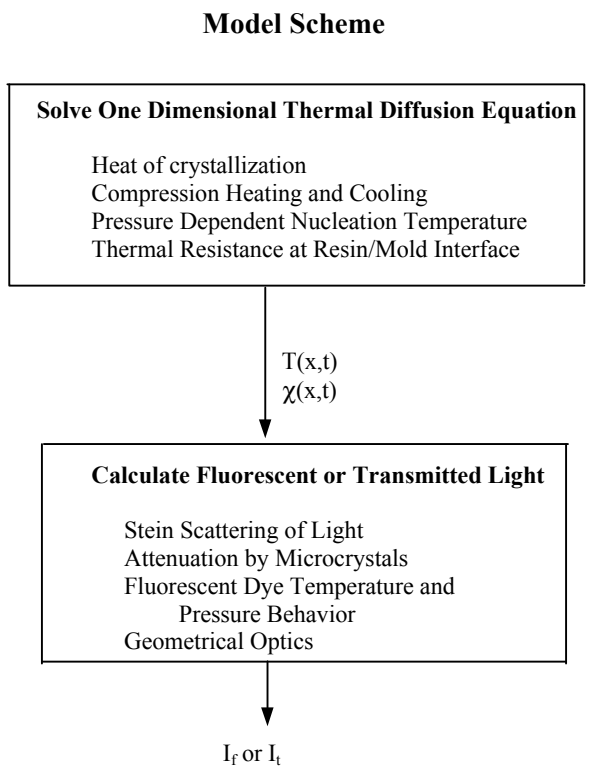


Figure 5. The model scheme for calculating fluorescence intensity during molding of semicrystalline polymers is shown.