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Imaging nylon polymerisation processes by applying electrical tomography

Tom Dyakowski[a,*,1], Trevor York[b], Michal Mikos[c], Dimiter Vlaev[a], Reg Mann[a], Gordon Follows[d], Arthur Boxman[d], Mike Wilson[e]

[a] *Department of Chemical Engineering, UMIST, PO Box 88, Manchester M60 1QD, UK*
[b] *Department of Electronics and Electrical Engineering, UMIST, PO Box 88, Manchester M60 1QD, UK*
[c] *Institute of Heat Engineering, Warsaw University of Technology, Warsaw, Poland*
[d] *DuPont (UK) PO Box 401, Middlesbrough TS6 8JE, UK*
[e] *DuPont (UK) Ltd., Gloucester GL4 3HP, UK*

Abstract

The paper presents an application of electrical tomography for imaging a nylon polymerisation process at elevated temperatures (up to 275°C) and pressures (up to 22 bar). The process was realised within a metal walled tank using a sensor constructed in the form of a ceramic sleeve with electrodes coated on the inner surface. The images obtained show the dynamic behaviour of the process and how the electrical properties of the material varied with time.

Keywords: Electrical tomography; Nylon polymerisation; Plasma technology

1. Introduction

Electrical tomography has been applied to imaging electrically conducting media (resistivity tomography) or dielectric media (capacitance tomography) at ambient temperature and pressure [1]. These applications were mainly concerned with imaging flow morphology of multi-phase flows: gas–solids (capacitance tomography) and solids–liquid (resistivity tomography). Non-homogeneities in phase distribution resulting from various types of interactions between phases were imaged and those images provided valuable information on the dynamic behaviour of multi-phase flow [2]. The results were obtained for flow conditions characterised by constant physical parameters (conductivity or permittivity). For such conditions the measured signals were only functions of material distribution in a pipe or a vessel cross-section. For example, for resistivity tomography, this significantly simplified the measurement protocol by using only one set of injecting currents.

This paper presents an application of electrical tomography, which is focused on imaging a nylon 6.6 polymerisation process. A key difference from earlier work is that the electrical properties of the material studied varies significantly during this process, the first step of which involves reacting hexamethylene diamine and adipic acid at low temperature to form hexamethylene diammonium adipate or nylon 6.6 'salt'. In the laboratory, polycondensation of this salt to polymer is carried out with a 85% salt : 15% water solution in a stainless steel autoclave and involves pressures approaching 20 bar and temperatures up to 275°C.

The polymerisation process itself maybe divided into four stages which can be described as heating, boiling, pressure reduction and equilibrium. During the first two stages, condensation commences but because of the high pressure the reaction mixture remains quite fluid and low molecular weight products remain in solution, albeit they become more and more viscous as the condensation proceeds. During the third stage, pressure reduction, heat continues to be applied to raise the temperature close to 275°C whilst simultaneously reducing pressure. After reaching atmospheric pressure the batch temperature is maintained at ca. 275°C to complete the polymerisation after which the molten polymer is extruded from the bottom of the autoclave.

It will be appreciated that as the condensation proceeds there is a progressive removal of water with a consequential significant impact on electrical properties.

2. Experimental facilities

An experimental set-up is shown in Fig. 1(a–b).To insulate the electrodes from the autoclave metal wall, a ceramic

* Corresponding author.
[1] The authors, Tom Dyakowski, Trevor York, Dimiter Vlaev and Reg Mann, are members of the Virtual Centre of Industrial Process Tomography.

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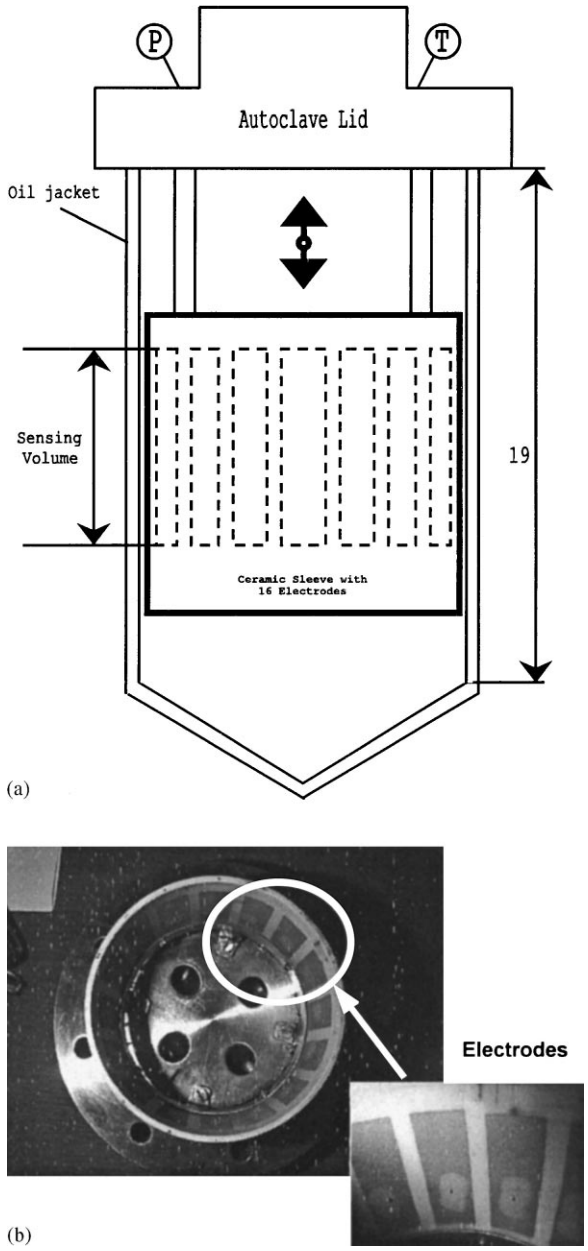

Fig. 1. (a) Ceramic sleeve design allowing suspension at various vertical positions, (b) ceramic sleeve (ϕ120) with 16 embedded electrodes.

sleeve with a set of 16 electrodes was inserted into the autoclave. Spraying a composite powder (80% nickel and 20% chromium) onto the sleeve inner surface formed the electrodes. This was achieved by applying a plasma technique at atmospheric pressure, the composite powder being introduced into the plasma jet, the inlet temperature of which was 15,000°C and the outlet temperature 8000°C. Solid particles were melted and liquid particles hit the inner surface with the velocity of about 300 ms^{-1}; to assure good adherence, the inner surface of the ceramic sleeve was rough. Additionally, a cooling system was applied to control the rate of solidification of melted particles. A full technical description is described elsewhere [3].

At the start of the heating stage, the mixture of salt and water is of low conductive but subsequently conductivity increases as the nylon salt dissolves in the water. However, at the end of the polymerisation process when nearly all of the water of solution has been removed, conductivity again approaches a value close to zero. Such variations in conductivity imposed some requirements concerned with the measurement techniques.

Here, a use of modalities: resistivity and capacitance for imaging the whole polymerisation process is presented. Both qualitative and quantitative results were obtained by using the two instruments. These were the ITS1000 data acquisition system with the injected current within the range 1–15 mA and the HP4284A LCR meter. In capacitance tomography, the neighbouring electrodes were coupled together and the switching between the resulting eight electrodes was carried out using a specially designed electronic switch matrix [4].

The aim of the experimental program was two-fold. Firstly, to measure the electrical properties (capacitance and conductance) during the polymerization process and on this basis to characterize its different stages. Secondly, to obtain information about the phase distribution at different polymerization stages by tomographic imaging.

The electrical conductance is a function of the material properties and sensor geometry. On the other hand, the electrical conductivity is only a function of material properties. Therefore, an additional experiment was carried out to relate, for our sensor, the electrical conductance to the electrical conductivity. A Sentek glass conductivity cell ($k = 1.0$) connected to the Jenway 4320 conductivity meter was used to measure the conductivity of the brine solution. Brine solutions of different conductivity were prepared and the conductance for each was measured by the impedance analyser. The autoclave was additionally filled to different levels of each of the brine solutions.

The relationship between the conductance and conductivity is shown in Fig. 2. As expected the conductance measured between various pairs of electrodes is slightly different. However, it is important to notice that the conductance strongly depends on the fluid level within an autoclave. For example, for an initial level (12 cm from the lid) and an adjacent pair of electrodes the conductance of 50 mS corresponds to conductivity of 22 mS/cm, (Fig. 2a). For a final level (14 cm from the lid) the same conductance corresponds to conductivity of 50 mS/cm. This seems to be caused by the three-dimensional character of the electrical field distribution.

Fig. 3 shows the conductance profile obtained from measurements between one adjacent pair of electrodes. The results are very similar for other pairs of electrodes. The process starts off in a relatively low conductance environment (about 5 mS) after which during the heating-up stage the measured conductance reaches its peak (about 75 mS) at about the 45th minute of the cycle at temperature 195°C and pressure 100 psi. The peak in conductance values is

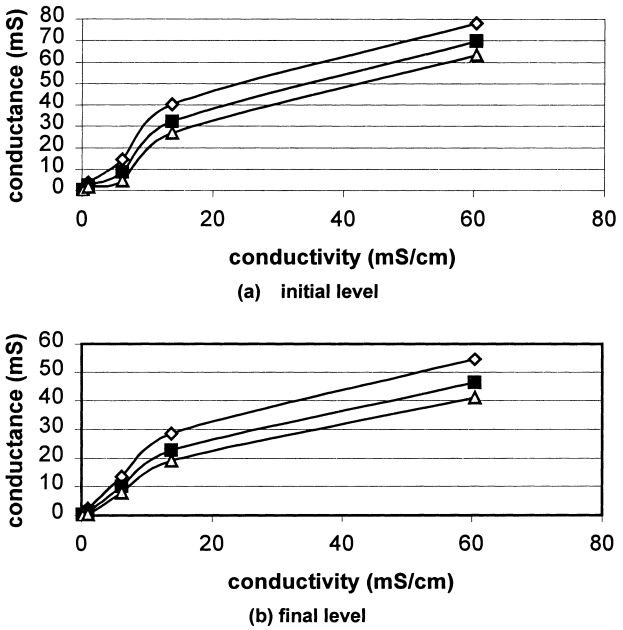

Fig. 2. Calibration curves for the 2L Wilton autoclave for three pairs of electrodes (adjacent: ◇; opposite: ■; next-but-one, i.e. electrodes 2 and 4: ▲).

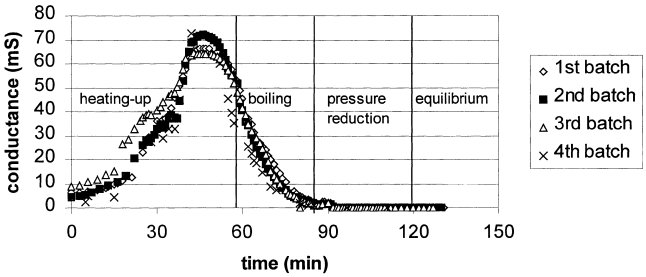

Fig. 3. Conductance profile throughout the nylon polymerisation batch.

followed by a steady decline which begins a little before the end of the heating-up stage and continues through the boiling and the pressure reduction stages. By the time the process enters the equilibrium stage, the conductance had reached very low values. The results presented in Fig. 3 confirm the earlier data reported in [5].

Within the heating up stage, the ERT system was set up with an injection current of 15 mA. The images presented in Fig. 4 show little variation, which corresponds to a nearly uniform distribution of the material within the vessel. During the following stages the injection current was adjusted according to the changes in the conductance as shown in Table 1.

Table 1
Injected current variations

Time (min)	45	72	86	97	110
Current (mA)	15	10	5	3	1

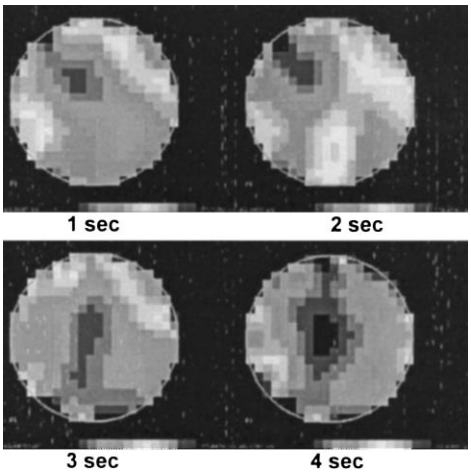

Fig. 4. Images obtained in a nylon producing autoclave (heating up).

It was observed that the boiling and pressure reduction stages were accompanied by more non-homogeneous material distribution than during the heating up stage, Fig. 5. During the boiling stage additional heat is applied and the pressure control valve bleeds off steam to maintain constant pressure. This results in drastic changes of conductance distribution as illustrated in Fig. 6.

2.1. Capacitance tomography imaging

The 28 capacitance measurements obtained from eight electrodes by the impedance analyser constitute a frame which could be used to reconstruct an image of the process medium in a cross-section of the autoclave. As the values of the measured capacitances show great variation throughout the process, the two reference images (for the maximum and minimum dielectric permittivity) had to be chosen for a period of time when the difference in the measured capaci-

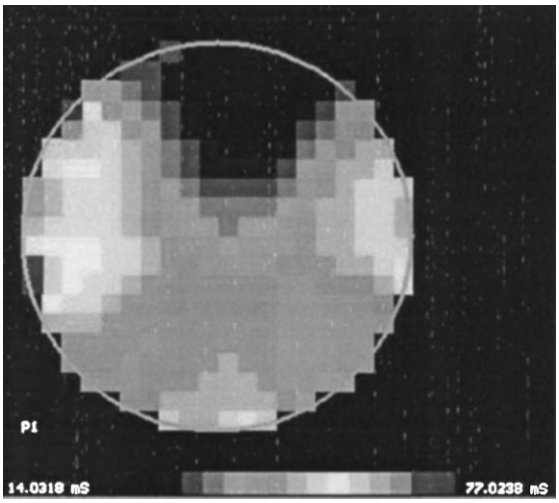

Fig. 5. Zone of low conductivity observed, during nylon polymerisation (boiling).

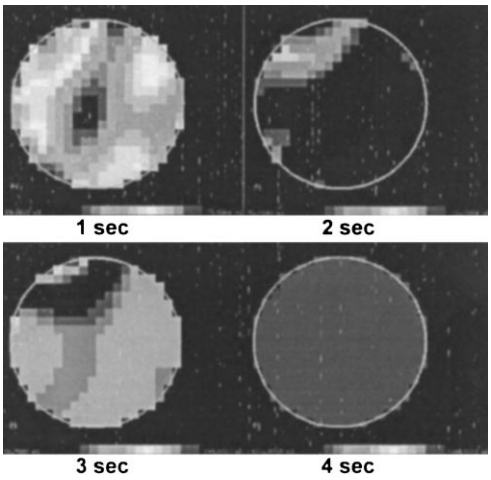

Fig. 6. Changes in the images coinciding with the valve bleeding off (pressure reduction).

tances was relatively small. In this way detail in the images is preserved. A convenient span of time is from the 95th minute onwards as Fig. 7 indicates.

Fig. 8 shows the imaging of the nylon polymerisation. The series of tomograms were produced off-line using a linear back-projection algorithm. The measurements were taken at 1 min increments, based on reference data collected at both ends of the measurement interval. The images show the dielectric permittivity distribution in the autoclave cross section. The distribution of moisture could be valued on this basis. The red colour, corresponding to the high permittivity of a mixture relatively rich in moisture, gradually disappears and by the end of the batch reaches the blue colour of a much drier polymer. The pattern of polymer demoisturising that all the images seem to suggest is a logical one. First the blue colour is established near the wall where the oil jacket (the heat source) is situated and only afterwards the moisture is driven out of the polymer in the centre of the vessel. Very similar findings were obtained from consecutive experiments.

3. Conclusions

The paper presents the first step in the application of electrical tomography for monitoring a chemical process at elevated temperatures and pressures. A specially designed sensor assembly enabled electrical signals to be taken from a metal walled vessel and through a metal lid. Plasma technology was utilized to fabricate a set of electrodes on the inner surface of the ceramic sleeve inserted into the metal walled autoclave and tests showed that the electrodes could withstand operating conditions within the autoclave.

The technique provides the basis for obtaining useful information about important stages of a nylon polymerization

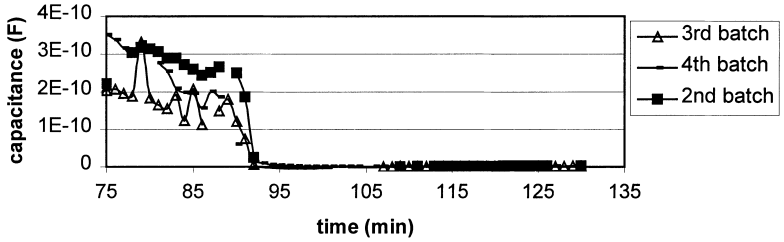

Fig. 7. Profile of the measured capacitances between electrodes 1 and 2 after the 75th minute of the nylon polymerisation cycle.

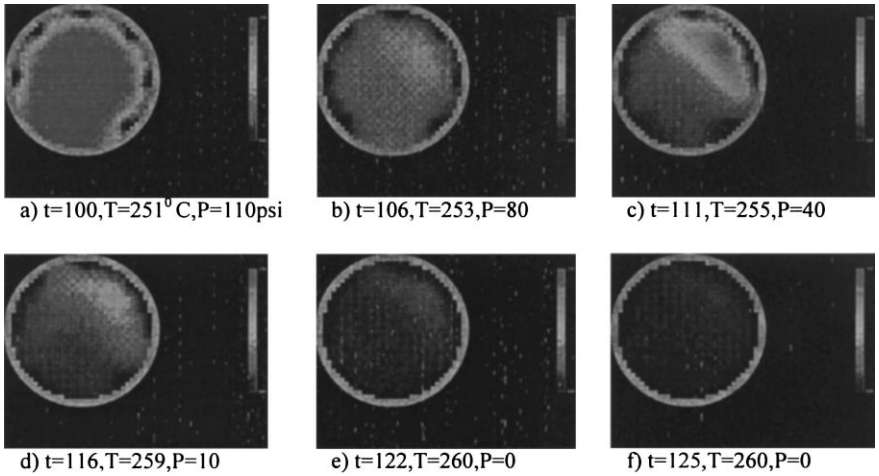

Fig. 8. ECT reconstruction of the data obtained from the first batch after the 100th minute of the nylon polymerization batch.

process. The quantitative and qualitative results were obtained during various stages of the nylon polymerization process. The electrical properties were characterized by measuring both conductance and capacitance, which are functions of the amount of 'salt', polymer and void fraction. The images show the material distribution during the heating up stage, the effect of opening the pressure control valve and the permittivity distribution at the last stage of the polymerization process. The future work program will focus on relating the obtained data to the physical modeling of the polymerization process.

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