

TEMPERATURE MODULATION IN PRESSURE DSC: A NEW TOOL TO INVESTIGATE THE PRESSURE EFFECT ON THE CURING

Ramón Artiaga, Carlos Gracia, Jorge López-Beceiro, Silvia Gómez-Barreiro, Javier Tarrío-Saavedra, Salvador Naya

Escola Politécnica Superior. Universidade da Coruña, Avda. Mendizábal s/n. 15403-Ferrol. Spain

Introduction

It was reported that the use of pressure during composite molding leads to a decrease in the void content and improvement of the mechanical properties. The optimum time to apply pressure is also very important in the optimization of epoxy cure. The effect of pressure on reactant volatilization has been investigated by pressure differential scanning calorimetry (PDSC) [1]. Hermetically sealed pans prevent reactants evaporation but pressure is not controlled [2]. Reactants evaporation can also be suppressed by PDSC [3]. The study of the pressure effect on the degree of curing was recently investigated on an epoxy system [4]. The aim of this work is to show how TMPDSC can be used to evaluate the effect of pressure on the curing reaction of a thermosetting system. TMDSC is a technique in which a sinusoidal temperature oscillation is superimposed upon a linear change in the underlying temperature or at an isothermal temperature (this latter condition is called quasi-isothermal operation). TMDSC is normally used at ambient pressure to determine the vitrification times and to setup the temperature curing profiles. Nevertheless, many composites are normally cured under pressure conditions and thus, TMPDSC would provide a more realistic measurement of the vitrification times.

Experimental

Materials

A two component high temperature cure epoxy system was chosen. The first component is composed of diglycidyl ether of bisphenol A (DGEBA) with a toughener, Nanostrength M52 N (Arkema). The second component contains dicyandiamide and 1-methyl imidazole.

Apparatus

DSC experiments were conducted in a TA Instruments MDSC Q2000 with cell pressure. Calibrations were performed at each of the pressures to be used in the measuring tests.

Procedures

The two components of the epoxy system were mixed at the stoichiometric proportion and manually stirred for 2 min. Samples of about 3 mg were extracted from the mixture and placed in Aluminum crucibles for DSC experiments. The experiments consisted of a modulated quasi-isothermal step followed by a modulated linear heating and then, by a non-modulated linear heating, all of them under pressure. For the temperature modulated quasi-isothermal PDSC tests, the samples were loaded into the cell at 60 °C for the isothermal curing. The program consisted of a quasi-isothermal stage at 105 °C, with 0.5 °C amplitude and a 80 s period. The experiments were stopped after the curing exotherm, when the heat flow trace presented a prolonged zero slope. Upon completion of the isothermal curing, the samples were subjected to a 2 °C/min modulated linear heating and then to a non-modulated ramp. The cured samples obtained in the modulated quasi-isothermal tests were allowed to cool in the PDSC cell and then heated from 60 to 205 °C at an underlying heating rate of 2 °C/min. The modulation amplitude was 0.5 °C and the period 60 s.

Results and discussion

Figure 1 shows the signals obtained in a quasi-isothermal curing experiment.

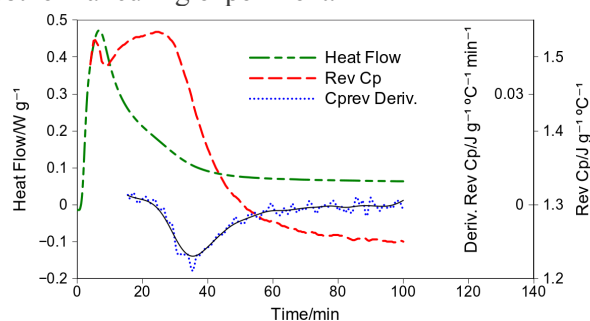


Figure 1. Typical signals obtained in a quasi-isothermal experiment.

The vitrification time is the time at the minimum of the reversing Cp derivative. The curing enthalpy is

calculated from the total heat flow curve using a flat baseline. Figure 2 shows that the heat of curing increases linearly with pressure for isothermal curing, while the vitrification time drastically drops with a small increase of pressure and then is much less sensitive to any further increase of pressure.

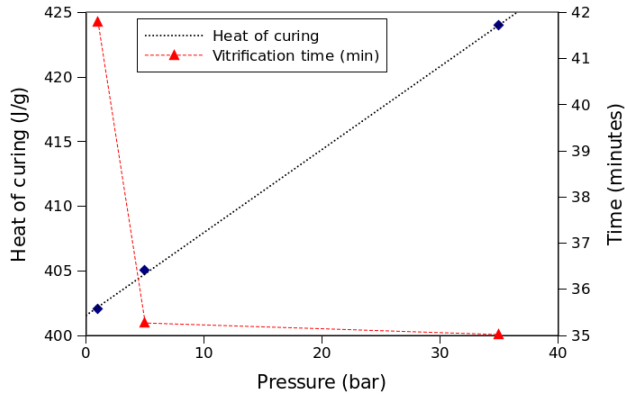


Table 1 shows the conversions at the vitrification times directly obtained at different pressures and the corresponding heat of curing. The vitrification occurs at about the 91% of conversion at any pressure. Nevertheless, the heat of curing measured up to tvit indicates that the extent of the reaction is higher at 35 bar.

Table 1. Conversions and heats of curing at the vitrification times observed at different pressures.

Pressure (bar)	Conversion at tvit (%)	Heat of curing at tvit (J/g)
1	92	369
5	90	363
35	92	390

Figure 4 shows how the onset, peak and endset points of the post-curing modulated ramp shift to lower temperature as pressure increases. We believe this is very important because the possibility of moving the curing at lower temperatures represents less energy consumption and less chance of degradation.

Conclusion

Vitrification times can be determined under pressure by means of TMPDSC. The vitrification time is very sensitive to pressure in the low pressure range. Further pressure increments do not seriously affect the vitrification time. The maximum heat of curing

obtained in isothermal experiments depends linearly on the pressure. The isothermal conversion at any given pressure is practically the same with respect to the maximum degree of curing reached at that pressure and temperature, but the heat of curing at tvit depends on the pressure. Pressure allows to move the curing at lower temperatures, which represents less energy consumption and less chance of degradation. The possibility of performing modulated experiments under pressure extends the great insight given by TMDSC to situations where pressure curing is needed to obtain high quality composites.

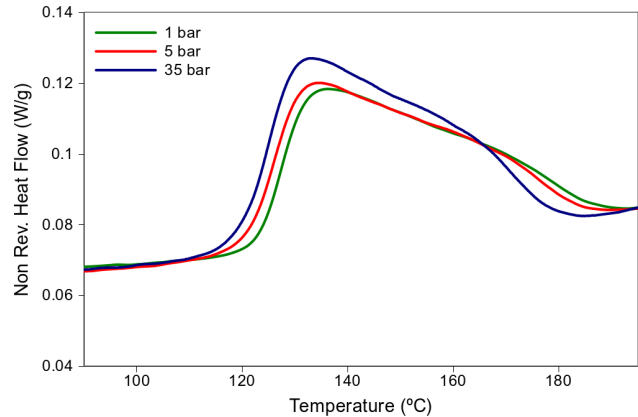


Figure 4. Non-reversing heat flow measured in the post-curing modulated ramp.

Acknowledgement

This work was partially funded by the Spanish Ministerio de Educacion y Ciencia MTM2008-00166 and additionally by FEDER.

References

- Hagstrand PO, Klason C, Svensson L, Lundmark S. Rheokinetic behavior of melamine-formaldehyde resins. *Polym Eng Sci.* 1999;39:2019–29.
- Van Mele B, Rahier H, Van Assche G, Swier S. In: Reading M, Hourston DJ, ed. *Modulated temperature differential scanning calorimetry. Theoretical and practical applications in polymer characterization.* Dordrecht: Springer; 2006. p. 83–160.
- Levy PF, Nieuweboer G, Semanski LC. Pressure differential scanning calorimetry. *Thermochim Acta.* 1970;1:429–39.
- Gracia-Fernandez C, Tarrío-Saavedra J, Lopez-Beceiro J, Gomez-Barreiro S, Naya S and Artiaga R, *J Therm Anal Calorim*, 2011, DOI 10.1007/s10973-011-1361-8.