Use of Dielectric Loss to Determine Blend Time for Organic Polymer Solutions

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When scaling up mixing applications, it is often important to measure blend time. In our application, we need to measure blend time in nonaqueous solutions of organic polymers in pilot- and plant-scale steel tanks. Techniques employing visual observations can be used in small-scale glass or Plexiglas tanks, but these methods are not applicable to large-scale operations. Another standard technique is to measure conductivity of a tracer material, which is useful particularly for aqueous systems, but does not provide an adequate response for our system.

A new technique that we established involves the measurement of the dielectric loss of a tracer material added to an acrylic polymer solution in mineral oil. It is demonstrated that the addition of N,N-dimethylformamide (DMF) results in mixing curves that give blend times equivalent to those measured by visual methods. Our preliminary studies were performed in a 2-L vessel over a temperature range of 30–120°C. The magnitude of the dielectric loss measurement is shown to depend on the scanning frequency of the measurement and the temperature of the polymer solution. The variation over a small temperature range is slight and will not interfere with the measurements.

Introduction

Mixing often plays a key role in the design and scale-up of industrial processes. In the case of a blending operation, mixing will determine the uniformity of the final blend. The choice of agitators and the processing time is critical to a successful scale-up. In the case of a chemical reaction, mixing will often determine the uniformity of the product, the rate of reaction, the extent of undesired side reactions, and the molecular weight and copolymer distributions for polymerization reactions. Once a process has been defined at the laboratory or pilot scale and it has been determined that mixing is important, we are then faced with the task of ensuring that we can achieve comparable mixing as we scale up the process. One key to this is the ability to measure blend time on both the laboratory scale and the plant scale.

There are a number of techniques available for blend time measurements for the laboratory or small pilot scale. Two that are widely used are dye injection and acid-base coloration-decoloration. Both techniques work well and provide similar results for blend time. They also have the advantage of allowing the experimenter to see the mixing patterns and the location of dead zones in the vessel. They do, however, have two major disadvantages: they are very subjective, relying on the observer to determine when the blending is complete; they are restricted to clear vessels, which renders them useless for plant-scale testing in metal tanks.

One commonly used method that can be applied to nontransparent vessels is temperature uniformity. Temperature uniformity measurements require only that temperature sensors be placed at various locations throughout the vessel. This has the advantage of being simple and reliable, but there are several drawbacks to this method. First, it requires the addition of a material that disturbs the temperature in the vessel enough to cause a measurable response. Second, it requires that the rate of thermal diffisivity is slower than that of mass diffusivity or bulk mixing. In general, it would be very difficult to be certain of this.

Another method that can be used in nontransparent vessels is conductivity measurements. A small amount of a conductive salt or an acid-base mixture is added to generate a conductive salt. The conductivity of the fluid can be monitored as the

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mixture reaches an equilibrium throughout the vessel and the mixing time can be measured as the time required to reach equilibrium or some fraction thereof. Furthermore, by knowing *a priori* the equilibrium conductivity, the experimenter can quantify the extent of mixing and whether or not dead zones exist in the vessel. This technique is rapidly becoming an accepted standard method for measuring blend time in mixing studies. Since this method requires the presence of a conductive salt, it lends itself quite readily to aqueous-phase systems.

The majority of industrial processes, however, are not done in aqueous solutions and therefore require a technique applicable to organic-phase solutions. Our application requires us to measure blend time during an organic-phase polymerization reaction, specifically the polymerization of acrylic monomers in an organic solvent.

Our initial attempts to measure blend time were by the conductivity method. We attempted to identify conductive salts that would give a sufficient signal for a blend time measurement. We were unable to find a salt sufficiently soluble and conductive to be used with this technique. Based on these results, we decided to try dielectric loss measurements, which are reportedly more applicable to low conductivity systems.

Introduction to Dielectric Measurements

A brief introduction to dielectric measurements is provided here as background. This is derived mainly from Sichina and Leckenby (1989) and Day (1987).

The two dielectric responses of a material are related to its capacitance (ability to store charge) and its conductance (ability to pass charge). These can be quantitatively expressed as the dielectric constant (ϵ') and the dielectric loss (ϵ''). The dielectric response is a result of a combination of several factors, including dipole interactions, ionic conduction, electrode polarization, and inhomogeneities in the material. Dielectric measurements are made over a range of frequencies, with the response dependent on the frequency. In general, high-frequency measurements detect primarily the dipole relaxations, while the lower frequencies tend to measure the ionic conduction. When measuring dielectric properties, a span of frequencies should be used. The trade-off is that lower frequencies often give a stronger response, but have a longer measurement time, while higher frequencies have a short measurement time, but give a weak signal. This often requires the determination of an optimum measurement frequency.

Dielectric measurements have found many uses in physical characterization of materials. These uses include the quantitative measurement of epoxy cure rates, thermal transitions, degree of crystallinity in polymers, and diffusion of solvents in and out of polymers. Dielectric measurements are influenced by temperature, viscosity and chemical composition of the materials under evaluation.

Equipment Description

The dielectric measurements were made using a Micromet Eumetric System II Microdielectrometer equipped with a Low Conductivity Interface. Micromet Low Conductivity Sensors were placed in the mixing vessel. The dielectrometer was interfaced with an AST 286 (IBM PC-compatible) computer for data acquisition using Micromet software.

The mixing vessel is a 1-L resin flask (10.5-cm-diameter) coated with a platinum-iridium resistance element to provide heating. The flask is equipped with a variable speed, variable torque motor. The injection point for the tracer materials and the location of the dielectric sensor was varied to test the effect of position on the mixing time curve. The agitation system is a set of three 45° pitched-blade turbines with a diameter of 6.3 cm. The impellers are spaced approximately one-half impeller diameter apart. A schematic of the equipment is shown in Figure 1.

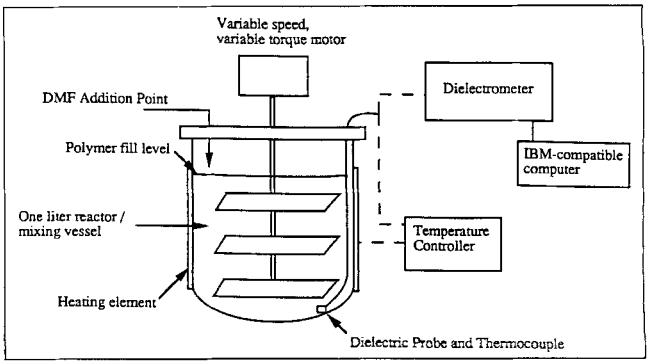

Figure 1. Mixing vessel showing location of feed point and dielectric probe.

Experimental Results

Since dielectric loss is temperature-dependent, it was necessary first to establish that any signal variation caused by small temperature changes was small relative to the overall response. The first response we measured was the relationship between ϵ'' and temperature for the polymer solution alone. Figure 2 shows a thousandfold increase in ϵ'' as the temperature varies from 30–130°C, measured at 1 Hz and 10 Hz. The next measurement was to determine whether small changes in temperature (±3°C), which are within our ability to control on a plant scale, would affect our ability to measure ϵ''. Although the slope of the temperature response in Figure 2 suggests a strong temperature effect, Figure 3 shows that in a separate

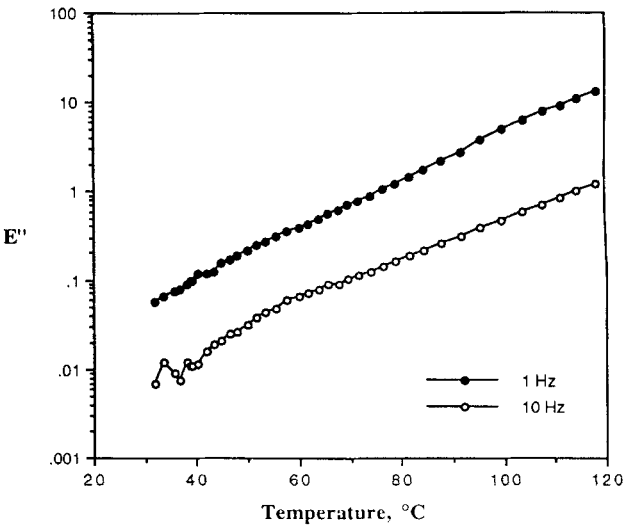

Figure 2. Temperature response of dielectric loss.

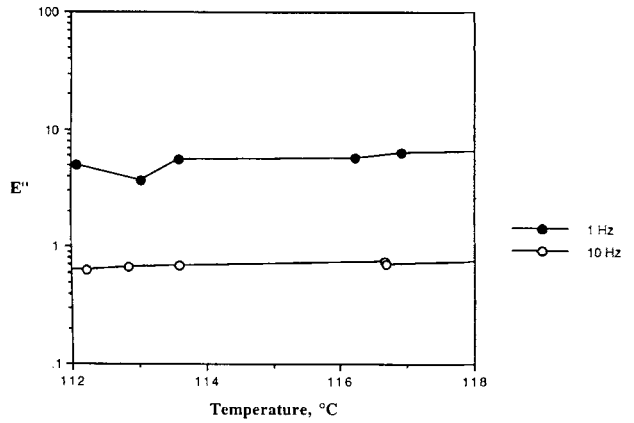

Figure 3. Variation of E'' with temperature fluctuation.

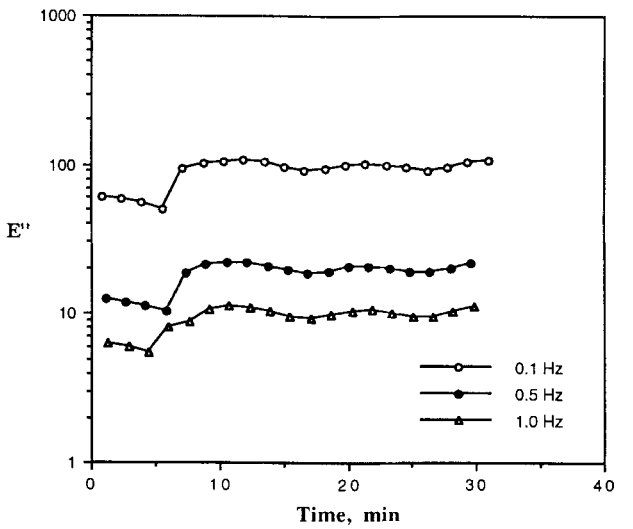

Figure 5. Mixing curves for polymer solution with 0.5% DMF added.

experiment, ϵ'' is nearly constant over a small temperature range for a given frequency. Therefore, small temperature variations will have only a slight effect on our measurements.

Our next goal was to find a suitable tracer that would alter the dielectric properties of the polymer solution sufficiently to provide a measurable, low-noise signal for the blend time determination. The solvents tested included toluene, xylene, heptane, dimethyl formamide (DMF), dimethyl sulfoxide, and tributyl phosphate. Our best results were achieved with DMF. Figures 4, 5 and 6 show the mixing curves for DMF levels of 0.25, 0.5 and 1.0 wt. % over the frequency range of 0.1 to 1.0 Hz. Selection of an appropriate solvent will depend on the system under study and should be based on solubility and differences in dielectric response compared to the polymer system being tested. There are two considerations in choosing the tracer level and scanning frequency. First, it is important to minimize the amount of any tracer added to a solution so it does not interfere with the fluid properties. Second, the scanning frequency should be chosen to give a measurement time much shorter than the blend time. We felt the best overall choice for our system was to add 0.25% DMF and use a scanning frequency of 0.5 Hz, which results in a measurement time of less than 1 min. As shown in Figure 6, this combination gives a very clear indication of when mixing is complete. Careful examination of the data will show that the time at which the response begins to change from the baseline is not the same for all freuqencies. This is because the scans at each frequency are taken sequentially and the time of the measurement will vary. For example, a scan of three frequencies will measure the 0.1 Hz value at 1.87 min, the 1.0 Hz value at 2.02 min, and the 10 Hz value at 2.13 min. Therefore, although ϵ'' has begun to increase for all three frequencies, a slight measurement lag occurs. Figure 5 also shows the minor instability of the dielectric response to slight temperature variations, as mentioned earlier. Despite this, it is still a simple matter to determine when blending is complete.

The blend time measured by the dielectric loss method under the conditions of Figure 6 is approximately 4 min. Previous studies by Shervin et al. (1991) gave similar results by visual

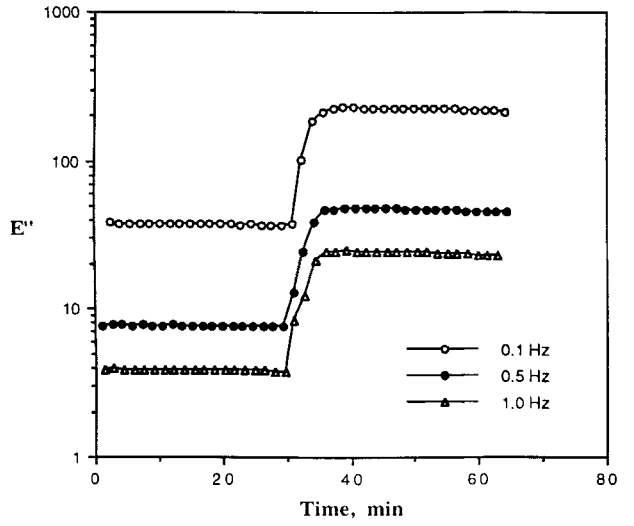

Figure 4. Mixing curves for polymer solution with 1% DMF added.

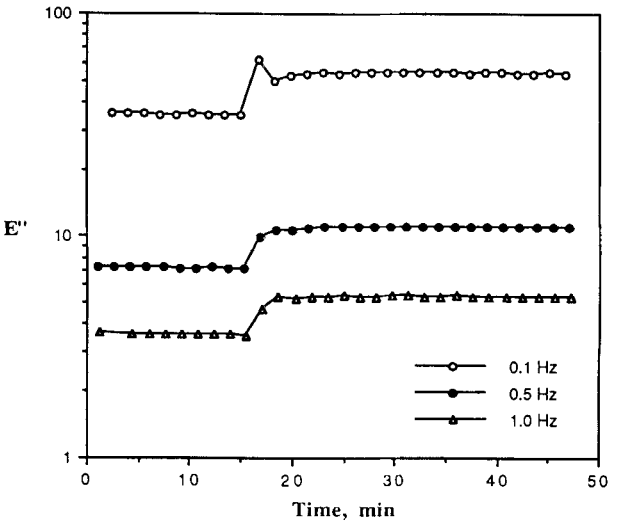

Figure 6. Mixing curves for polymer solution with 0.25% DMF added.

methods for the same polymer solutions under similar mixing conditions. In addition, dielectric measurements have the advantage of being more quantitative and reproducible than the visual methods.

Another point to note is that the baseline value of ϵ'' varies slightly among experiments. For example, the value at 1.0 Hz ranges from approximately 3 to 7 in different experiments. This is caused most likely by the condition of the dielectric probe. The probes are cleaned and reused when possible and may be altered slightly by the cleaning process. Generally a probe will survive only one or two cleanings before the circuit delaminates and the probe is discarded.

Conclusions

A new technique has been developed to measure blend time, which is particularly useful for organic solutions with low conductivity. This technique uses the measurement of dielectric loss as an indication of the mixing time. Mixing curves generated by this method are consistent and the blend times are easy to determine. Temperature effects on the dielectric loss are minimal as long as the temperature is controlled within a few degrees as the measurement is being made. We have further shown that DMF acts as a useful tracer material in the blend time determination. The tracer concentration and measurement frequency should be optimized independently for any system under study. We have also determined that this method gives blend times very similar to those obtained by visual methods.

In a small-scale laboratory vessel, where it is easy to achieve good mixing, a single probe proved sufficient to determine blend time. On a larger scale, where significant dead zones could exist in the vessel, multiple probes will be required. This would allow for comparison of mixing effectiveness in different locations in the vessel, identify locations of dead zones, and give a quantitative measure of the overall mixing in the vessel. Further work will be necessary to design a scaled-up version of the probe for use in a plant-scale vessel and to determine the optimum number and location of measurement points.

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