

Fluorescence Temperature Measurements: Methodology for Applications to Process Monitoring

ANTHONY J. BUR* and STEVEN C. ROTH

*Materials Science and Engineering Laboratory
National Institute of Standards and Technology
Gaithersburg, MD 20899-8542*

In previous publications, we described a technique based on fluorescence spectroscopy to monitor resin temperature during processing. The method consists of using optical fiber sensors to monitor fluorescence from a fluorescent dye that has been doped into the processed resin. Temperature is derived from temperature-induced changes in the fluorescence spectrum. In practice, a temperature calibration function is obtained from the temperature dependence of the ratio of fluorescence intensities at two wavelengths. In this paper, we address several experimental design issues: (a) the supportive role of fluorescence anisotropy measurements to the measuring concept, (b) the experimental setup used for noncontact measurements during capillary rheometry testing, and (c) molecular-level environmental issues that arise during reactive processing and temperature profiling. We find that fluorescence anisotropy of the dye bis(2,5-tert-butylphenyl)-3,4,9,10-perylenedicarboximide (BTBP) is independent of shear rate up to 250 s^{-1} , implying that isotropic orientation of the dye is maintained as the matrix resin undergoes dynamic shear flow, i.e. the calibration function made under quiescent conditions applies to dynamic shear flow conditions. Using this technique in a noncontact application to monitor temperature of the extrudate from a capillary rheometer required an optical design that neutralized the focusing attributes of the cylindrical extrudate. Application to reactive processing is complicated by changes in polarization that accompany the reaction, and, in some cases, produce wavelength shifts in the fluorescence spectrum. We overcome these effects by using a dye that yields a calibration independent of the polarization effects and by averaging over a large dataset to reduce measurement uncertainty. *Polym. Eng. Sci.* 44:898–908, 2004. © 2004 Society of Plastics Engineers.

INTRODUCTION

In previous publications, we described a process monitoring technique for measuring resin temperature (1–4). The method, based on fluorescence spectroscopy, employs an organic fluorescent dye that is mixed with the resin at very low concentrations, less than 10^{-5} mass fraction of dye in the resin. At this low concentration, the dyes are soluble in organic resins and their presence does not affect the overall performance of the resin product. We use temperature-sensitive fluorescent dyes that are called band definition dyes because their fluorescence is characterized by distinct bands in specific wavelength regions (4). The intensities of the spectral bands are temperature-dependent, and this dependence is used

for real-time resin-temperature monitoring. The concept is portrayed in *Fig. 1*, where we have plotted fluorescence spectra for perylene doped into polycarbonate for temperatures ranging from 180°C to 295°C . *Figure 1b* shows a plot of the ratio of intensities at 466 nm and 476 nm versus temperature that is the basis for the temperature calibration. Similar results have been obtained from two other band definition dyes, benzoxazolyl stilbene (BOS) and bis (di-tert butylphenyl) perylenedicarboximide (BTBP). These three dyes were chosen for process-monitoring applications because they are stable at typical processing temperatures, up to 300°C .

The technique has been used to monitor resins during injection molding and extrusion, and we have shown how confocal optics can be used to measure temperature profiles (1–3). In this paper we examine several issues that pose potential problems for the application of the method. Results from three experiments are presented: (a) fluorescence anisotropy was measured as a function of shear rate in order to justify

*To whom correspondence should be addressed. E-mail: abur@nist.gov
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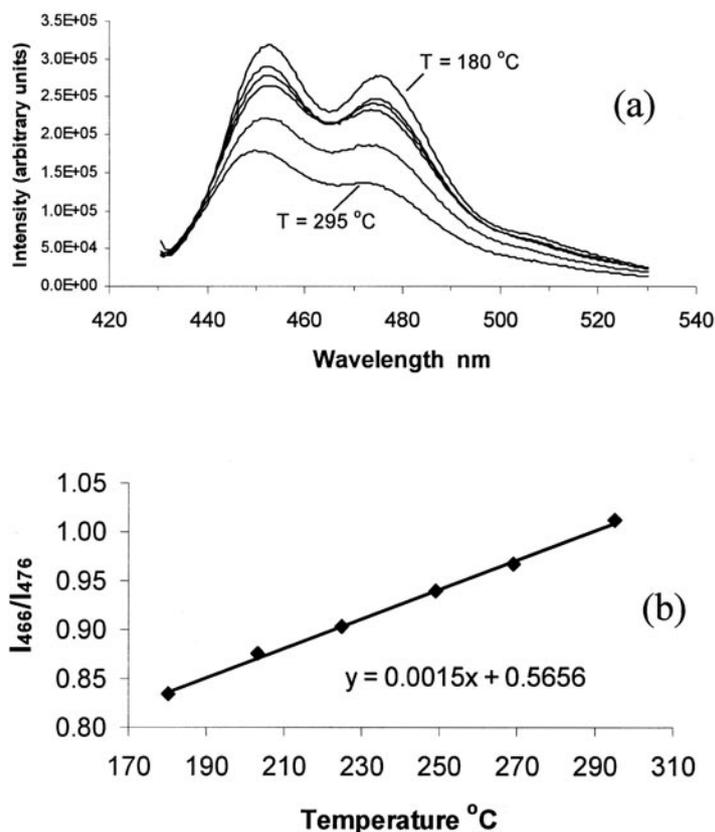


Fig. 1. Fluorescence intensity versus wavelength for perylene doped into polycarbonate at temperatures ranging between 180°C and 295°C. The inset is a plot of the ratio of fluorescence intensities at 464 nm and 473 nm versus temperature.

using a calibration function, obtained under quiescent conditions, to measure resin temperature under conditions of dynamic shear flow; (b) we discuss the details of the optics design for noncontact temperature measurements, and (c) we present results obtained during reactive extrusion to show that the method can be used in a molecular environment that changes its polarization.

Fluorescence Anisotropy. Fluorescence anisotropy measurements yield information about both orientation and molecular dynamics of the dye molecule (5–9). The measurement has been used to measure molecular orientation in polymer melts, and in solid polymer films and fibers. To measure fluorescence anisotropy, excitation light polarized with respect to a laboratory coordinate system is incident upon the resin sample and fluorescence emission is analyzed for its polarization. Fluorescence anisotropy, r , is defined as

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

where I_{vv} and I_{vh} are, respectively, vertically and horizontally polarized fluorescent light, which are produced by vertically polarized excitation light. In the experiments described below, v is the direction of resin flow during extrusion processing.

Orientation is defined by θ and ϕ angles of the dye absorption dipole moment where θ and ϕ are spherical coordinates of the laboratory reference coordinate system. Several authors have developed molecular models that yield a relationship between r and fluorescent dye orientation (10–15). This relationship is somewhat complicated involving the second and fourth moments of the cosine orientation factors. In general,

$$r_{cw} = f\left(\langle \cos^2\theta \rangle, \langle \cos^2\phi \rangle, \frac{\tau_f}{\tau_r}\right) \quad (2)$$

where r_{cw} is anisotropy measured with continuous illumination, τ_f is the fluorescence decay time and τ_r is the rotational relaxation time of the molecule. The term τ_f/τ_r appears because a molecule with small τ_r relative to τ_f will randomize its orientation before radiating fluorescence and, therefore, show no anisotropy. The ideal situation is $\tau_r \gg \tau_f$ for which the molecule is stationary while it fluoresces. Usually, $\tau_r \approx \tau_f$ for which some reorientation of the molecule occurs during fluorescence emission. Interpretation of r measurements must take into account temperature and pressure dependence of the τ_f/τ_r ratio.

In the special case of isotropic distribution of a freely rotating dye and when the excitation and emission dipoles are coincident in direction as is the case for BTBP, then,

$$r_{cw} = 2/5(\tau_f/\tau_r + 1)^{-1} \quad (3)$$

where the factor $2/5$ results from calculating the spatial averages of the Legendre orientation terms when orientation is random (16). r_{cw} will be reduced from 0.4 if the ratio τ_f/τ_r is significantly greater than zero, a situation that is demonstrated below.

Noncontact Temperature Measurements. Noncontact measurements involve the transmission of light across the free surface of a resin sample that, in general, will have curvature that focuses (or defocuses) the light. For example, we are engaged in a project to monitor temperature during capillary rheometry testing using a noncontact technique. This requires an optical design that neutralizes the focusing effects of the cylindrically shaped extrudate. Our approach is to deliver a focused fluorescence light beam through an aperture to photomultiplier detectors. We present data acquired from two extremes of free surface, a cylindrically shaped extrudate from a capillary die and a flat ribbon extrudate from a slit die.

Monitoring Reactive Processing. Another problem to be addressed here is fluorescence temperature measurements in a reactive processing environment. During reactive polymer processing, the polarization and the viscosity of the medium change as the reaction proceeds, which influences the magnitude of the Stokes shift of the fluorescence spectrum, i.e. the difference between excitation and emission wavelengths. Some researchers have utilized this effect to monitor the progression of epoxy curing (17). In our application, it is important that the ratio of intensities used to measure temperature be unaffected by polarization changes that accompany the reaction. Our approach has been to examine several dyes, searching each fluorescence spectrum for intensity ratios that depend only on temperature, and to modify the experimental procedure to accommodate polarization effects.

EXPERIMENTAL PROCEDURES¹

Materials. Three fluorescent dyes were used in this study: bis(2-benzoxazolyl) stilbene (BOS), perylene, and bis(2,5-tert-butylphenyl)-3,4,9,10-perylenedicarboximide (BTBP). They were chosen for polymer-processing applications because they can be used at processing temperatures up to 300°C. Their molecular structures are shown in Fig. 2. All three dyes were obtained from Aldrich Chemicals. We have also obtained BOS from Eastman Chemicals sold under the trade name Eastobrite. BOS is used in large-scale commercial applications, primarily as a whitener in detergents and as an additive in food and consumer packaging; it has a blue fluorescence when excited by the mercury line at 365 nm. The excitation wavelength for perylene

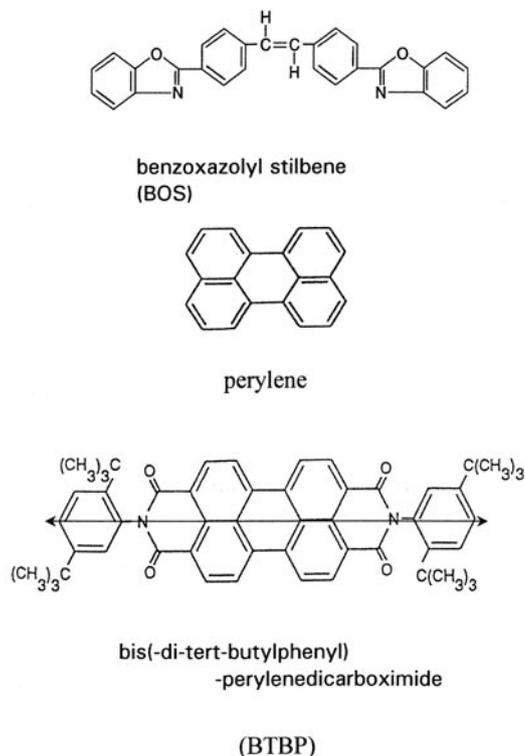


Fig. 2. The molecular structures of perylene, bis-benzoxazolyl stilbene (BOS) and bis (di-tert butylphenyl) perylenedicarboximide (BTBP).

is 405 nm, for BOS it is 365 nm to 370 nm, and for BTBP the excitation is 488 nm. BTBP was chosen for fluorescence anisotropy studies because of its geometric anisotropy. The arrow shown in Fig. 2 lies along the direction of the absorption and emission dipoles so that geometrical and fluorescence anisotropy are referenced to the same direction. Under applied extensional stress we have observed that the long axis of the molecule orients in the direction of orientation of the matrix polymer (5). In this paper, we report on its response in a polymer matrix (polyethylene) as the matrix is subjected to shear flow. All three dyes were used for temperature measurements, and in the case of BTBP, simultaneous measurements of temperature and anisotropy were obtained.

Two polymers were employed in our study: Polyethylene (type 640 I) that was obtained from Dow Chemical; and polyhydroxyl amino ether (PHAE), the product of reactive processing, which is a Dow Chemical product sold under the tradename BLOX. It is a linear epoxy that is used as a barrier resin. The chemistry, which involves reacting ethanolamine with diglycidyl ether of bisphenol-A (DGEBA), is described in Reference 18.

For the preparation of polyethylene doped with BTBP, a 5 kg batch of PE pellets was prepared by pouring a solution of dye (toluene solvent) over 25% of the pellets, allowing the solvent to evaporate, leaving behind BTBP coated pellets. The coated pellets were

¹ Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or imply that it is necessarily the best product for the experiment.

then tumble mixed with the other 75% of uncoated pellets so that the overall average mass fraction of dye in polymer was 5×10^{-6} . The PE pellets were used in extrusion experiments during which additional mixing of the dye occurred during screw translation in the extrusion machine. In the case of PHAE, the BOS dye was mixed with one of the reactants and fed into the twin-screw extruder at one of the feed ports. Mass fraction of BOS dye in the PHAE product was approximately 1×10^{-5} , twice as high as the recommended concentration of 5×10^{-6} mass fraction of dye in resin. This had an impact on the uncertainty in the measurement of the temperature profile to be described below.

Optics for Fluorescence Temperature Measurements (3, 4). The primary modules of the measurement apparatus, depicted in Fig. 3, are a light source that is either a laser or a xenon arc lamp, a bifurcated optical fiber cable, the optical sensor, and a light detector consisting of a monochromator with CCD detector or a beamsplitter (for separating spectra into different wavelength regimes) with filtered photomultiplier tube (PMT) detectors. For BTBP, an air-cooled argon ion laser tuned to 488 nm (Melles Griot) was used, and for BOS and perylene, a xenon arc lamp, filtered with 10 nm bandpass filters centered at 365 nm and 405 nm, respectively, was used for excitation. The sensor consists of a single bundle of fibers, which, upon exiting the sensor, are bifurcated into two bundles, one for carrying excitation light to the resin, and the other for transmitting fluorescence to the detector. For obtaining detailed spectra, the optical signal is sent to a monochromator with CCD detector. In order to maximize the rate of data acquisition during process monitoring, however, only the intensities at two wavelengths are monitored. This is accomplished by splitting the optical signal with a beamsplitter and filtering the two separated intensities with specific band

pass filters before PMT detection. For perylene, 5 nm band pass filters centered at 464 nm and 473 nm were used; for BOS, 10 nm bandpass filters centered at 420 nm and 436 nm were used; and for BTBP, 10 nm bandpass filters centered at 530 nm and 550 nm were used. In each case the bandpass filters were chosen in accordance with the temperature dependencies observed in the full spectrum for each dye.

The designs of the bifurcated optical fiber cables that are used in the half-inch sensor bolt² for extrusion and for the noncontact measurement are different. For the half-inch sensor bolt, the cable consists of nineteen 200 μm core fused silica fibers, of which six carried excitation light to the resin and thirteen carried fluorescence light to the detector. For noncontact measurements, the arrangement was: nineteen 200 μm core fibers—one fiber for excitation light and eighteen fibers for fluorescence collection. The single fiber for excitation light was positioned in the middle of the sensor head fiber bundle. This arrangement allowed precise control of the size and position of the focused excitation light, an important consideration for noncontact measurements.

Unless otherwise stated below, the standard uncertainty in the temperature measurements was 2°C using perylene and 3°C using BOS.

Half-Inch Bolt Sensor. Sensor access to extrusion machines is achieved using the standard half-inch diameter sensor port that is normally used for temperature and pressure sensors. For our application, the bolt is machined into a sleeve that can receive optical fibers and a focusing lens. A sketch of the sensor is shown in Fig. 4. The sensor design has confocal optics geometry that we have used to measure temperature

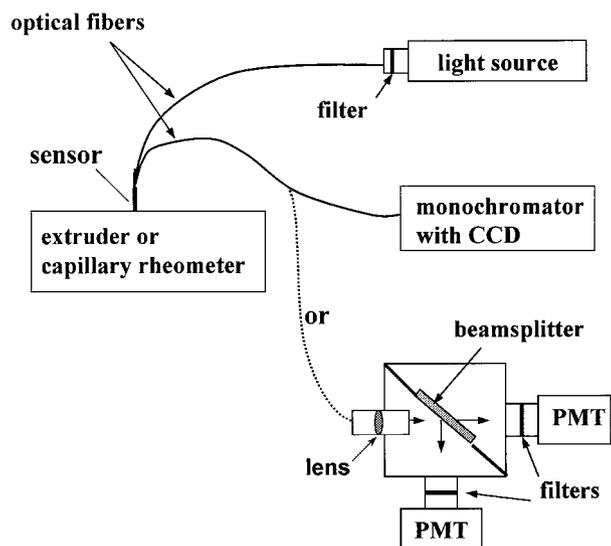


Fig. 3. A schematic of the experimental apparatus.

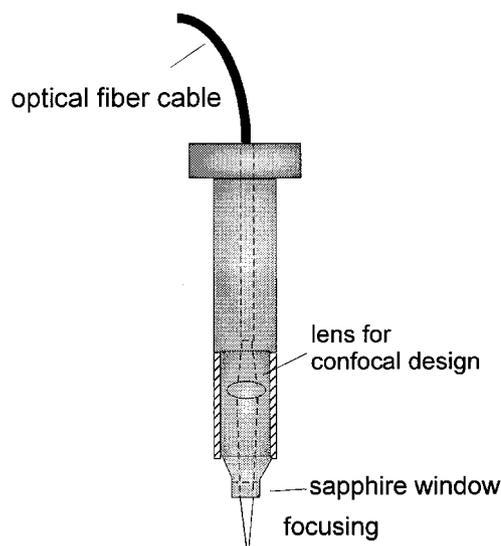


Fig. 4. An optical sensor bolt showing lens, window and fiber optic.

² The "half-inch sensor bolt" is the name of a commercial product. Therefore, SI units are not used.

profiles in a flowing resin. The spatial resolution achieved with this sensor is 0.5 mm. A full description of the sensor design is presented in a previous publication (2).

Fluorescence Anisotropy Sensor. Fluorescence anisotropy measurements require a sensor head containing polarizing elements (5). This sensor is a stainless steel block of two halves that are bolted together. One half of the sensor head has been machined with channels and compartments that receive the optical fibers, lenses, and the calcite polarizing crystal. The assembled piece is 65 cm long with a square cross section (2.54 cm) that aids in establishing a recognizable direction of the light polarization. Light exiting this sensor is polarized with direction parallel to a side of the square. The sensor head contains a Glan-Taylor polarizer consisting of two calcite crystals separated by a fixed air space of approximately 0.1 mm. When assembled, the polarizer has a 6 mm square cross section and is approximately 8 mm in length. One side surface of the calcite crystal is polished in order to allow horizontally polarized fluorescence to exit to the side. I_{vv} and I_{vh} are obtained simultaneously from this arrangement. More details of its design and operation can be found in Reference 5.

The major source of uncertainty in the measured value of anisotropy is subtraction of the background signal. After background correction, fluorescence

intensities were measured with a relative standard uncertainty of 0.4%. The relative standard uncertainty of the anisotropy measurements reported below is 1.6%.

Slit Die Rheometer. The slit die rheometer, shown in Fig. 5, contains instrumentation ports for pressure, temperature and optical sensors. During processing, the slit die is attached to the exit of a single-screw extruder (3). Implementation of the device as a rheometer requires acquisition of pressure drop, flow rate and temperature data. A weighing pan is positioned at the exit of the slit die in order to measure the mass flow rate and a pressure transducer is placed at the first position in the slit die, 101.6 cm upstream from the exit. Fluorescence temperature measurements are obtained using the sleeved half-inch bolt positioned at 50.8 cm upstream from the exit. A 2.54 cm square well in the slit die receives the anisotropy sensor. Measurements of fluorescence anisotropy of BTBP doped into polyethylene were carried out as a function of pressure drop (shear stress) during extrusion through the die. The standard uncertainty in the pressure measurements was 0.05 MPa and the relative standard uncertainty in the mass flow rate was 4%.

Capillary Rheometer. A Goettfert 2003 servo-hydraulic rheometer was used in conjunction with a capillary die 1 mm diameter by 20 mm long and a slit die with die length of 100 mm and slit size of 10 mm

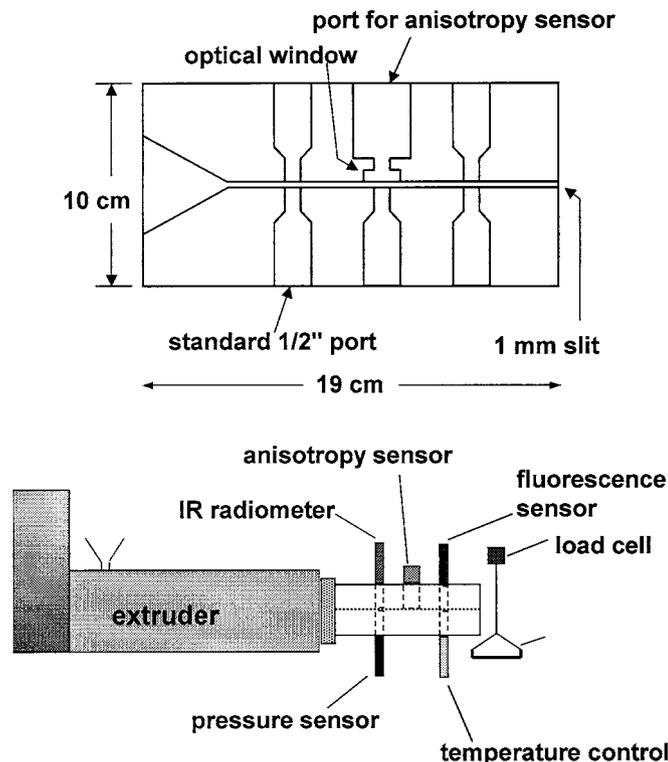


Fig. 5. The slit die rheometer containing a 2.54 cm (1 inch) square port for the anisotropy sensor is shown. The other ports are standard 1/2 inch ports for temperature and pressure sensors.

wide by 0.5 mm high. Figure 6 shows the experimental setup for interfacing with the optical sensor. The optical fiber is positioned to interrogate the resin flow stream at a point 0.5 cm beyond the orifice of the capillary or slit die. The sensing tip is in the shape of a long rod with outer diameter of 6.35 mm (0.25 inch). It contains a small lens at its end with 6 mm focal length that focuses the excitation light onto the extruded strand of resin. As noted above, a single 200 μm core diameter optical fiber transmits the excitation light and eighteen fibers collect the fluorescence.

When using the slit die, excitation light is directed normal to and focused onto the ribbon extrudate. But when using the capillary die, the situation is distinctly different because the cylindrical shape of the extrudate focuses both the excitation light and the fluorescence. The extruded cylinder focuses the excitation beam over and above that achieved by the sensor lens. A beam tracing exercise shows that it is fluorescence from the middle to far side of the cylinder that is focused into the collection fibers. Thus, the measured temperature is a bulk average of the extrudate stream. The optical design is not refined enough to produce spatial profiles of the temperature.

During the course of the capillary rheometer experiment, it is possible for the extrudate string to vibrate or wiggle, and because the extrudate string acts as a lens, small changes in its position can translate into changes in the relative amount of light entering the 18 collection fibers, which in turn will change the pattern of light incident upon the photosensitive surface of the PMTs. The calibration of the instrument will hold only if the ratio of the two targeted fluorescence intensities is independent of vibration in the extrudate string. To address this problem, a 12 mm diameter lens and 3 mm aperture are positioned at the entrance to the beamsplitter, and fluorescence light is focused to a small spot on the photosensitive surface of the two PMTs. The tight focus of this beam is

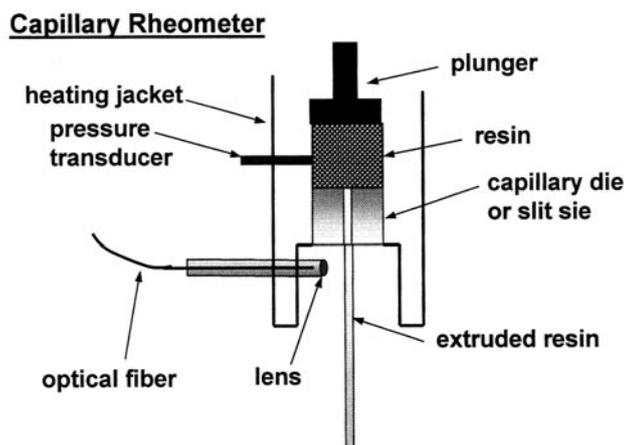


Fig. 6. The experimental setup for capillary rheometer monitoring.

needed because the sensitivity of the photosurface is a function of position. With this arrangement, variations in intensity from the individual fibers do not translate into erroneous signal variations that are due to changes in sensitivity of the photoactive surface.

RESULTS AND DISCUSSION

Anisotropy Measurements. In Fig. 7, we plot the results from extrusion of polyethylene doped with BTBP dye. The data are anisotropy and mass versus time where mass is the sawtooth curve that is the result of continuously emptying the weighing pan after it had filled with resin. Simultaneously with removing the resin from weighing pan, we changed the rpm (revolutions per minute) of the screw and rpm remained constant until the weighing pan was full. Thus, the slope of the individual teeth is equal to the mass flow rate and is proportional to the shear rate expressed in the slit die. In carrying out this experiment, rpm was selected and changed at random over a range of 0 rpm to 112 rpm so that the resin was subjected to significant and large changes in shear stress. In spite of the fact that we are operating in the shear-thinning regime for this polymer, anisotropy remained constant over the course of this run. The standard deviation of all the anisotropy measurements of Fig. 7 (over 2000 data points) is 1.6%. Thus, we can assert with reasonable certainty that there was no significant change in anisotropy for shear rates over the range 0 s^{-1} to 250 s^{-1} . If we assume that the BTBP molecule has isotropic orientation in the polyethylene matrix at zero shear rate, then these results tell us that isotropic orientation is maintained up to 250 s^{-1} without any indication of departure from the isotropic state. The result suggests that the BTBP molecules occupy free volume regions within the polymer matrix that are too small to be impacted by orientation that takes place on a larger scale at the macromolecular entanglement regime. We conclude that fluorescence temperature measurements that are based on a calibration obtained under quiescent (isotropic orientation) conditions will also be valid at higher shear rates. But, we have not been able to establish the upper limit on shear rate because of the limitations of the experimental setup.

Resin temperature measurements obtained from the ratio of fluorescence intensities at 535 nm and 550 nm for a sensor located in the slit die 2.54 cm downstream from the anisotropy sensor are shown in Fig. 8. These data taken simultaneously with the measurements of Fig. 7 show that temperature remained constant during the anisotropy measurement. The standard uncertainty in the temperature measurements of Fig. 8 is 2°C .

The value of anisotropy for BTBP in polyethylene at 180°C , 0.32, is lower than the possible maximum of 0.40 (see Eq 6) because the BTBP molecule has some rotational freedom during its fluorescence decay that causes depolarization. Using 0.32 as the value for r ,

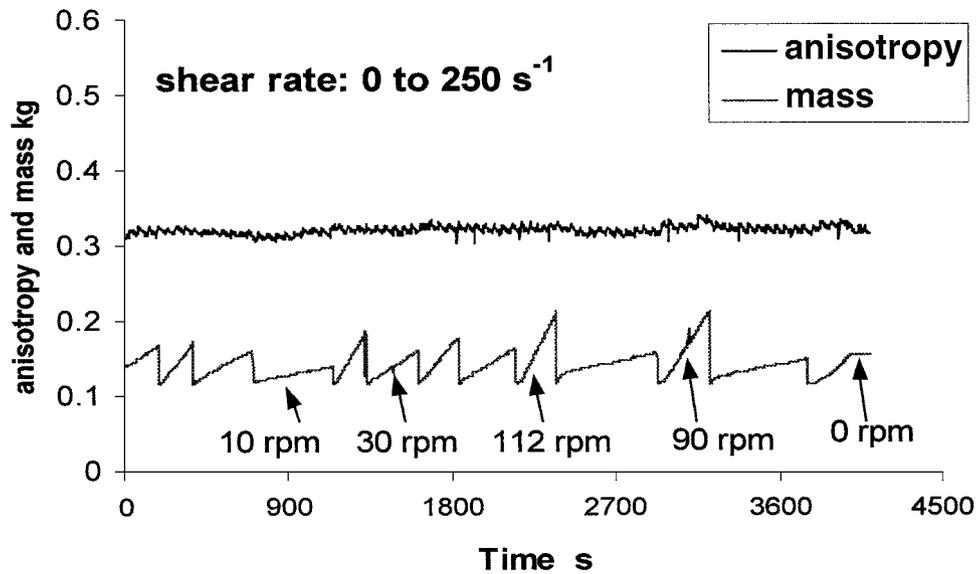


Fig. 7. Anisotropy and mass versus time for extrusion of polyethylene doped with BTBP. The sawtooth curve is the output from the weighing pan that is repeatedly emptied during the run.

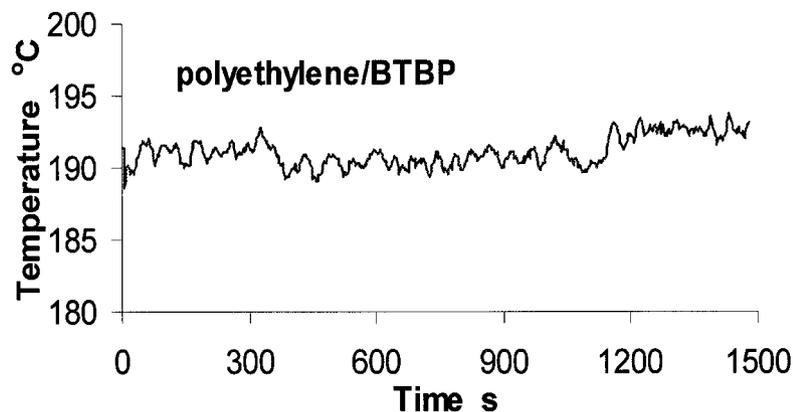


Fig. 8. The temperature in the slit die during the experiment of Fig. 7 is monitored using fluorescence from BTBP.

we obtain $\tau_f/\tau_r = 0.25$ or $\tau_r = 4\tau_f$. Using the literature value of $\tau_f = 3.7$ ns yields $\tau_r = 14.8$ ns (19). This relatively large rotational relaxation time for BTBP is a consequence of its molecular size. It is the largest of the molecules that we use for fluorescence temperature applications, and it was selected for this experiment because of its potential to interact with the polymer matrix and orient under applied shear stress. The fact that it did not show orientation works to our advantage for this measurement, and from this result we infer that molecules smaller than BTBP, e.g. perylene and BOS, will also be unaffected by shear stress during extrusion processing at these shear rates.

For the case of extensional stress, the situation is quite different because much higher stress levels can be achieved. For example, during film stretching, the force is applied over a small cross-sectional area, producing extensional stress on the order of 10^6 N/m²

and larger, orders of magnitude greater than shear stress experienced by the resin during extrusion through a 1 mm slit die. Indeed, using fluorescence anisotropy observations, we have observed significant dye orientation in a matrix of extensionally stretched crosslinked polybutadiene, and polypropylene and polyethylene terephthalate films (5, 11). Early work by Ward and co-workers using BOS doped into uniaxially stretched polyethylene terephthalate showed that orientation as measured with fluorescence anisotropy correlates well with X-ray and birefringence results (12, 20). The impact of an extensionally stressed medium on fluorescence temperature measurements centers on effects at the molecular level, whereby matrix extension causes a change in local polarization, thus inducing a change in Stokes shift of the fluorescent spectrum. Under these circumstances, one must be careful about using a calibration function involving

the ratio of two wavelengths that was obtained under quiescent (unoriented matrix) conditions. For example, fluorescence temperature measurements of stretched polypropylene doped with BTBP can be made using the ratio of intensities at 544 nm and 577 nm, but another wavelength pair (535 nm and 550 nm) are used for measurements of an unoriented polypropylene matrix.

Noncontact Temperature Monitoring of Capillary and Slit Die Rheometry. The results of the capillary and slit die rheometer experiments on polyethylene doped with perylene are shown in Figs. 9 and 10. For each experiment, the oven temperature was set at 180°C and the rheology test run was carried out by ramping up the shear rate in 2, 5, 10 ... increments to a maximum of approximately 10,000 s⁻¹. The results from the capillary run, Fig. 9, show two excursions in

the temperature reading at 10 s and at 120 s. These excursions were attributed to excessive wiggle in the extruded 1 mm diameter resin string. Otherwise, the reading remained stable over the duration of the run, demonstrating that the extruded resin stream remained centered in position with respect to the excitation light beam. Temperature remained constant over most of the run, rising slightly at the highest shear rates. Shear heating effects were not observed below 2000 s⁻¹.

In contrast, the results from the slit die rheometer, Fig. 10, display significant shear heating effects at the shear rates greater than 100 s⁻¹. Even though the capillary and slit die runs were carried out at the same oven temperature, 180°C, shear heating is significant for the slit die because its length, 100 mm, is five times the length of the capillary. Energy is dissipated

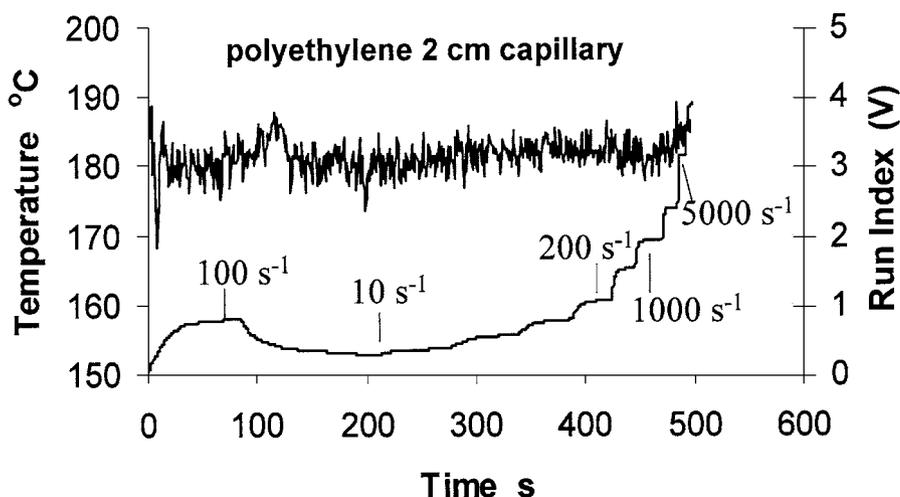


Fig. 9. Temperature versus time for a capillary rheometer experiment using a 1 mm diameter by 2 cm long capillary. The run index shows the stepwise manner in which shear rate increased during the experiment. Polyethylene doped with perylene.

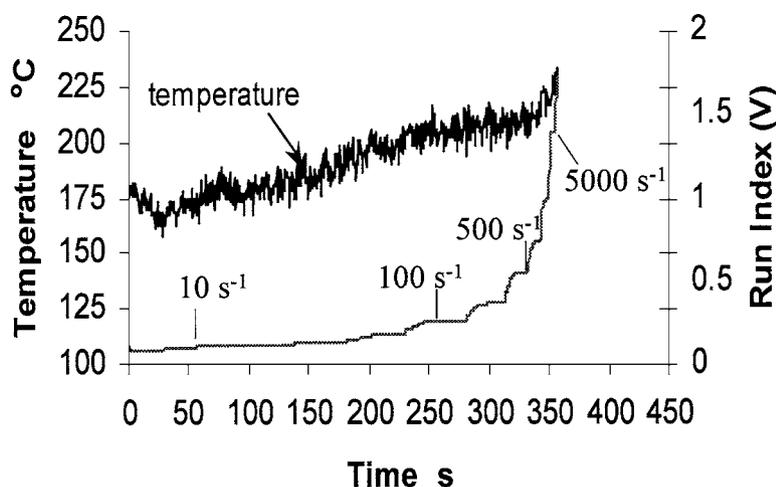


Fig. 10. Temperature versus time for a slit die rheometer experiment using a 0.5 mm by 10 mm wide by 100 mm long slit die. The run index shows the stepwise manner in which shear rate increased during the experiment. Polyethylene doped with perylene.

in the flow stream through the slit die over a much larger distance. The maximum temperature observed at the end of the slit die experiment was 225°C at 10,000 s⁻¹. Resin temperature had increased by 45°C over the oven set-point, a situation that has significant impact on the calculation of viscosity values from the rheometer test. A full study of shear heating effects during rheometer testing is being carried out in our laboratory.

Monitoring Reactive Processing. For this measurement we used a confocal sensor positioned near the exit of a twin-screw extruder during the reactive processing of a linear PHAE thermoplastic linear epoxy. The measurements are based on the calibration curve shown in Fig. 11, where we have plotted temperature versus the ratio I_{420}/I_{436} . A linear regression of these data is used for the calibration function. Fluctuations seen in the calibration data dictate that averages from several minutes of observation time were needed for the real-time observations.

With the confocal sensor situated near the exit of the extruder as shown in Fig. 12a, we obtained a temperature profile for the resin flow stream within 5 mm of the wall during steady state conditions. Each data point of Fig. 12b is an average over 5 min of observations yielding standard uncertainties as indicated by the error bars. Close to the wall, the uncertainty in the measurements is approximately 3.5°C. For measurements at the far side of the profile, 5 mm from the wall, uncertainty is as high as 10°C because the intensity of the fluorescence signal was diminished by absorption of the excitation light and by resorption of the fluorescence as it traversed through the resin to the fiber-optic sensor. The absorption/resorption phenomenon is a consequence of a higher-than-usual concentration of dye in the resin, a situation that should be avoided in order to maintain an acceptable measurement uncertainty over the entire profile.

The profile of Fig. 12b was obtained over the course of time while moving the focus of the excitation light away from the wall to a position 5 mm away and then moving back to the wall according to the arrows on

the plot. Some hysteresis was observed in the profile that was due to drift in the processing conditions over the period of 1.5 h needed for the experiment. A rough comparison to thermocouple measurements was made by inserting a hand-held thermocouple probe into the exit stream, yielding readings that ranged from 210°C to 220°C, temperatures much lower than the fluorescence temperature values, 240°C to 285°C. The problem with the thermocouple measurements was that the steel-jacketed probe conducted heat away from the point of the measurement, giving an erroneous low value. The standard uncertainty in the thermocouple measurements is 1°C.

Figure 13 is a plot of temperature versus time for focus position at 0.635 mm from the wall. Each data point is an average from 10 s of photon counting. The observations were made while the fluorescent dye was being purged from the system. At long times, fluctuations in the data were larger than those at short times because there was less fluorescence intensity at each measurement as the dye concentration decreased. Also, we observed a slight increase in average temperature with time, which we interpreted as a drift in processing conditions that resulted in a higher-viscosity product with enhanced shear heating. The standard uncertainty in temperature measurements for the first 3000 s is 3.5°C, and at the end of the run it is 4.7°C. The large negative spike in the data at 1000 s was due to a bubble in the flow stream.

In summary, we have carried out a set of experiments that demonstrate the versatility of the fluorescence temperature-monitoring technique. The rationale for using a calibration function obtained under quiescent conditions for dynamic processing situations was justified by the results from the anisotropy measurements. For BTBP doped into polyethylene, the anisotropy measurements showed that, during shear flow, the dye molecule maintains an isotropic orientation and does not orient with the entanglement network of the resin matrix. For noncontact temperature measurements, it is important that the geometrical optics incorporate tight focusing of the fluorescence

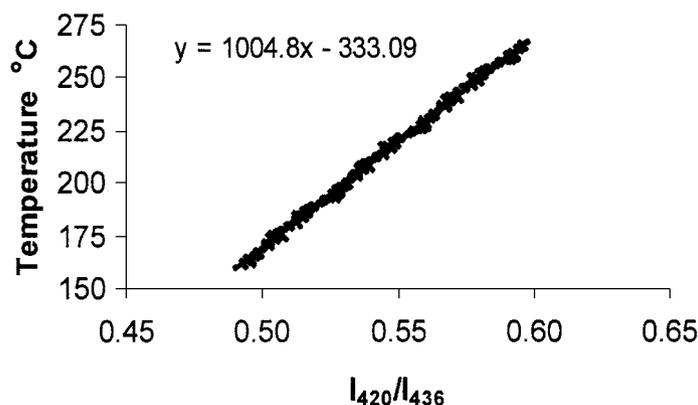


Fig. 11. Temperature versus the ratio I_{422}/I_{436} for BOS doped into PHAE.

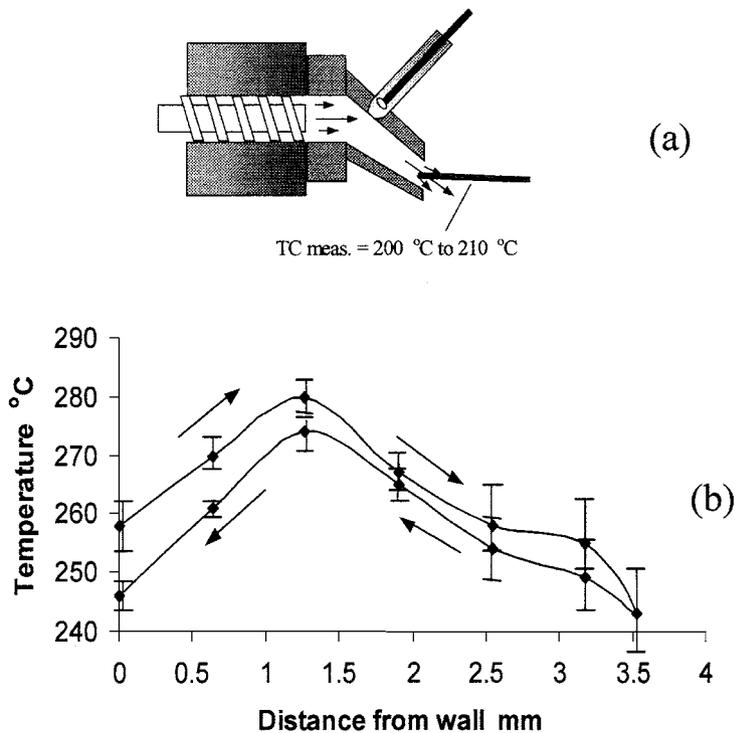


Fig. 12. (a) Sensor placement for monitoring reactive extrusion of PHAE. (b) Temperature versus distance into the PHAE resin flow stream.

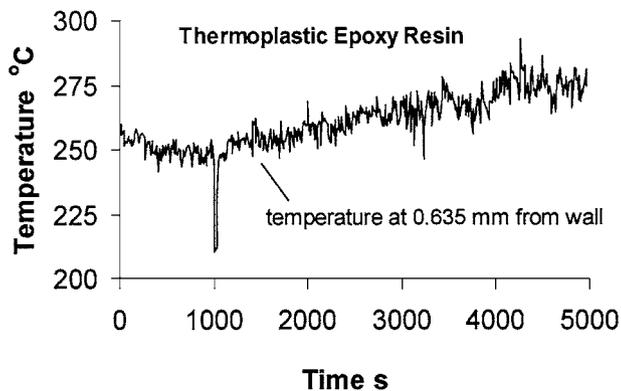


Fig. 13. Temperature versus time for PHAE extrusion during purge of the fluorescent dye. The focus of the confocal sensor was set at 0.635 mm from wall.

light onto the photosensitive surface of the photomultiplier. For monitoring reactive processing, it is important to understand the impact of polarization changes on fluorescence spectra and to tailor the experimental protocol accordingly. For temperature profile measurements, the problem of resorption of fluorescent light can be avoided by keeping dye concentrations below 5×10^{-6} mol of dye per monomer mol of resin. Every application has its own set of important parameters that must be examined in order to achieve optimum measurement accuracy.

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