Inline Conversion Monitoring in MMA High Solid Content Polymerization Process

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Abstract: Inline conversion measurements in chemical reactions are in general and especially in polymerization reactions necessary for process monitoring and control. For polymerization monitoring, the sound propagation (UPV) can be related to the texture of the bulk with a high accuracy. As the monomer is transformed to polymer, both the density and adiabatic compressibility change, making the UPV closely related to the monomer conversion. This technique is based on the increase of UPV with rising elasticity of the medium due to the polymerization. The application of the UPV technique to follow the composition evolution of the solution during the polymerization reaction in a recycle tubular reactor is presented. The sensor can be directly inserted in the tubular reactor and does not require a sampling circuit. This makes its use particularly simple and suitable for laboratory and industrial purposes.

Keywords: Conversion monitoring · MMA polymerization · PMMA · Ultrasound measurement

1. Theoretical

The ultrasound propagation velocity (UPV) in gases, liquids or solids depends on the density and the adiabatic compressibility of the media. The functional relationship is as follows [1][2]:

$$c^2 = \frac{1}{\varrho \beta}$$  \hspace{1cm} (1)

Where \(c\) is the propagation velocity and \(\varrho, \beta\) are the mean values of the density and the adiabatic compressibility. The major influence on the propagation velocity comes from the compressibility; this means that in case of increasing velocity the density and compressibility can be contradictory. This also means that in case of small density differences a large difference in sound propagation velocity occurs.

The mean values of the density and compressibility are estimated as follows:

$$\varrho = \sum_i \Phi_i \varrho_i$$  \hspace{1cm} (2a)
$$\beta = \sum_i \Phi_i \beta_i$$  \hspace{1cm} (2b)

\(\Phi_i\) is the volume fraction of the \(i\) component in the medium and \(\varrho_i, \beta_i\) respectively, the density and the adiabatic compressibility of the pure component. These equations express the additivity rule when calculating the average density and the average compressibility [3][4].

The volume fraction \(\Phi_i\) can be expressed as a function of the mass fraction \(w_i\):

$$\Phi_i = \frac{w_i \varrho_i}{\sum_i w_i \varrho_i}$$  \hspace{1cm} (3)

The densities and compressibilities are calculated from polynomial equations like [5]:

$$\rho_i, \beta_i, = A + B T + C T^2 \hspace{1cm} (4)$$

except for the polymer compressibility where we used the values taken from [6] and fitted with an equation of the form:

$$\beta_{PMMA} = \frac{A + C T + E T^2}{1 + B T + D T^2 + F T^3}$$  \hspace{1cm} (5)

If one takes into account a linear relationship between UPV and the pressure:

$$c_0 = c - \alpha P$$  \hspace{1cm} (6)

the final equation that has to be solved for \(w_p\), the polymer mass fraction, derived from Eqs 1, 2a, b, 3 and 6 is:

$$\sum_i \frac{w_i}{\varrho_i} \varrho_i = \frac{w_p \varrho_p + w_m \varrho_m + w_i \varrho_i}{\varrho_p + \varrho_m + \varrho_i}$$  \hspace{1cm} (7)

2. UPV Measurement Equipment

Until now there was no possibility to measure at temperatures higher than 110 °C [7]. The new sensor-setup (Sensotech, D) gives us the opportunity to follow the polymerization of PMMA up to 150 °C in a pilot plant reactor. Fig. 1a,b shows the new sensor where the parts in contact with hot temperature of the emitter and receiver are separated from the electronic supply via a temperature resistant cable.
3. Pilot Plant

The pilot plant for free radical polymerization of MMA is shown schematically in Fig. 2. It consists of a recycle tubular reactor for pre-polymerization [A], in series with the postpolymerization tubular reactor [B] the preheater [C] and the devolatilization unit [D]. It is constructed entirely of stainless steel 316. The inner diameter of the tubes is 22 mm. The whole reactor contains static mixing elements also in stainless steel 316 of the type SULZER SMXL.

The whole reactor is constructed from jacketed tubes assembled in a way that the recycle loop, the postpolymerization tube, the preheater and the devolatilization unit can be separately heated (T1, T2, T3, T4). The temperature inside the reactor is measured by means of several thermocouples.

Two pressure transducers are used for pressure drop measurements. Polymer samples can be taken through valves at three different points along the reactor in addition to the exit.

4. Results and Discussion

The value for \( \alpha \) in Eqn 6 is fitted to the slope values of this UPV-pressure dependence for various temperatures and polymer mass fractions. The derived equation is as follows:

\[
\alpha = 0.471 + 0.00252^{T} - 0.2145^{w_p}(8)
\]

Fig. 3 shows the comparison of the analytical methods between:
- offline multiple head space gas chromatography MHE-GC analysis
- inline UPV measurements solved from Eqn 6

The free radical polymerization of methylmethacrylate in a continuous process can be monitored inline by measuring the UPV in the polymeric medium. This technique allows the following of the solution composition evolution during the polymerization as well as the residence time distribution determination [8] opening the way to online reactor control.

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