ELSEVIER

Thermochimica Acta 269/270 (1995) 145–157

thermochimica
acta

Forced-adiabatic sampling environments: useful tools for the study of structure development during polymerization [☆], [1]

M.J. Elwell

Manchester Materials Science Centre, UMIST, Grosvenor Street, Manchester M1 7HS, UK

Received 16 September 1994; accepted 7 February 1995

Abstract

Forced-adiabatic conditions are shown to be an essential requirement for following chemical and morphological changes during bulk copolymerizations such that erroneous conclusions are avoided. Results are described for segmented block copoly(urethane-urea) foams analysed in spectroscopic (FT-IR), synchrotron X-ray scattering (SAXS) and rheological sampling environments.

Keywords: Forced-adiabatic conditions; FT-IR; Rheology; Sample environment; SAXS; Structure development kinetics

1. Introduction

The existing morphology of a polymeric article, be it a thermoplastic or thermosetting polymer, is determined by the processing thermal history. In order to have some degree of control over the resultant polymer morphology, the molecular response of the polymer or evolving polymer (depending on the processing route) to changes in temperature must be clearly understood. For thermoplastic polymers, in the majority of cases, a polymer in pelletized or powdered form is processed [1]. However, for some thermoplastics (for example thermoplastic elastomers) and the majority of thermoset-

---

[☆] Presented at the 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 11–16 September 1994.

[1] RSC Thermal Methods Group 7th TMG Award Paper

SSDI 0040-6031(95)02357-7

ting polymers, the situation is somewhat different. Here, the polymerization takes place within the confines of a mould that yields the eventual polymer article [2].

The reactive processing of thermoplastic/thermosetting materials from liquid monomers and oligomers involves a complex combination of both chemical and physical events [3, 4]. Within a short time interval, a liquid mixture of relatively low molecular weight components is transformed into a solid polymer. The temperature of the mould will determine the initial reaction kinetics and, thus, influence the reaction exotherm. The process thermal history determines the morphology evolved and, thus, the final properties of the polymer. Information regarding the reaction kinetics and the morphology is essential to obtain an objective description of the events taking place such that selective control of the process can be achieved.

Fast reactions put limitations on the techniques that can be employed for their analysis. It is very difficult to measure isothermal reaction kinetics during a fast bulk copolymerization. During rapid solidification with chemical gelation or vitrification times of ten minutes or less, there are two factors in particular that are inherent to the system which becomes overwhelming:

(i) The highly exothermic nature of such systems.

(ii) The low thermal conductivities which prevent heat transfer or temperature being controlled.

Due to these factors, the use of titrimetric methods is not applicable because they are only suitable for slow reacting or relatively soluble systems. Thermal methods that are based upon the enthalpy of reaction are much simpler but are also much cruder in their arrangment. DSC has been employed previously for thermally activated thermosetting resins [5]. However, for reactions that are activated by mixing (cf. reaction injection moulding (RIM) based systems [6–13]), this renders the method less useful. In terms of reaction chemistry and morphology development, time-resolved FT-IR spectroscopy has the ability to analyse fast reactions (< 10 s) and can monitor several chemical changes simultaneously. The implementation of time-resolved synchrotron SAXS is an excellent means for the characterization of the bulk sample morphology and also for the determination of the nature of microphase separated structure in segmented block copolymers [14]. The technique can be applied to measure structural features of size 20–1000 Å provided that sufficient phase contrast exists. On a more macroscopic scale, time-resolved rheological techniques have been employed previously for monitoring the development of polymer morphology, extent of curing, chemical gelation and vitrification [15–24].

2. The need for forced-adiabatic conditions

To study the reaction chemistry and development of morphology during fast bulk copolymerizations (RIM) that yield both thermoplastic and thermosetting polymers is difficult. The material undergoes a large reaction exotherm, typically in the range of 75–300°C and the viscosity of the reaction medium increases from approximately

10 Pa s to 10^5 Pa s in less than five minutes [6, 7, 9], in some instances less than 10 seconds [8, 10–13]. The low thermal conductivity of the polymer evolved reduces the heat loss from the material even further. The highly exothermic nature of the reaction provides a temperature rise that is quite easy to measure. Measurement of the adiabatic temperature rise has been employed previously by Stonecypher and co-workers [25] and Allen [26] for the polymerization of solid propellant binders. Macosko and co-workers [12, 16–23, 27–30] have also used this method to follow isocyanate conversion in rapid reacting urethane systems for RIM technology. The chemical reactions are usually over within a matter of minutes for urethane [4, 6, 7, 19–21, 30], and in seconds in the case of epoxy resin and polyurea RIM [4, 8–13, 27].

Although the extents of conversion of the component monomers can be evaluated from the adiabatic temperature rise profile, this reveals nothing about the reaction chemistry sequence, morphological changes or macroscopic properties as a function of the extent of reaction. However, if information about the system is required in terms of the sequence of chemical reactions taking place, changes in the sample morphology or the development of macroscopic properties as a function of the extent of reaction, a major problem arises. The problem is the nature of the sampling environment. The methods of analysis previously discussed only require very small amounts ($\leq 5\ \mathrm{cm}^3$) of sample material. However, the amount of material that is required to achieve self-insulation (typcially $\geq 100\ \mathrm{cm}^3$) cannot be contained within the sampling cell of an FT-IR spectrophotometer. Furthermore, the fact that many polymerized samples are opaque, results in the need for attenuated total reflectance (a.t.r.) as the sampling method rather than transmission. Similarly, the amount of material that is required to achieve self-insulation cannot be contained within the sampling stage, positioned in the optical bench of a synchrotron SAXS beamline, nor can it be contained between the parallel oscillatory plates in a conventional rheometer.

To be able to obtain physically and chemically meaningful data about the polymerizing system, the temperature of the reaction 'probe', be it an attenuated total reflectance element for an FT-IR spectrophotometer, a reaction cell for time-resolved SAXS or the parallel plates in a conventional rheometer, must be identical to that of the bulk material throughout the reaction exotherm. If not, and the temperature is lower than that of the material in contact with the surface of the 'probe', the surface of the 'probe' acts as heat sink and as a consequence will decrease the reaction exotherm, delay the reaction chemistry and disrupt the development of morphology. This leads to erroneous results both in terms of the reaction chemistry taking place [31, 32] and the extents of conversion at which critical events occur [28, 29], such as microphase separation, vitrification and chemical gelation.

Rapid heating of the 'probe' for the reaction is necessary in order to replicate the reaction exotherm (simulate forced-adiabatic conditions) of the polymerizing material, and thus effectively monitor the development of structure during the chemical reaction. Fig. 1 illustrates the effect of the attenuated total reflectance element for an FT-IR spectrophotometer acting as a heat sink and the subsequent delay in the observed onset of microphase separation (MST) of urea hard segments during flexible polyurethane foam formation [28, 29].

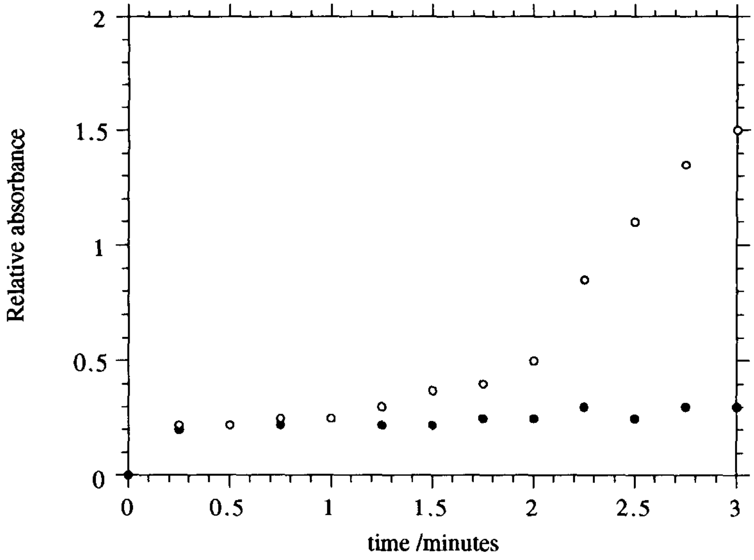

Fig. 1. Evolution of hard-segment D-urea (1640–1630 cm^{-1}) under different thermal histories: isothermal foaming at 25 °C (●) and forced-adiabatic foaming (○). The onset of microphase separation (MST) of D-urea hard segments was observed at about 90 s into the reaction [28, 29].

3. Development of the sampling environments

3.1. *FT-IR spectroscopy*

Previous investigations employing infra-red spectroscopy to study reaction kinetics during the formation of flexible polyurethane foam have been reported by Merten and co-workers [33], Bailey and Critchfield [31] and Rossmy and co-workers [34]. The studies were all carried out under isothermal foaming conditions and the exothermic nature of the foaming reaction was disregarded. A forced-adiabatic FT-IR cell, contained in the sample compartment of an FT-IR spectrophotometer, was first reported by Artavia and Macosko [28] for analysing the reaction kinetics during formation of TDI-based polyurethane foam. More recently, Van Lieshout et al. [35] have developed a different design whereby sampling takes place outside the spectrophotometer. This latter arrangement was also employed by Elwell and coworkers [36, 37] to study structure development in MDI-based polyurethane foams. Further details, regarding the experimental arrangement and procedure adopted can be found elsewhere [36, 37].

3.2. *Synchrotron SAXS*

To be able to study real-time morphological changes during fast, bulk copolymerization reactions (cf. reaction injection moulding, RIM) involving multiphase materials and how the processes of microphase separation/crystallization interact to affect the

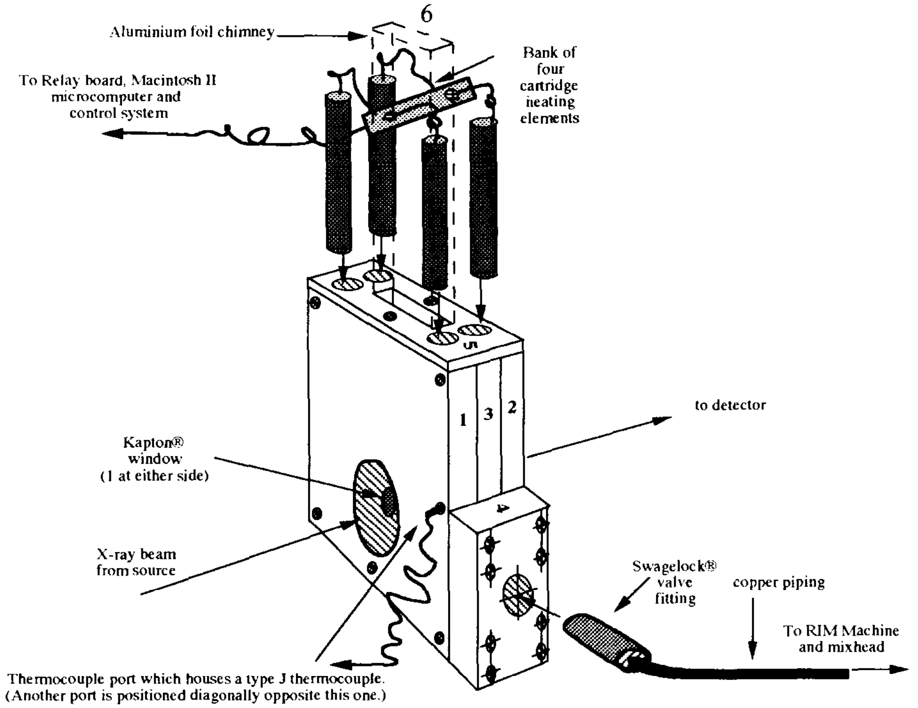

Fig. 2. 3-D schematic diagram of the forced-adiabatic SAXS sampling cell.

resultant copolymer morphology, it is necessary to probe the structure development kinetics by conducting time-resolved, forced-adiabatic SAXS measurements during the bulk copolymerization. Ryan and co-workers [38] studied the evolution of microphase separation during the bulk polymerization of a copolyurethane. More recently, a forced-adiabatic SAXS sampling cell that can be positioned in the optical bench assembly of a beamline has been designed and constructed at UMIST [37, 39]. A schematic diagram of the SAXS sampling cell is illustrated in Fig. 2. Further details regarding the specifications of the SAXS sampling cell, the experimental arrangement and procedure adopted are described elsewhere [37, 39].

3.3. Rheology

Although there have been numerous studies on the rheological behaviour of bulk copolymerizing systems [15–24], all the information presented pertains to isothermal conditions. There is a lack of information for forced-adiabatic conditions. However, the application of electrical heating devices built into/around the disposable fixtures/plates for rheometers is not widespread [23, 37]. Furthermore, such devices, i.e. attachable temperature-controlled rheometer plates, are not commercially available. A forced-adiabatic rheometer plate that can be attached to a modified lower fixture for the Rheometrics® RMS 800 series rheometer has recently been designed at UMIST [37].

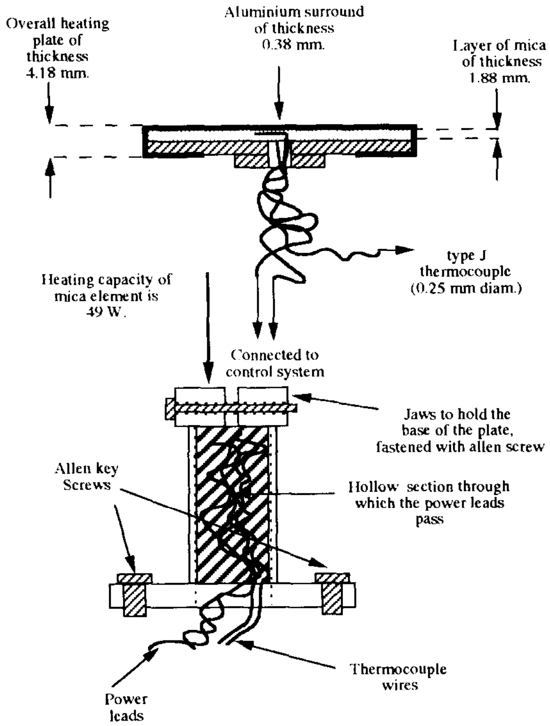

Fig. 3. Schematic diagram illustrating the design of the temperature-controlled lower plate for attachment to the modified fixture of the rheometer.

A schematic diagram of the modified rheometer plate is illustrated in Fig. 3. Further details regarding the specifications of the temperature-controlled plate, the experimental arrangement and procedures adopted are described elsewhere [37].

4. Temperature control of the sampling cells

A temperature control system has been developed [37] to enable the adiabatic temperature rise profiles of reacting foams to be replicated by the SAXS cell and the modified lower parallel plate for the rheometer. The temperatures of both the small-angle X-ray scattering cell and the modified lower parallel plate for the rheometer were controlled by a Macintosh® II microcomputer equipped with Strawberry Tree Incorporated Workbench™ V3.1 system software and ACM2-12-8 (T51) data acquisition A-D hardware. The adiabatic temperature rise profile of a reacting polyurethane foam was recorded employing a type J thermocouple (Omega Eng. Corp., diameter 0.25 mm). The temperature was recorded at a frequency of 1 Hz over a period of 1000 s. This previously recorded temperature profile was then used as the movable 'set-point' in the control circuit. The temperature of the cell was measured at two positions, diagonally opposite, on both sides of the SAXS cell (refer to Fig. 2). At each time interval, the circuit calculates the difference between the reference temperature and that of the mean temperature of the cell. The difference signal is then proportionalized and fed back to the four heating elements positioned in the cell via a relay circuit system linked between the analogue output of the terminal panel (T51) and the electricity supply connection of the heating elements. In the case of the rheometer plate, the signal is fed back to a mica plate heating element. Reproducible temperature control of both the SAXS cell and the rheometer plate to within ± 3°C of the reference temperature was achievable over a wide range of exotherms.

5. Results

5.1. FT-IR spectroscopy

Artavia and Macosko [28, 29], Priester and co-workers [40], and Elwell and co-workers [36] have conducted forced-adiabatic, time-resolved FT-IR spectroscopic measurements during polyurethane foam formation. Their results demonstrated that formation of both urethane and soluble urea occurred in the initial stages of the foaming reaction rather than in sequence, as suggested from earlier studies conducted under isothermal conditions [31, 33, 34]. The onset of microphase separation (MST) of urea hard-segment sequence lengths occurred early in the reaction at 50–60% conversion of isocyanate functional groups [28, 36, 37, 40]. This was well before a covalent network could be developed. Such hard-segment sequence lengths grow and eventually domains comprised of hydrogen-bonded urea hard-segment sequences are evolved.

Fig. 4 shows a plot comparing sets of isocyanate conversion data calculated from the forced-adiabatic FT-IR spectroscopy data with that calculated from the normalization of the foam reaction exotherm at both low and intermediate water concentrations [36, 37]. The correlation between the isocyanate conversion calculated from adiabatic temperature rise and infra-red spectroscopy data is within ± 3% after approximately 40 s of the reaction. Fig. 5 is a plot of soluble urea and hydrogen-bonded urea concentration versus time for a low water concentration foam formulation [36, 37]. The onset of microphase separation (MST) is indicated. The rate of association of the microphase separated urea hard-segment sequences has been observed to increase with increasing water concentration (higher ratio of urea to urethane groups) [36, 37]. The rate of association passes through a maximum in close vicinity to the onset of vitrification of the urea hard segments [37], as the system passes through the Berghmans point [41].

5.2. Synchrotron SAXS

A comparison of the temperature profiles for the reference temperature, the thermal response of the cell and the polyurethane foam within the SAXS sampling cell are illustrated in Fig. 6, for foam formulations at low (2.10 g per 100.0 g polyol) and high

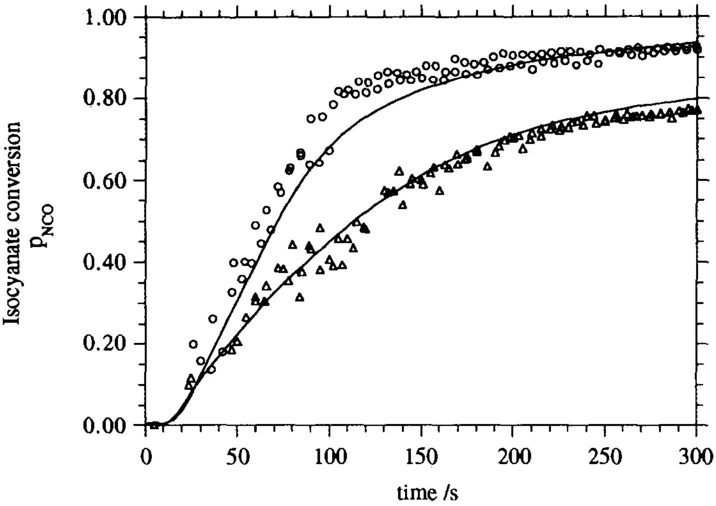

Fig. 4. Isocyanate conversion as a function of time illustrating the correlation between infra-red spectroscopy data (open symbols) and adiabatic temperature rise data (solid lines) for a low water concentration (Δ) and an intermediate water concentration foam formulation (○) respectively [36, 37].

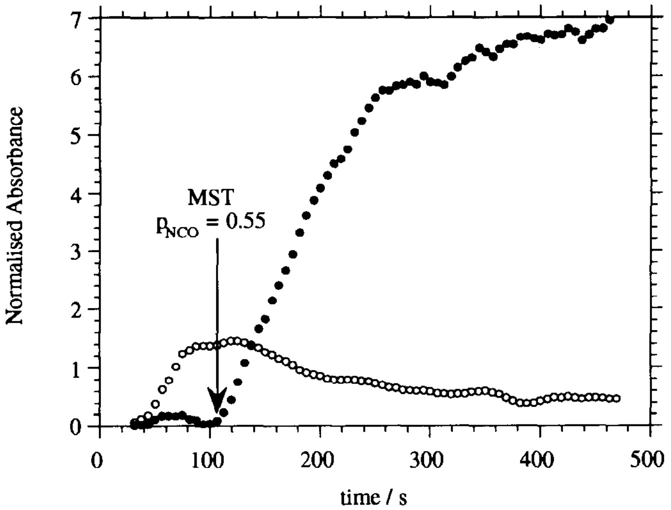

Fig. 5. Plot of normalized soluble urea (1715 cm^{-1}, open symbols) and normalized hydrogen-bonded urea (1654 cm^{-1}, closed symbols) as a function of time for a low water concentration foam formulation [36, 37].

(4.19 g per 100.0 g polyol) water concentrations [37, 39]. For both systems, there is an initial short delay in the response of the cell of approximately 5–10 s. This results from the finite time required for relaying the signal around the circuit and the initial response of the heating elements. The difference in temperature between the reference and the cell

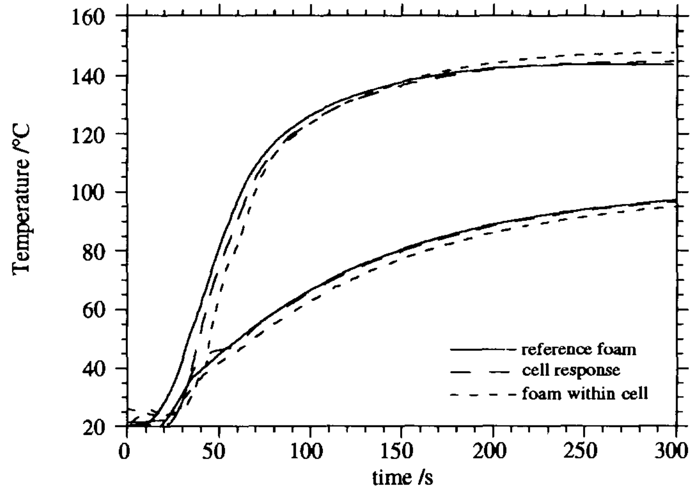

Fig. 6. Comparison of the temperature profiles for the reference, cell response and the foam within the SAXS cell for the low water formulation (lower curves) and the high water formulation (upper curves) [37, 39].

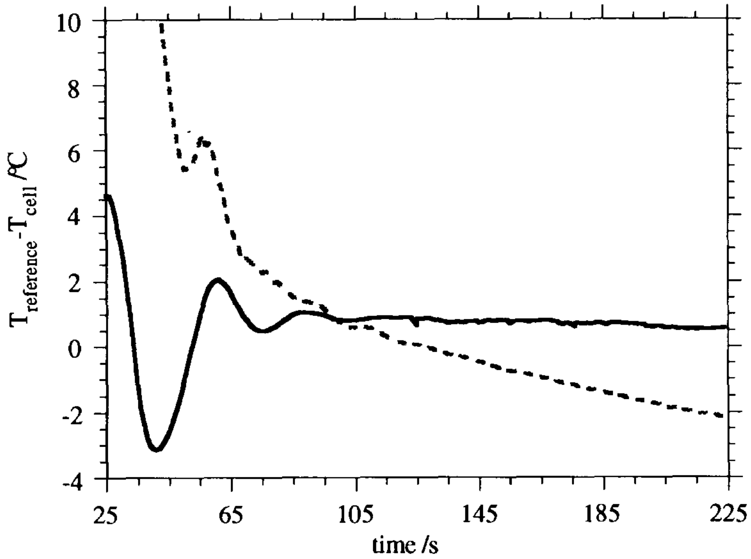

Fig. 7. Comparison of the temperature difference between the reference and the cell for the low water concentration formulation (solid line) and the high water concentration formulation (broken line) [37].

as a function of time is illustrated in Fig. 7 for both low and high water concentration formulations [37, 39]. For the low water system, within 60 s of the reaction, the cell is within 1 °C of the reference temperature. For the high water system, after 60 s of the reaction, the cell is within 5 °C of the reference temperature, and at 80 s the difference is 1–2 °C.

Fig. 8 illustrates a plot of the error in the value of isocyanate conversion as measured from the thermal response of the SAXS cell for the low water concentration formulation. Beyond the initial 30 s of data acquisition, the error in the value of isocyanate conversion calculated from the response of the cell is within 2%.

Marked on the plot are the points at which the key structuring transitions have been observed to take place [36, 37, 39]. The error in the isocyanate conversion at these points is within 1%.

Representative time-resolved SAXS data that were collected during foam formation are illustrated in Fig. 9 for a high water concentration formulation [37, 39]. It is illustrated as a three-dimensional plot of intensity $I(\mathbf{q}, t)$ versus the scattering vector, $\mathbf{q} = (4\pi/\lambda) \sin(\theta/2)$ where θ is the scattering angle, versus time t.

5.3. Rheology

The temperature control of the rheometer plate was as accurate as that of the SAXS reaction cell [37]. The effect of temperature on the rate of reaction and the development of morphology, illustrating the importance of being able to reproduce the adiabatic conditions during the analysis of the foaming reaction, have been described earlier. In terms of the rheological behaviour of the foam, this is clearly illustrated in Fig. 10, which shows the development of the elastic shear modulus as a function of reaction time under both isothermal (broken lines) and forced-adiabatic (solid lines) conditions for two independent runs under each condition on a low water concentration foam

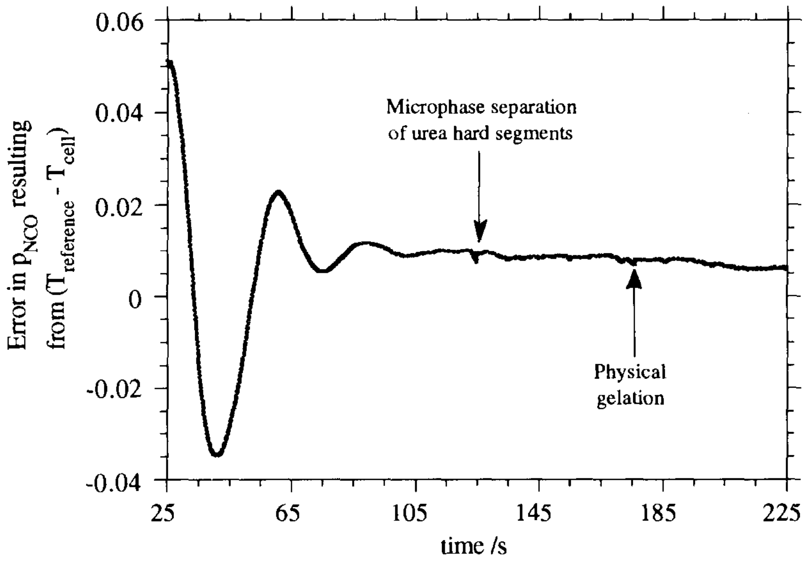

Fig. 8. Plot of the error in isocyanate conversion, p_{NCO}, resulting from the temperature difference between the reference and the cell for the low water concentration formulation [37].

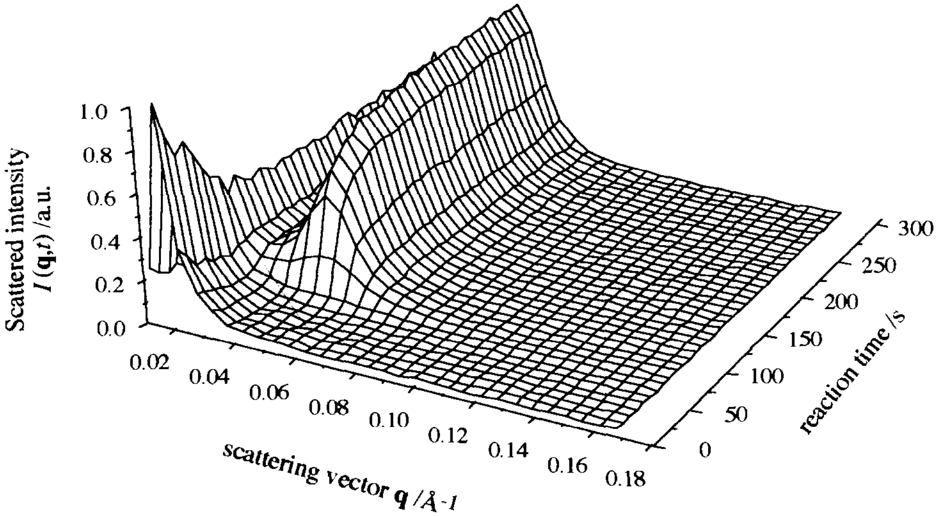

Fig. 9. Three-dimensional plot of intensity $I(q, t)$ versus scattering vector, $q = (4\pi/\lambda)\sin(\theta/2)$ where θ is the scattering angle, versus time t for a high water concentration formulation [37, 39].

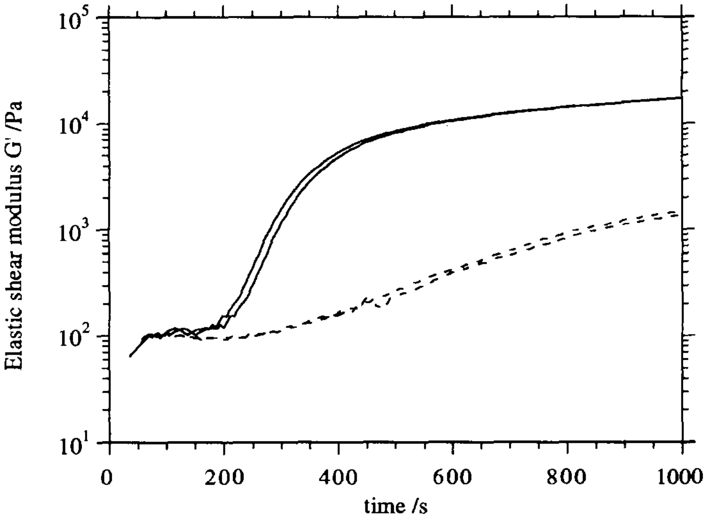

Fig. 10. Growth in elastic shear modulus (G') as a function of reaction time under isothermal (broken lines) and forced-adiabatic (solid lines) conditions for two independent runs under each condition on a low water concentration foam formulation [37].

formulation [37]. It is apparent that the time at which the elastic shear modulus shows a sharp increase is markedly different depending upon the preveailing conditions.

It is also apparent that the rate of growth of modulus is very different under the two conditions. The reproducibility and accuracy of the rheological data obtained with the temperature-controlled flooded fixture, for a series of independent runs on two different water concentration formulations, yielded values of the elastic shear modulus that were reproducible to within ± 5% [37]. The value of the elastic shear modulus in the liquid foam plateau region [37] was observed to compare well to data available in the literature on both reactive [23, 42] and non-reactive systems [43, 44].

6. Summary and conclusions

Forced-adiabatic sampling environments have been shown to be useful tools for the study of structure development during fast bulk copolymerizations. A forced-adiabatic SAXS reaction cell that can be positioned in the optical bench assembly of a synchrotron SAXS beamline has been described. Reproducible temperature control of the cell to within ± 3 °C of the reaction exotherm over a period of 500 s was observed, resulting in a small error in the isocyanate conversion obtained from the thermal response of the cell. A modified rheometer plate with an integral mica plate heating element has been described for enabling forced-adiabatic rheological measurements during bulk copolymerization to be made. Reproducible temperature control of the rheometer plate to within ± 3 °C of the reaction exotherm over a period of 500 s was observed for a wide range of exotherms. The importance of the process thermal history on the development of the elastic shear modulus (G') was clearly demonstrated. The value of the elastic shear modulus (G') in the liquid foam plateau region compared well to data available in the literature on both reactive and non-reactive systems.

Finally, the application of these types of reaction cells to investigations of other fast, bulk copolymerizing systems, such as RIM polyurethane elastomers, interpenetrating polymer networks, epoxy resin systems and reinforced composite materials of these particular systems, are readily feasible.

References

[1] R.J. Young and P.A. Lovell, Introduction to Polymers, 2nd edn., Chapman and Hall, London, 1991.
[2] J.M.G. Cowie, Polymers: Chemistry and Physics of Modern Materials, 2nd edn., Chapman and Hall, New York, 1991.
[3] F.W. Billmeyer, Jr., Textbook of Polymer Science, 3rd edn., Wiley Interscience, New York, 1984.
[4] C.W. Macosko, RIM: Fundamentals of Reaction Injection Molding, Carl Hanser Verlag, Munich, 1988.
[5] R.B. Prime, Thermosets in E.A. Turi (Ed.), Thermal Characterisation of Polymeric Materials, Academic Press, New York, 1981, p. 435–571.
[6] A.J. Ryan, J.L. Stanford and R.H. Still, Plas. Rubb. Proc. Appl., 13(2) (1990) 99.
[7] J.L. Stanford, A.N. Wilkinson, D.K. Lee and A.J. Ryan, Plas. Rubb. Proc. Appl., 13(2) (1990) 111.
[8] A.J. Ryan, Polymer 31 (1990) 707.
[9] A.J. Ryan, J.L. Stanford and R.H. Still, Polym. Bull., 18 (1987) 517.
[10] A.J. Birch, J.L. Stanford and A.J. Ryan, Polym. Bull., 22 (1989) 629.
[11] Z.S. Chen, W.P. Wang and C.W. Macosko, Rubber. Chem. Technol., 61 (1988) 86.
[12] C.W. Macosko and M.C. Pannone, Polym. Eng. Sci., 28 (1988) 660.
[13] W.R. Wilkomm, Z.S. Chen, C.W. Macosko, D.A. Gobran and E.L. Thomas, Polym. Eng. Sci., 28 (1988) 888.

[14] A.J. Ryan, J. Therm. Anal., 40 (1993) 887.
[15] F.G. Mussatti, C.W. Macosko, Polym. Eng. Sci., 13 (1973) 236.
[16] S.D. Lipshitz, C.W. Macosko, Polym. Eng. Sci., 16 (1976) 803.
[17] J.M. Castro, C.W. Macosko, S.J. Perry, Polym. Commun., 25 (1984) 82.
[18] S.J. Perry, J.M. Castro, C.W. Macosko, J. Rheol., 29 (1985) 19.
[19] W.P. Yang, Ph. D. Thesis, University of Minnesota, 1987.
[20] J.W. Blake, W.P. Yang, R.D. Anderson and C.W. Macosko, Polym. Eng. Sci., 27 (1987) 1238.
[21] W.P. Yang and C.W. Macosko, Makromol. Chem., Macromol. Symp., 25 (1989) 23.
[22] E. Mora, L.D. Artavia and C.W. Macosko, J. Rheol., 35 (1991) 921.
[23] E. Mora, MSc. Dissertation, University of Minnesota, 1991.
[24] A.Y. Malkin, S.A. Bolgov, V.P. Begishev and V.A. Mansurov, Rheol. Acta., 31 (1992) 345.
[25] T.E. Stonecypher, E.L. Allen, D.E. Mastin and D.A. Willoughby, Chem. Eng. Prog. Symp. Ser. 62(61) (1966) 7.
[26] E.L. Allen, Ind. Eng. Chem. Fundam. 8 (1969) 828.
[27] M.C. Pannone and C.W. Macosko, J. Appl. Polym. Sci., 34 (1987) 2409.
[28] L.D. Artavia and C.W. Macosko, J. Cell. Plast., 26 (1990) 490.
[29] L.D. Artavia, Ph. D. Thesis, University of Minnesota, 1991.
[30] R.E. Camargo, Ph. D. Thesis, University of Minnesota, 1984.
[31] F.E. Bailey and F.E. Critchfield, J. Cell. Plast., 17 (1981) 333.
[32] P. Van Gheluwe and J. Leroux, J. Appl. Polym. Sci., 28 (1983) 2053.
[33] R. Merten, D. Lauerer, M. Dham, J. Cell. Plast., 5 (1969) 262.
[34] G.R. Rossmy, H.J. Kollmeier, W. Lidy, H. Schator and M. Wiemann, J. Cell. Plast., 13 (1977) 26.
[35] H.C. Van Lieshout, H.J.M. Grünbauer and J.A. Thoen, Appl. Spectrosc., in press.
[36] M.J.A. Elwell, A.J. Ryan, H.J.M. Grünbauer, H.C. Van Lieshout and J.A. Thoen, Prog. Rubb. Plast. Technol., 9 (1993) 120.
[37] M.J.A. Elwell, Ph.D. Thesis, Victoria University of Manchester, 1993.
[38] A.J. Ryan, W.R. Willkomm, T.B. Bergstrom, C.W. Macosko, J.T. Koberstein, C.C. Yu and T.P. Russell, Macromolecules, 24 (1991) 2883.
[39] M.J.A. Elwell, A.J. Ryan and S. Mortimer, Macromolecules, 27 (1994) 5428.
[40] R.D. Priester, Jr., J.V. McClusky, R.E. O'Neill, R.B. Turner, M.A. Harthcock and B.L. Davis, J. Cell. Plast., 26 (1990) 346.
[41] S. Callister, A. Keller and R.M. Hikmet, Makromol. Chem. Makromol. Symp., 39 (1990) 19.
[42] M.D. Bessette and D.W. Sundstrom, Polym. Process. Eng., 3 (1985) 25.
[43] S.A. Khan, C.A. Schnepper and R.C. Armstrong, J. Rheol., 32 (1988) 69.
[44] H.M. Princen and A.D. Kiss, J. Coll. Interface Sci., 112 (1986) 427.