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Automatic Ultrasonic Monitoring of Vinyl Chloride Polymerization

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Abstract

An automatic method and apparatus for continuous monitoring of vinyl chloride suspension polymerization was developed and built, which enables a parallel measurements of attenuation changes and velocity of ultrasonic propagation in frequency range from hundreds of kHz to units of MHz and in dynamic range greater than 60 dB. The results of automatic measurements were compared and tested by previous results obtained manually by means of MATEC Model 6000/755 ultrasonic comparator and have showed many substantial advantages of ultrasonic attenuation measurements for checking through the suspension polymerization of vinyl chloride e.g. possibility of indication of very fast phase changes during the process as well as the prediction of the PVC particles final morphology properties including eventual undesirable polymerization courses.

Introduction

Recently we have shown the feasibility of the measurements of ultrasonic attenuation of 1 MHz longitudinal waves during the suspension polymerization of vinyl chloride. The measurements were carried out manually by means of MATEC ultrasonic comparator and revealed some correlation between the ultrasonic attenuation as a function of polymerization time and physical properties of the final PVC particles (SLADKY et al. 1979). On the ground of this experimental results we have proposed simple qualitative interpretation of the interaction of longitudinal ultrasonic waves of a given frequency range during the various

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stages of the polymerization process. The interpretation was based on the model of local phase transitions of the polymerizying monomer from liquid to gaseous state and vice versa within the particle beads (SLADKY 1979, ZDRAZIL 1978).

On the other hand our results have shown a necessity of the measurements of acoustic spectra for more detailed understanding of the interaction as well as the effective automation of our experimental technique.

The purpose of our present contribution is to show some preliminary results of the automatic monitoring of ultrasonic attenuation during vinyl chloride suspension polymerization process and to compare them with previous results recorded manually.Such a comparison will reveal clearly all advantages of this new technique for studying various stages of the vinyl chloride suspension polymerization.

Experimental

Polymerization was carried out in 8 liter stainless steel reactor provided with variable frequency stirrer, thermostating mantle and electronic temperature controller of standard type.

The reactor was filled with 4.2 l of the water phase together with 2.4 l of vinyl chloride. A mixture of methylhydroxyprophyl celulose in concentration of 0.14 weight % per monomer was used as the emulsifying agent. The iniciator was diacethylperoxidicarbonate in 2.2 mmol concentration. pH of the water phase was adjusted between 10 to 11. After filling the reactor with water the space in the reactor was stripped with nitrogen gas and evacuated subsequently to about 2 kPa prior to monomer adding. Stirring frequency was set to 5.5 Hz. The polymerization temperature was 54 ± 0.5 °C, the pressure 0.8 MPa. After about 220 minutes of the polymerization process the drop of the pressure in the reactor was observed. The polymerization was yet running for about one hour and than was stopped by cooling the system and releasing the nonpolymerized monomer out of the reactor.

At the end of polymerization the conversion degree of the system was 87 ± 1 %. Polyvinyl chloride was than washed carefully and after drying it was analysed according to the Czechoslovak standard No. 643200. The viscose number of the final product was (124 ± 4) . $10^{-3}m^3kg^{-1}$ which corresponds to the value of K = 70 ± 1.

The ultrasonic part of our apparatus was already described in detail on another place (SLADKY et al 1979). The electronic part consists of the standart type r.f. gated ultrasonic generator - reciever with buffer amplifier and impedance matching networks to the transducers and electronic detection stage based on peak detection system with more than 60 dB dynamic range. The detailed description of the electronic part of the automatic apparatus for attenuation and velocity measurements is described on another place (PARMA et al. 1980).

Results and discussion

In the first part of verifying the function of our automatic apparatus we focused on measurements of the ultrasonic attenuation only. We have carried out the measurements with ultrasonic pulses of the frequency of 0.83 MHz that means at the frequency, which is a little lower than in the previous measurements with MATEC comparator. The curves of the time dependence of the ultrasonic attenuation $\alpha(t)$ were recorded during the polymerization by standard laboratory pen recorder. Results of the measurements are shown in Fig. 1. For to appreciate the measurement reproducibility and errors the courses of the dependence $\alpha(t)$ for two independent polymerization of the same prescription and above described technology are here compared. The polymerization described by the lower curve was stopped approximately after two hours since the beginning of the measurements. Because the long therm stability of the apparatus was better than 1 %, we can say, that the individual changes of the time course $\alpha(t)$ are given above all by the divergences in prescription and polymerization technology. That is obvious e.g. from the point (14) on the upper curve $\alpha(t)$ in Fig. 1 when compared with the same place on the lower curve. We succeeded to record the similar structure in manual measurements only partly, as can be seen from Fig. 2 where the results of the measurements for four polymerizations of nominally the same prescription and technology are compared. The larger time resolution of automatic measurements regards especially the beginning phase o polymerization, as can be seen from comparison of Fig. 1 and Fig. 2.

In the next discussion we will show further advantages of automatic recording of the ultrasonic attenuation curves during polymerization from the point of view of description and identification of single technologic operations and process events. The advantages of automatic measurement appear above all in the monitoring of the fast changes of the polymerization process including its preparation phase. For that purpose there are significant moments of laboratory preparations and of given course of vinyl chloride suspension polymerization numbered on the α (t) curve in Fig. 1.

The ultrasonic probes placed approximately on the level of half reactor depth are in the very beginning of measurement (1) surrounded by air. At this time only the ultrasonic crosstalk occures which is caused by spreading the ultrasound through the probes and reactor constructions. These signals are well below 60 dB. During the filling of the reactor with water phase the partial dip of the probes takes place and the attenuation of ultrasound sharply falls down (2). During further filling the surface of water phase shortly waves around the mean axis of the ultrasonic beam, which presents sharp oscillations in the moment (2). The end of the filling and closing the filling neck calls up also a little discontinuity in attenuation changes (3). In the moment (4) the stirrer is switched on. The strong agitation of water phase appears and the polymerization ingredients mix together, which is connected with producing the foam. Attenuation extremely grows up, practically on the noise level due to great unsonorousness of the system in certain time interval (5) - (11). During this interval rinsing the reactor and its contents by nitrogen and the evacuation of air rests takes place.

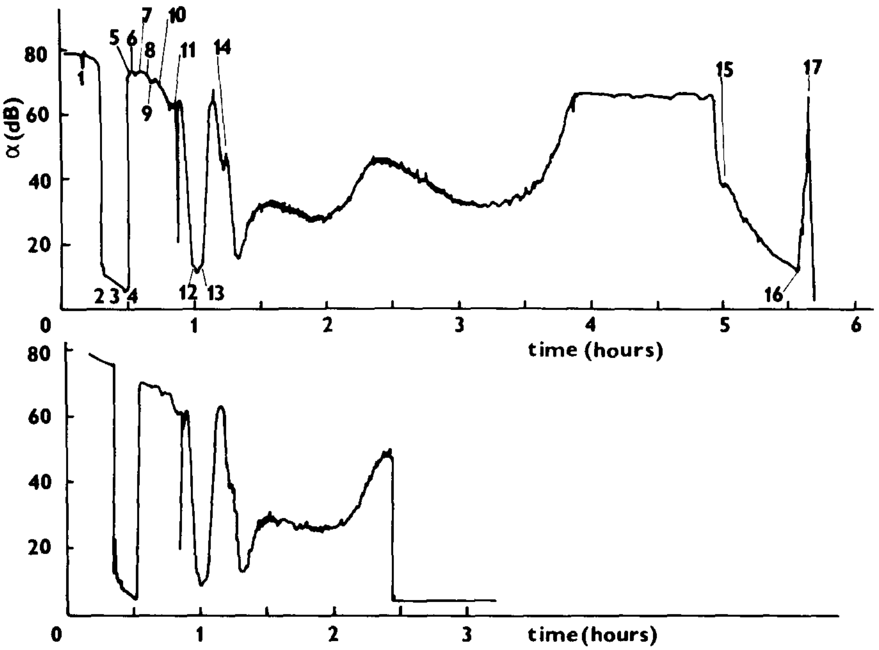

Fig. 1. Time dependence of ultrasound attenuation taken during polymerization of vinyl chloride. Points of interest are numbered (for legend see text).

Pressure changes provoked by given operations become evident as effective changes on the smooth course of the attenuation curve. The ultrasonic probes connected with the apparatus work than also as a differencial pressure gauge. In the moment (11) the liquid monomer begins to fill in. The filling passes under continual stirring of the set. Stirring the monomer into water phase stops producing the foam for a short time and the attenuation intensively drops down (see the vicinity of the point (11)). By further stirring a part of monomer evaporates for a moment. This state lasts approximately 5 minutes, and after it the attenuation gradually declines to the minimum corresponding to the end of dosing (12). After the beginning of heating the set of a temporary evaporation of monomer occures again (13). Due to this a maximum appears, which presents discontinuous drop arround the point (14).

During the previous manual reading of the attenuation from the oscilloscope screen we started the measurements from the point (13) that means after filling the reactor (see also Fig. 2). The great attenuation changes (2), (4) or, on the contrary, very small changes (5) - (10) we were not able to record manually.

Further course of the attenuation curve in time qualitatively agrees with the course of manually recorded curves (Fig. 2). Comparing both pictures the difference in the curves (x,▲,●, o) from the last curve marked (o) is evident. This difference is caused by the reactor filling technology modification. The same technology is used also for present automatic measurements as follows from the comparison of curve (o) in Fig. 2 and the curves in the Fig. 1 at the time 20 minutes after the beginning of the heating.

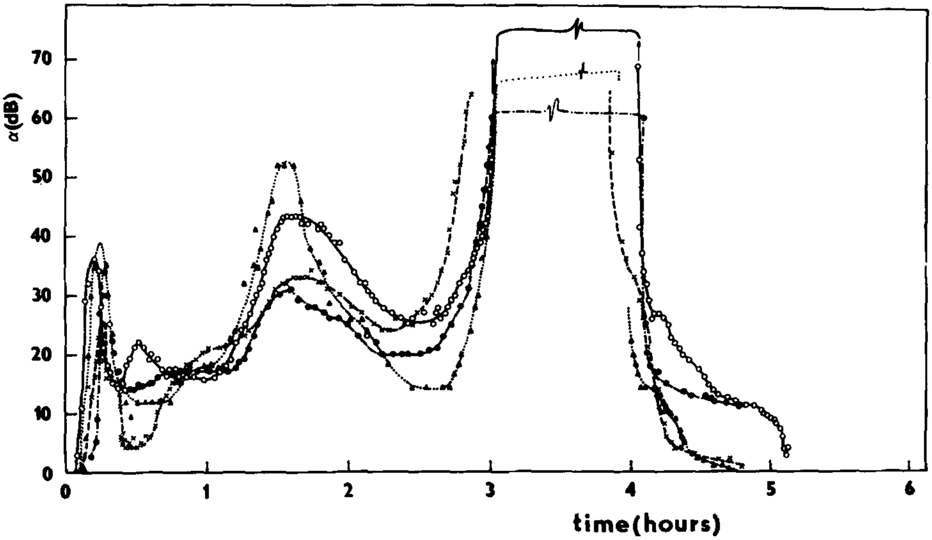

Fig. 2. Time dependence of ultrasound attenuation as gained manually by means of MATEC.

Because of little space here, we would not discuss in details the origin of the maximum on the α (t) curve in the interval (14) - (15), because this is the aim of next studies. We would like to add only, that the main maximum on the attenuation curve for given technology and prescription appears 40 minutes before the pressure drop. Because in this maximum the ultrasonic attenuation, due to the scattering on gas centres in the system, reaches substantially higher values than the dynamic range of our apparatus, plateau on 70 dB level appears on the attenuation curve, here. Few minutes before the pressure drop in the polymerizying system the attenuation decreases substantially for a given prescription and technology, with gradual retards in the vicinity of the point (15). This temporary attenuation raising was also recorded during the manual measurements (see Fig. 2, curve (o)). It corresponds within the 3 min. accuracy to the point of pressure drop in the reactor. After pressure drop the attenuation continues to decrease until the polymerization stops due to additional cooling of the system. After it the pressure in reactor is decreased finally by releasing the nonpolymerized monomer (16). The gas outlet from the final PVC suspension results in producing great bubbling. That presents an extreme nonsonorousness of the system until the pressure repeats to increase by e.g. closing the releasing valve (17).

More detailed discussion of the course of ultrasonic attenuation as a function of pressure at the end of polymerization process was given in (SLADKY et al. 1979).

Conclusions

Method and apparatus for automatic continuous monitoring of vinyl chloride suspension polymerization was developed and built, which enables a parallel measurement of attenuation changes and velocity of ultrasonic propagation in frequency range of hundreds of kHz and with dynamic range greater than 60 dB. The automatic monitoring of vinyl chloride suspension polymerization was examined in industrial laboratory practise. The results of automatic measurements were compared and tested by previous results obtained manually by means of MATEC Model 6000/755 ultrasonic comparator and showed many substantial advantages of those ultrasonic attenuation measurements for checking during suspension polymerization of vinyl chloride. The advantages can be summarized as follows:

1. High reproducibility of the measurements of ultrasonic attenuation coefficient changes during the individual polymerization process as well as during its preparation stage.
2. Possibility of indication of very fast changes (in second scale) during the polymerization as e.g. local phase changes due to evaporating monomer, foaming and boiling of the system and other temperature or pressure changes in polymerizying system.
3. Possibility of prediction of the PVC particles final morphology properties including eventual undesirable polymerization courses.

Besides that the results of measurement proved that the automatic monitoring of polymerization process by ultrasound brings new, qualitatively and quantitatively higher degree of process description and control in general sense of the word. It supplements and substantially extends the information obtained until now on the base of measuring temperature and pressure during polymerization, especially as far as the recording data speed and resolution capabilities in prescription composition and technology of the process are concerned. Further significant advantage is also the nondestructive character of ultrasonic measurements and the high degree of electric spark security in comparison with the pure electric measurements. Thanks to this, the ultrasonic automatic monitoring appears to be very advantageous also for the control and description of other suspension or block polymerizations. In future it can be justifiably awaited to be used not only for developing new ways of polymerization but above all for their automatic control.

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