NON-DESTRUCTIVE EVALUATION MEASUREMENT TECHNOLOGY FOR POLYMER PROCESSING BASED ON FLUORESCENCE SPECTROSCOPY

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INTRODUCTION

We are employing fluorescence spectroscopy as a tool to monitor polymer processing parameters which are important for understanding process behavior. The measurements involve the detection of fluorescence spectra from fluorescent dyes which have been doped into the processed polymer material. The character of the fluorescence, i.e. its intensity, polarization, and wavelength distribution, yields information about the state of the polymer matrix. We have concentrated on developing concepts and methods to measure molecular orientation, shear stress, shear rate, non-Newtonian viscosity, velocity, residence time distribution, flow instabilities, quality-of-mix of ingredients, and intersegmental mixing. Work on each of these measurement problems is ongoing and in various stages of development.[1-2] In this paper, we describe some recent work on quality-of-mix and intersegmental mixing.

MEASUREMENT PROGRAMS

Measurements of Quality-of-Mix of Ingredients

Many polymer products are manufactured from a combination of several different raw materials which are mixed into a homogeneous state during the mixing phase of the process. Reaching a homogeneous state can be a critical criterion for attaining specified materials characteristics and performance of the product. Definitions of the quality-of-mix or the "goodness of mix" have been presented by many authors.[3,4] These definitions stress either the randomness or the spatial distribution of the mixture. In all cases, the scale or volume of examination must be sufficiently large to allow a random or uniform distribution to exist, i.e. it must be much larger than the size of the individual components. The definition of the quality of mix which we will use emphasizes the uniformity of the distribution. Our definition refers to the mixing of solid particulate in a liquid and states that a uniform mixture is one for which the standard deviation of the average number of particles per unit volume is minimized.

Our experimental method uses fluorescence radiation intensity from an excited fluorescent chromophore (or dye), which has been well dispersed in a polymer melt, to determine the state of mixture uniformity. To create fluorescence, a dye is subjected to excitation light energy of short wavelength which is absorbed by the chromophore and emitted as fluorescence radiation at a

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longer wavelength. A material which contains a uniform spatial distribution of fluorescent chromophores will display constant fluorescence from any randomly selected constant volume of the material. If components A and B are mixed together and if component A possesses an active fluorescent chromophore and B does not, then uniform mixing of the two components will result in constant fluorescence intensity radiating from equal probe volumes. Thus, the mixing hypothesis for this measurement method is: given a material mixture for which one of the components contains an active chromophore, uniform mixing is achieved when the fluorescence intensity is constant with time.

Two experiments relating to the quality-of-mix are described. First, we report on the measurement of fluorescence intensity as a function of time from a polymer/particulate mixture as it undergoes mixing in a small laboratory mixer. Second, by using an optical fiber, we examine the depth of the optical field of view into filled specimens in order to demonstrate that the fluorescence measurement method gathers information from beyond the surface or interface.

Experimental Procedure for Quality-of-Mix Measurement

The materials which we used for these experiments were a polymer binder known as PBAN, aluminum oxide particulate (14 μm grain size), and a fluorophore, coumarin 30. PBAN is a polybutadiene based terpolymer; it was obtained from American Synthetic Rubber,[5] and, according to the supplier's specifications, it has a weight average molecular weight of 6000 and a viscosity of 369 poise at 25°C. The fluorophore, coumarin 30, was obtained from Eastman-Kodak.[5] It was chosen because it satisfies the following criteria which we have established for the dopant fluorophore:

- o The chromophore must be chemically stable and not susceptible to photobleaching by the excitation photons;
- o Excitation and emission must occur at visible wavelengths.

The last criterion is not a necessary condition but one of convenience. The fluorescence emission spectrum for coumarin 30 and its molecular structure are shown in Figure 1. The excitation wavelength for this spectrum and for the mixing experiments was 458 nm which is a discrete line of an argon ion laser. During the mixing experiments, we did not scan the full spectrum of emission fluorescence, but we set the monochromator to 500 nm at which there is ample fluorescence intensity. The monochromator bandwidth was 6 nm.

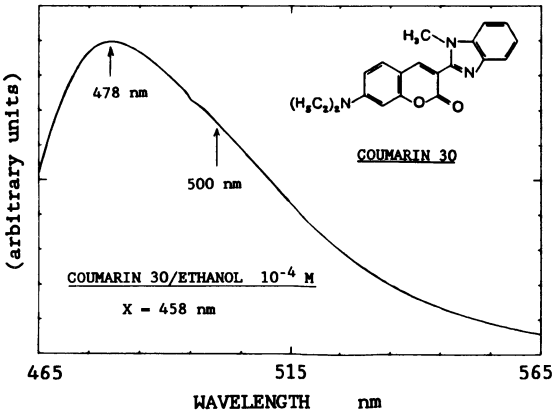


Figure 1. The molecular structure and the fluorescence spectrum for coumarin 30 in ethanol at a concentration of 10^{-4} molar is shown. The excitation wavelength was 458 nm.

Prior to mixing PBAN and aluminum oxide, PBAN was doped with coumarin 30 to a concentration of 10^{-4} molar. To do this, a few milligrams of coumarin were dissolved in a few drops of a 50/50 ethanol/toluene mixture and then mixed with PBAN. This mixing was carried out with ease because the materials are miscible and both were in the liquid state.

Mixing of the doped PBAN and Al_2O_3 was carried out in a mixer which was constructed in our laboratory and is diagrammed in Figure 2. The mixer was designed so that the material is subjected to both shear and translational forces, thus satisfying the conditions to achieve good mixing. The cylindrical wall of the mixer is a glass tube which is approximately 2.54 cm in diameter by 7 cm in length. The specimen volume in the mixer is 42 cm^3. There are two sets of mixing blades which can be driven in co-rotating or counter-rotating modes of motion by the motors shown. One set of blades rotates at the outer circumference of the mixer near the glass wall. This set is connected to the uni-directional motor and contains a flat brass piece which functions as a scraper and prevents material from accumulating at the wall. The other set consists of a single twisted brass piece which is connected to the bi-directional motor and rotates on the cylindrical axis of the mixer. Both motors rotate at approximately 10 rpm, i.e. with a period of revolution equal to 6 sec. In operation, the movements of two sets of blades create a shearing force and the twisted central blade creates a translational force.

In Figure 3, we show the optical arrangement for collecting the fluorescence during mixing. Excitation radiation of 458 nm light beam from an argon ion laser was directed through the beam splitter to the glass wall of the mixer. The diameter of the light beam was approximately 1 mm, and its penetration into the sample varies with the amount of particle scattering, a factor which we examine below. The beam splitter is employed in order to detect fluorescence emitted at 0°. The fluorescence signal was detected by a photomultiplier tube and counter, and stored in a computer. The data sampling time was set at 0.2 seconds so that 30 data points were obtained for each revolution of the mixer motors.

The optical depth of view for this measurement method was obtained using a bifurcated optical fiber bundle in the arrangement shown in Figure 4. Fluorescence intensity was measured as a function of the distance d, between the optical fiber tip and the non-fluorescent surface at the bottom of the specimen vessel. Distance d was measured using a mechenical micrometer. It is seen that the same optical fiber bundle is used for both excitation and collection of the fluorescent light as would be the case for on-line measuremment. The bundle consists of 50 μm diameter fibers wrapped into a sheaf 1.58 mm in diameter.

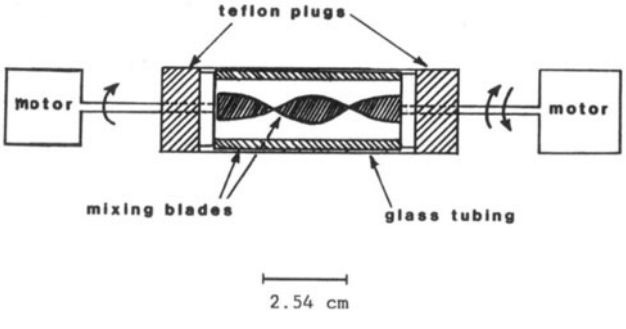


Figure 2. A diagram of the mixer is shown. The twisted blade, which rotates on the central axis of the mixer, is driven by the bi-directional motor. Three blades, driven by the uni-directional motor, are at the outer circumference of the mixer, near the glass wall.

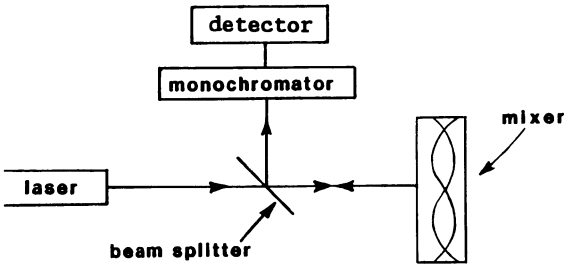


Figure 3. The optical arrangement for the fluorescence mixing experiment is shown.

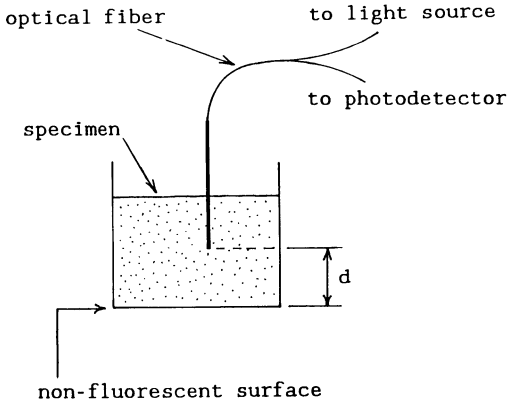


Figure 4. The experiment to measure the depth of view of the fluorescence optical fiber probe is depicted. A mechanical micrometer is used to measure the distance d.

The specimens examined were PBAN mixed with aluminum oxide (14 μm grain size) and sodium chloride (grain size less than 75 μm). These fillers were chosen for their differences in index of refraction, 1.67 and 1.544 respectively, compared to 1.519 for PBAN. These specimens had viscosities greater than 300 Pa·s (3,000 poise) so that sedimentation during the time scale of the measurements could be neglected.

Results and Discussion of Quality-of-Mix Experiment

In Figure 5 we show fluorescence intensity versus time for the mixing of the coumarin doped PBAN with aluminum oxide at 67% by weight. At the start of mixing, large variations in intensity were observed. These variations are seen as spikes in the data which have a period of six seconds and occur with each revolution of the scraper blade as it brings chromophore rich and poor regions of the specimen into the volume of the excitation light beam. The magnitude of the spikes was observed to decrease as the mixing proceeded indicating that uniformity of the mixture was being approached. After nine minutes of mixing, there remains intensity spiking of approximately 1 kilocount/s, but, after 100 minutes, the intensity is constant to within the sensitivity of our measurement. The fluctuations in the fluorescence intensity after 100 minutes have a standard

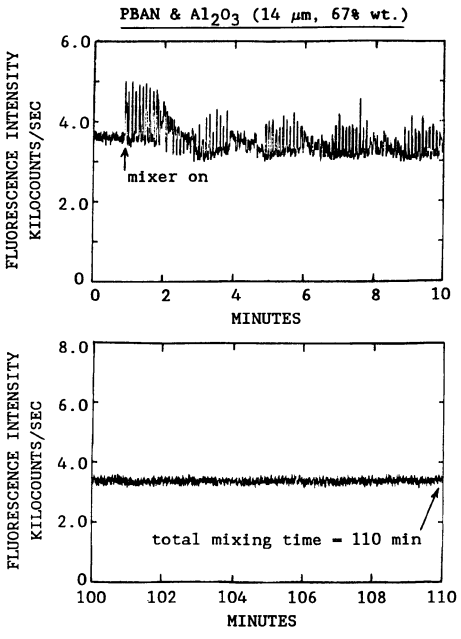


Figure 5. Fluorescence intensity versus time is plotted for mixing of PBAN with 67% aluminum oxide by weight. The plot for 0 to 10 minutes shows the intensity variations at the beginning of mixing. The plot from 100 to 110 minutes shows the intensity at the end of mixing.

deviation of ± 2% and are due to inherent noise in the signal. An improved signal to noise ratio would permit a calculation of the standard deviation and a quantitative measure of the quality of mix. For this case, we can state that the standard deviation of the fluorescence intensity is less than ± 2%. This observation was interpreted as a demonstration of the mixing hypothesis, i.e. constant fluorescence intensity as a function of time is an indication that uniform mixing has been achieved.

A rigorous test of our fluorescence/mixing hypothesis was carried out using an epifluorescence microscope to observe both optical transmittance and fluorescence from microscopic regions of poor and well mixed specimens. This work is described in a previous publication.[1]

Results and Discussion of Optical Fiber Depth of View Experiment

We view the neighborhood at the end of the fiber bundle (Figure 4) as a probe front consisting of light excitation and fluorescence which extends into the specimen and defines the depth of view. When d is much larger than the depth of view, the probe front is fully involved in the specimen and the intensity is constant, independent of d. As the fiber bundle is inserted further into the specimen, the probe front impinges upon the non-fluorescent bottom surface of the specimen vessel; fluorescence intensity decreases and continues to do so as d approaches zero.

This effect is seen in Figure 6, where we have plotted normalized fluorescence intensity versus d for three well mixed specimens containing coumarin 30 dye: unfilled PBAN, PBAN filled sodium chloride at 29% by

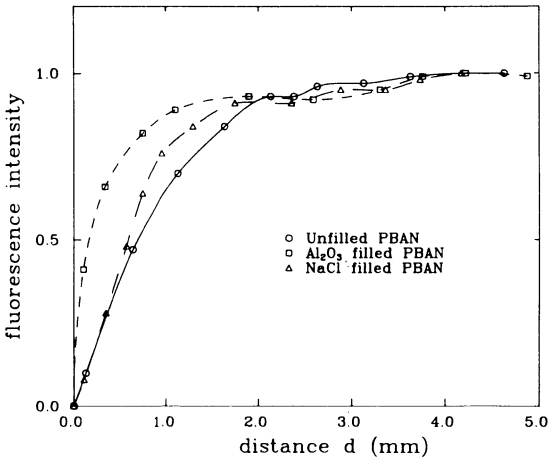


Figure 6. Normalized fluorescence intensity is plotted against distance d for unfilled PBAN (circles), NaCl filled PBAN (triangles), and Al_2O_3 filled PBAN (squares). All specimens were doped with coumarin 30 dye.

volume, and PBAN filled with aluminum oxide (14 μm grain size) at 29% by volume. We recall that the index of refraction n of these materials is 1.519 for PBAN, 1.544 for NaCl, and 1.67 for Al_2O_3. The depth of view is defined as the maximum distance for which the probe is affected by the presence of the bottom surface of the vessel; it is found to be 2.5 mm for unfilled PBAN, 1.5 mm for NaCl filled PBAN, and 1.0 mm for Al_2O_3 filled PBAN. The difference in the depth of view for the two filled specimens is due to the difference between values of n for particulate and filler. Thus, for the case of NaCl in PBAN, the probe front extends further into the specimen than for Al_2O_3 in PBAN. In each case, the depth of view is much larger than the grain size of the particulate and we conclude that the probe can sense beyond the wall interface.

Continuation of Mixing Studies

The ultimate application of this measurement method is to monitor mixing phenomena in real time on a mixer or processing line. Indeed, we have constructed an optical fiber sensor which has been inserted into the standard transducer port of a twin screw extruder. Fluorescence is being used to monitor residence time distributions, quality-of-mix, and flow instabilities. Here, we must give consideration to the presence of UV absorbers, stabilizers, impurities etc. in the processed material which may interfere with the fluorescence observations. Such problems can be overcome by choosing the proper fluorescent chromophore, by isolating excitation light to wavelengths absorbed only by the chromophore, and by limiting the detector to a narrow band of wavelengths which are characteristic of the chromophore fluorescence. Results of these experiments will be the subject of a future publication.

Intersegmental Mixing

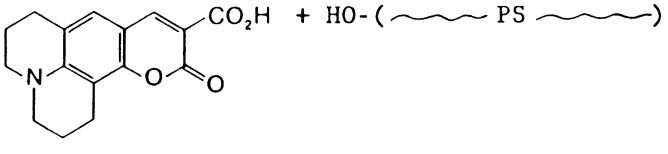
The phenomenon of intersegmental mixing occurs in a two component material which undergoes a transition from phase separated to homogeneous at a critical shear stress. Detection of this transition has application to the processing of block copolymers and polymer blends. Of specific interest to us is the block copolymer styrene-ethylene/1-butene-styrene (SEBS). To detect intersegmental mixing via fluorescence observations we will use a fluorescent dye which has a thermodynamic preference to reside in one phase of the phase separated material and whose spectrum is sensitive to the polarity of its molecular neighborhood. Upon application of the critical shear stress the degree of

homogeneity can be monitored via the fluorescence spectrum of the tracer dye as it is drawn into molecular contact with a variety of polarity environments.

Experimental Procedure for Intersegmental Mixing

For SEBS we have synthesized a tagged polystyrene which has a polarity sensitive coumarin dye as the end group. The starting materials were coumarin 343 (Eastman Kodak) which contained a functional carboxy group, and monocarboxy terminated polystyrene (Aldrich).[5] Tagging was carried out through an esterification reaction which is depicted in Figure 7.

In order to examine polarity dependence, tagged polystyrene was doped into toluene, cyclohexane, and into solutions and cast films of polystyrene. Toluene and cyclohexane were chosen as model solvents because they are expected to simulate the polarity effect of stryene (toluene) and ethylene/1-butene random copolymer (cyclohexane). Fluorescence spectra were measured over a wavelength range from 410 to 460 nm using a Spex fluorimeter with excitation at 400 nm.[5] The bandwidth of the monochromator and detector was approximately 6 nm.



Coumarin

Figure 7. The monocarboxy polystyrene (PS) and coumarin 343 with the carboxy functional group are shown. An esterification reaction completes the addition of coumarin to the end group of the polystryrene molecule.

Results and Discussion of Intersegmental Mixing Study

As an example of the effect of polarity on the fluorescence spectrum, we show spectra of toluene and cyclohexane doped with tagged polystyrene in Figure 8. The results show a 26 nm wavelength shift in the two spectra which peak at 451 nm for toluene and 425 nm for cyclohexane. Such calibration data can be used to assess the homogeneity of an SEBS specimen by noting the position of the peak fluorescence.

Other results from intersegmental mixing experiments on neat SEBS doped with the tagged molecule will be the subject of a future publication.

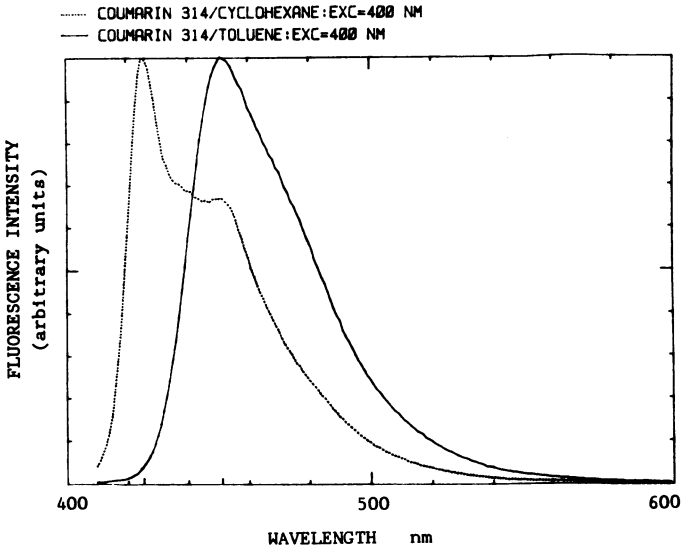


Figure 8. Fluorescence spectra for dilute solutions of tagged polystryrene in toluene (solid curve) and cyclohexane (dashed curve) are shown. The excitation wavelength was 400 nm.

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