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Inline Dielectric Monitoring of MMA/BuA Copolymerization Reactions

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Abstract: Dielectric analysis has become an effective instrumental means for monitoring a variety of polymer resin processing properties. This is because the dielectric properties are sensitive to the changes of resins properties linked to the mobility of the polymer molecules. In the present work, dielectric analysis is used for in-line evaluation of monomer conversion and overall conversion during MMA/BuA solution copolymerization carried out in batch. An empirical model was derived to correlate the dielectric loss factor and monomer conversion. The effects of inhibitor and MMA concentration on the dielectric properties are also investigated. It is shown here that this technique allows the successful real-time evaluation of monomer conversion in lab-scale MMA/BuA solution polymerization reactors, but that limitations do exist, and in particular the need for experiment-specific calibrations.

Keywords: Dielectric analysis · In-line measurements · MMA/BuA copolymerization · Solution

1. Introduction

The increasing requirements of quality, safety and economic operation are all reasons for the ever-growing interest in the development of in-line sensors and techniques for monitoring process variables and product properties.

Monitoring techniques based on dielectric analysis are well suited to provide real-time data with simple hardware and software tools. A small sensor that provides an effective instrumental means for monitoring a variety of polymer resin processing properties can be inserted into an existing reactor system without time-consuming modifications. In some systems this type of probe can be very useful because the dielectric properties such as permittivity (dielectric constant) and loss factor are sensitive to changes in polymer properties such as varying viscosity or the formation of a crossed-linked insoluble solids [1][2].

Recently, a relatively large number of publications presenting experimental in-line measurements of dielectric properties have been reported in the literature. However, most of these investigations refer to cure monitoring applications and very little is known about the in-line evaluation of these properties for estimating homo/copolymerization progress. Crowley and Choi [3] reported the use of dielectric sensor as an in-line monitoring device for monomer conversion measurement. However, their study looked only at the homopolymerization of MMA (methyl methacrylate).

In the present work, dielectric analysis is used for in-line evaluation of monomer conversion and overall conversion during MMA and BuA (butyl acrylate) batch solution copolymerizations. An empirical model was derived to correlate dielectric loss factor and monomer conversion.

2. Experimental

Solution MMA/BuA polymerization batches were carried out at 60 °C with toluene (Laurylab-France, 99%) as solvent and AIBN (Acros Organics, 99%) as initiator, using a 1 l stirred tank reactor. Samples were occasionally collected from the reactor for off-line determination of monomer conversion by gravimetry. Gas chromatography analysis (CG 5890 Hewell Packard) was used to determine individual monomers conversion. The monomers used were MMA (Acros Organics, 99%), BuA (Acros Organics, 99+%). Chemicals were used as received. Both the MMA and BuA used in the batches contain 10 and 20 ppm of MEHQ (monomethyl ether of hydroquinone).

Dielectric measurements at frequencies of 1 Hz were collected at regular intervals of 1 min using an impedance analyzer/gain-phase SI 1260 (SOLARTRON INSTRUMENTS) controlled by a microcomputer, connected to a planar wafer-thin sensor inserted into the reactor. The sensor is inert and has 2 cm x 1 cm area and 1mm thick. For all the batches, a sinusoidal voltage with amplitude of 1 V was imposed across the sensor. The resulting current traversing the sensor was also sinusoidal but out of phase with the voltage signal. The instrument measures the amplitude ratio and phase difference of the signals and, from these, calculates the equivalent capacitance and conductance. These two values are used to calculate the permittivity (ε') and loss factor (ε'') for the polymer solution in contact to the sensor, as described elsewhere [1–3].

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3. Results and Discussion

For the sake of the dielectric signal calibration, solution MMA/BuA polymerization batches with different initial compositions were carried out. Table 1 shows experimental conditions for the polymerization runs, where *w* represents the initial weight fraction of MMA in the monomer mixture.

Fig. 1 shows the typical evolution of loss factor dielectric signal at a frequency of 1Hz when homo/copolymerization batches are carried out. Loss factor values change dramatically as polymer is formed, indicating high sensitivity to the resistance imposed by reactor media to the mobility of ions. This is to be expected because a low frequency electric field was applied. It can also be noted that a maximum value of loss factor occurs at each polymerization run, at different reaction times. This behavior was also observed by Choi and Crowley [3], and was attributed to the induction period of the process, due to the consumption of inhibitor molecules by initiator radicals. In this case, the maximum value of loss factor dielectric signal represents the start-up of the polymerization process. To minimize batch-to-batch variations, calibration tests must be done with normalized dielectric data.

For practical applications, the monitoring of normalized loss factor should be done only after the evaluation of $\varepsilon''(\omega)_{max}$. This constraint may be unimportant, as $\varepsilon''(\omega)_{max}$ is generally observed during initial instants of the polymerization

Table 1. Experimental conditions of the polymerization runs: calibration data set

Run[a]	MMA [g]	BuA [g]	w
Exp1 - MMA	320	–	1.00
Exp2 – MMA/ABu	240	80	0.75
Exp3 – MMA/ABu	160	160	0.50
Exp4 – MMA/ABu	80	240	0.25

[a] Solvent: toluene (480 g); solids content = 40%; T = 60 °C; [AIBN] = 3 g/l

The influence of induction period can be clearly seen in Fig. 1 and Table 2. Dielectric measurements are more delayed as *w* decreases. This occurs because as *w* decreases, we add more BuA, and thus more inhibitor w.r.t the initiator concentration.

Table 2. Inhibitor concentration in the media

w	MEHQ ppm	Inhibition time
1.00	10.0	2.0 min
0.75	12.5	4.0 min
0.50	15.0	10.0 min
0.25	17.5	14.0 min

Gravimetric measurements of conversion and normalized loss factor values were correlated by an empirical model described by Eqn (1), where the parameters k_1 and k_2 (with 95% confidence interval) are given by $k_1 = 1.05E\text{-}2 \pm 3.0E\text{-}4$ and $k_2 = 4.288 \pm 0.121$.

$$x_g = k_1.\exp(k_2.\varepsilon'') \qquad (1)$$

This empirical approach can account for the different compositions in the batch, and the overall gravimetric conversion. Thus, MMA conversion was regarded as dependent of a sort of parameters p_i and variables Φ_i in a polynomial

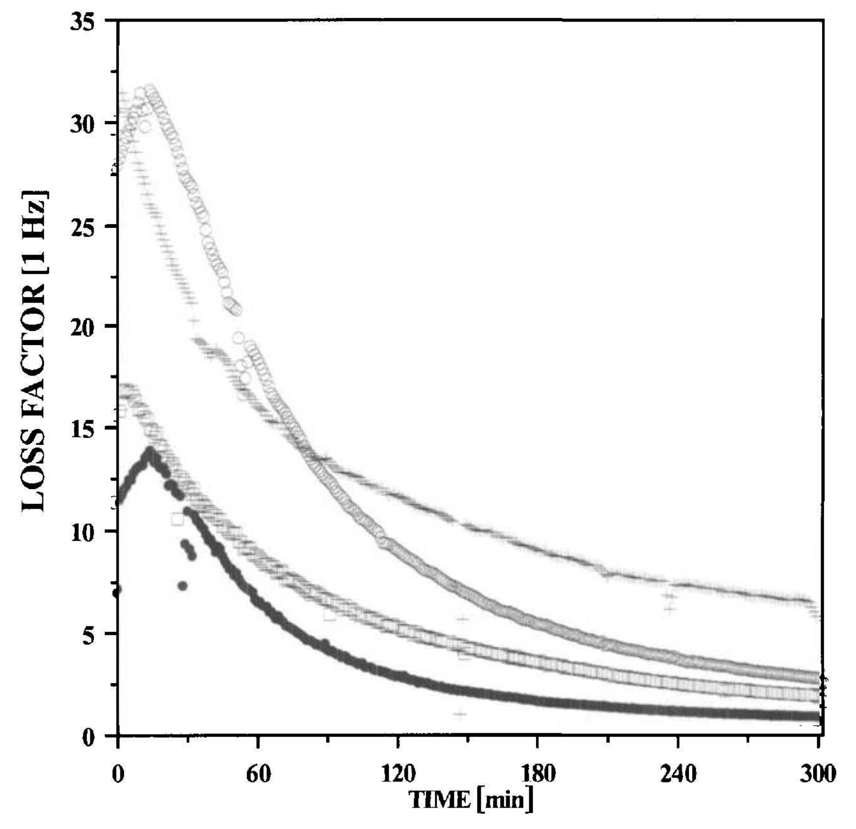

Fig. 1: Dielectric signal monitoring during polymerization runs, *w* = 1.0 (+), *w* = 0.75 (□), *w* = 0.50 (○), *w* = 0.25 (●).

approach, described by Eqn (2). The variables were chosen by the trial-and-error method, and a minimization of the difference between chromatographic and predicted values for MMA conversion. The p_i parameters calculated from such approach are (0.354, -0.620, 0.555, -0.375, 0.163, 1.048). The Φ_i variables used in the regression are [1, ε'', ε''^2, w, w^2, x_g]. These variables were found to provide the best agreement between predictions and calibration data set.

$$x_{mma} = \sum p_i \cdot \Phi_i \qquad (2)$$

Fig. 2 (A,B) shows the estimation of the overall and MMA conversions for copolymerization batches. It can be observed that the model fits quite well overall conversion values, some difficulties are observed for MMA individual conversion at initial times due to the presence of inhibitor molecules, as discussed above.

An extra MMA/BuA copolymerization (w = *0.50*) run was carried out in order to validate the empirical model, as shown in Fig. 2 (C). It can be observed that, particularly for the MMA conversion, predicted values are underestimated. However, overall conversion predicted values are in good agreement with observed values.

4. Conclusions

An empirical model was derived to correlate dielectric loss factor and monomer conversion. The effects of inhibitor contents and MMA concentration on the dielectric properties were also investigated, showing that this technique allows the identification of the induction time. The empirical model can be used at different MMA contents. However, further calibration is needed if we are to treat a wider range of conditions.

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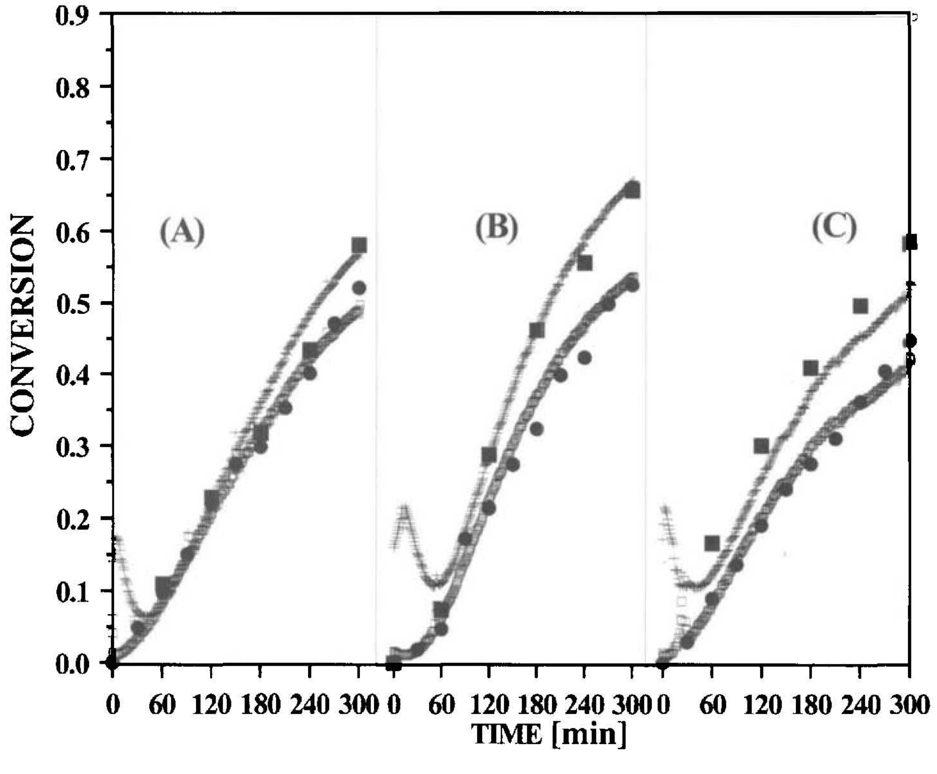

Fig. 2: Estimation of the overall (□) and MMA (+) conversion, and comparison with x_g (●) and x_{mma} (■) experimental values: (A) w=*0.75*, (B) w=*0.50*; (C) validation results for an extra batch with w=*0.50*