Temperature modulation in PDSC for monitoring the curing under pressure

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Abstract The use of pressure cell attached to a temperature modulated differential scanning calorimeter (TMDSC) is investigated to perform modulated DSC experiments at high pressures (TMPDSC). No previous reports were found on the use of TMPDSC. In this study, the proposed method is applied to the study of the pressure effect on the curing reaction of an epoxy system. Curing quasi-isothermal modulated experiments were performed at different pressures to evaluate the vitrification time. Linear heating modulated tests were also successfully performed at different pressures to separate the reversing glass transition effect from the residual exothermic cure reaction. The curing enthalpy, conversion versus temperature, and glass transition of the fully cured thermoset were also evaluated. All the studied parameters resulted to be affected by the pressure in the range from atmospheric pressure to 35 bar. It was observed that the curing enthalpy, the reaction rate and the conversion at any given time increase with any pressure increment. The usefulness of TMDSC to characterize the curing of thermosets is extended by PTMDSC to situations, i.e., aeronautics industry, where pressure curing is needed.

Keywords Pressure · Modulated temperature · DSC · TMDSC · PDSC · TMPDSC

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Introduction

Epoxies find application in many industrial fields, including bond technology and structural composites [1, 2]. The outstanding physical properties exhibited by cured epoxy include low cure shrinkage, no volatiles given off during cure, compatibility with a great number of materials, strength and durability, adhesion, corrosion and chemical resistance, and electrical insulation. Owing to their outstanding mechanical properties, epoxy composites are one of the most important choices as lightweight materials for structural applications. In fact, epoxies are frequently used as matrix material for aeronautics composites [1, 3, 4]. It is well known that the use of pressure during composite molding leads to a decrease in the void content and improvement of the mechanical properties [5–7]. Issues such as the optimum time to apply pressure in an autoclave process are also very important in the optimization of epoxy cure processes [8]. The effect of pressure on reactant volatilization has been investigated by pressure differential scanning calorimetry (PDSC) [9–11]. Hermetically sealed pans are usually adequate to contain the small amount of reaction products associated with cure. Some workers prefer the use of stainless steel high-pressure crucibles that withstand much higher pressures [12]. But, although this kind of crucibles prevents the reactants evaporation in some materials as melamine–formaldehyde resins [13],

pressure is not controlled. Phenomena such as volatiles and reactants endothermic evaporation can also be suppressed using PDSC [14]. Nevertheless, the study of the pressure effect on the degree of curing was little investigated. The degree of curing of resins cured under pressure was evaluated by DSC [7, 15]. Several works have studied the influences of pressure over the kinetic reaction of epoxy resins using pressure-volume-temperature analysis (PVT) [6, 16]. The pressure effect in the curing of polyester resins or polyurethane has been also reported in several studies using PDSC [17–19]. But there is not any report of evaluating the curing enthalpy by PDSC and measuring the vitrification time by temperature modulated PDSC (TMPDSC) in epoxy systems. The aim of this work is to investigate the ability of TMPDSC to evaluate the effect of pressure on the curing reaction of an epoxy 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). The aeronautic industry makes use of TMDSC at ambient pressure to determine the vitrification times and to setup the temperature curing profiles. Nevertheless, their composites are normally cured under pressure conditions and thus, TMPDSC would provide a more realistic measurement of the vitrification times.

Experimental

The epoxy system

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), product of a new family of self-assembling block copolymers [2]. The second component contents dicyandiamide and 1-methyl imidazole [2]. Dicyandiamide, with particle size ≤6 μm, provides long gel times. 1-methyl imidazol provides elevated values of T_g^∞. The high cure temperature of the system, along with the high glass-transition temperature, T_g, of the fully cured material, makes it suitable for the study of curing under pressure, allowing the testing of isothermal curing at a relatively high temperature (>100 °C). The stoichiometric weight ratio between first and second component is 111/1.

Instruments

DSC experiments were conducted in a TA Instruments MDSC Q2000 with cell pressure. The range of temperature of the pressure cell to operate under pressure is −130 to 725 °C. Its maximum pressure specification is 7 MPa.

Baseline, temperature and enthalpy calibrations were performed, with empty crucibles, corundum, and indium, at each of the pressures to be used in the measuring tests [20, 21].In addition, a thermogravimetric (TG) test was performed in a TA Instruments SDT 2960.

Sample preparation

The first and second components were mixed at the stoichiometric proportion and manually stirred for 2 min. In the case of DSC experiments, samples of about 3 mg were extracted from the mixture and placed in the crucible. Open aluminum Tzero (TM) crucibles were used. A fresh mixture was prepared for each set of experiments. Then, two sets of DSC experiments were performed: standard PDSC with linear heating and modulated quasi-isothermal followed by a modulated linear heating and then, by a non-modulated linear heating, all of them under pressure. A preliminary TG test was performed to insure that no hardener volatilization takes place simultaneously to the curing reaction. The sample in this case was prepared in the same way than for the DSC experiments, except that the sample mass was about 7 mg.

TG test

The sample was placed in open alumina pans. A 10 °C/min heating rate was applied from room temperature to 800 °C under a 100 mL/min nitrogen purge.

Standard PDSC with linear heating

All the experiments were performed at three pressure levels: 1, 5, and 35 bar. In all cases, a linear heating from room temperature to 260 °C at 10 °C/min was programmed, although the experiments were manually stopped upon reaching a constant slope baseline after the exotherm. The final temperature was chosen high enough to observe the complete curing reaction, and low enough to avoid degradation of the resin. A 50 mL/min nitrogen flow was kept in all experiments. Two replicates of each experiment were performed. The instrument was previously calibrated for temperature and enthalpy, according to the manufacturer procedure, at each pressure level.

Temperature modulated quasi-isothermal PDSC tests

Temperature modulation was used both in linear heating and quasi-isothermal tests so that the samples were cured in quasi-isothermal mode and then the degree of curing was evaluated in ramp. 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. The temperature of 105 °C was chosen as it corresponds to the beginning of the curing reaction in the modulated linear heating test, and it is also low enough so that degradation of the resin is not expected. All the experiments have been performed at 1, 5, and 35 bar. The nitrogen flow was 50 mL/min in all cases. 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. In between the experiments, the samples were allowed to cool inside the PDSC cell under similar pressure level.

Temperature modulated PDSC 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. Finally, sample cooled and rerun is tested using non-modulated mode.

Non-modulated DSC linear heating

The samples that underwent quasi-isothermal and modulated linear heating experiments were also subjected to a non-modulated linear heating. A 10 °C/min heating rate was used and the same pressure levels than in the previous experiments.

Results and discussion

Thermogravimetric analysis

Figure 1 shows that there is no mass loss in the 100 to 200 °C range, where further analysis of the curing will be focused. Thus, no hardener volatilization is expected to interfere with the curing. The sample is thermally stable up to 280 °C.
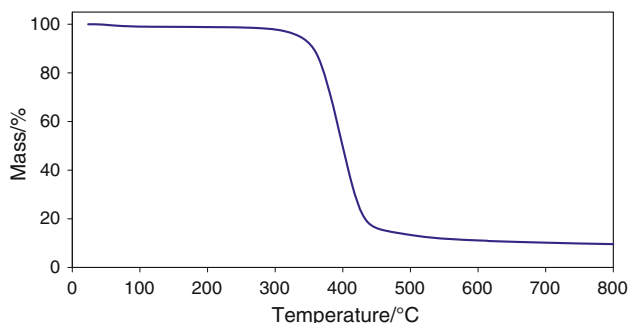
Standard PDSC using linear heating

Standard PDSC was used to evaluate the cure conversion and cure enthalpy at 1, 5, and 35 bar.

Figure 2 displays an overlay of the heat flow curves obtained from the curing experiments, where the broad exotherms correspond to the cure reactions. The curing peaks corresponding to 5 and 35 bar tests are displaced to lower temperatures with respect to those obtained at ambient pressure. However, the differences between the curves obtained at 5 and 35 bar are much smaller. The curing enthalpy, ΔH_{RXN}, was calculated with the Universal Analysis software by integration of the exothermal peak using a sigmoid baseline. Table 1 shows that ΔH_{RXN} increases with increasing pressure. The analysis of variance (ANOVA) and F test revealed that there are significant differences in ΔH_{RXN} when increasing the pressure (p-value $= 0.013 < 0.05$) assuming a significance level of 0.05 [22]. This dependence is statistically significant. It confirms that the pressurized curing produces a higher degree of curing than the obtained at atmospheric pressure.

Figure 2 shows that the curing reaction begins at the same temperature independently of the pressure, but it proceeds faster when increasing the pressure. This observation is confirmed by the onset temperature and the temperature at which a maximum slope is observed, which are shown in Table 1. The last column of Table 1 also shows the maximum slope of heat flow versus time, dH/dt. While this slope appreciably changes from 1 to 5 bar, only a slight increment is observed in the range from 5 to 35 bar.

Figure 3 displays an overlay of the conversion curves obtained by integration from the curing experiments at three pressure levels. The conversions were normalized with respect to the largest curing enthalpy obtained in any
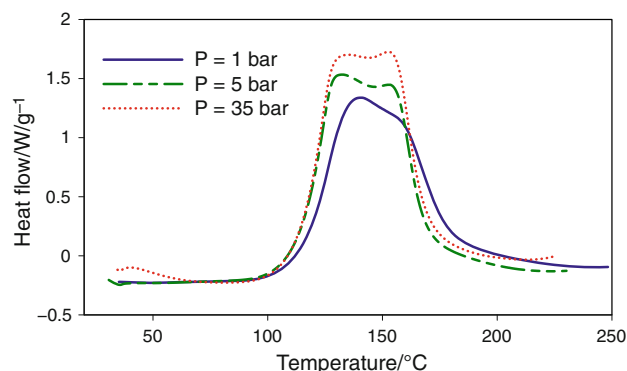

Fig. 1 TG curve corresponding to fresh epoxy formulation

Fig. 2 Heat flow curves obtained from the curing experiments at three pressure levels

Table 1 Values of the curing enthalpy, onset temperature, temperature at the maximum of dH/dt and dH/dt obtained in the ramp curing experiments at different pressures
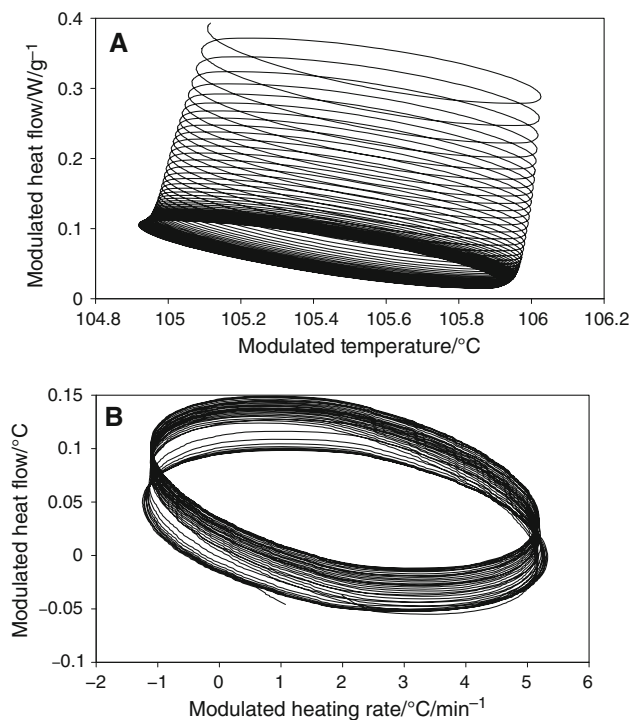
Pressure/bar	ΔH_{RXN}/J g^{-1}	Onset temperature/°C	T at the max. of dH/dt/°C	Maximum dH/dt/W g^{-1}/min^{-1}
1	455 ± 12	114.01 ± 0.97	125.9 ± 1.3	0.899 ± 0.047
5	481.00 ± 0.42	113.29 ± 0.13	124.19 ± 0.31	1.297 ± 0.025
35	512.3 ± 4.9	113.31 ± 0.09	124.04 ± 0.20	1.400 ± 0.016

of the experiments. It is clear that increasing pressure shifts the curing reaction to lower temperatures and produces an increase in the slope of the curves. Thus, the curing rate increases as a consequence of the pressure increment, which agrees with an earlier report [23].

Modulated Quasi-isothermal

A simple verification of the instrument performance in the actual modulated measuring tests consists in checking the stability of the cycles in the Lissajous figures what is presented. Figure 4 plots the Lissajous figures obtained in a modulated quasi-isothermal and a modulated linear heating experiment. Each ellipse corresponds to a modulation cycle. In both cases, the ellipses are almost perfect. The shifting of the ellipses corresponds to the change of the average heat flow, which changes owing to the progress of the curing reaction. If the sample could not follow the modulation conditions, it would produce some loss of the ellipsoidal shape. The fact that there are neither large thermal delays nor loss of system linearity is a confirmation that the modulation conditions were adequately chosen.

Figure 5 displays the total heat flow, reversing heat capacity, Cp_{rev}, and time derivative of Cp_{rev}, obtained from a 5 bar quasi-isothermal curing experiment at 105 °C. The total heat flow is calculated as the average value of the modulated heat flow signal, and it is similar to the heat flow obtained in conventional DSC. Cp_{rev} is the heat capacity without any kinetic events or reactions, and it can be calculated using $Cp_{rev} = $ K · heat flow amplitude/heating rate amplitude,
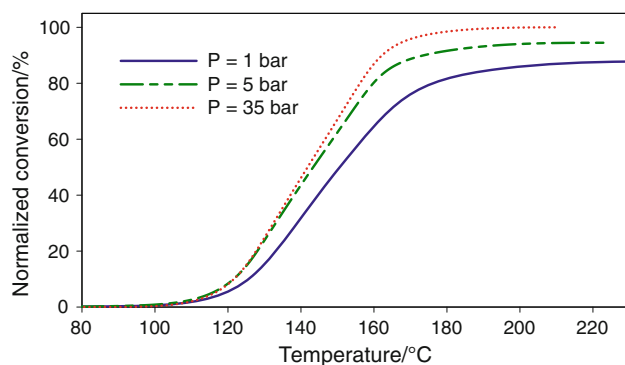
Fig. 3 Normalized conversion curves obtained from the ramp curing experiments at the three considered pressure levels

Fig. 4 Lissajoux figures obtained in a modulated quasi-isothermal (**a**) and a modulated ramp (**b**) experiments
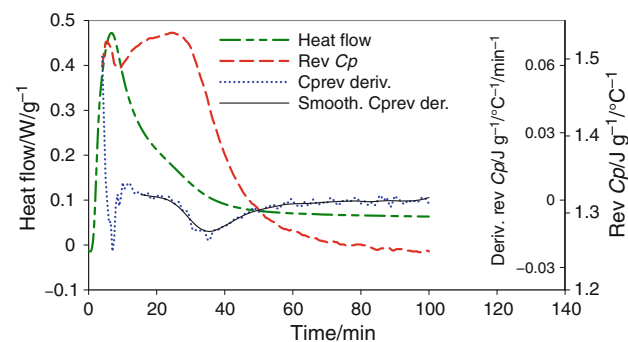
Fig. 5 Total heat flow, reversing heat capacity, Cp_{rev}, and time derivative of Cp_{rev}, obtained from a 5 bar quasi-isothermal curing experiment at 105 °C

where K is a calibration constant [8]. In order to obtain a smooth signal of the Cp_{rev} derivative, a linear local polynomial nonparametric model [24–26] of the Cp_{rev} was performed. A direct plug-in methodology was used to select the

Table 2 Heat of reaction and t_{vit} obtained in quasi-isothermal tests

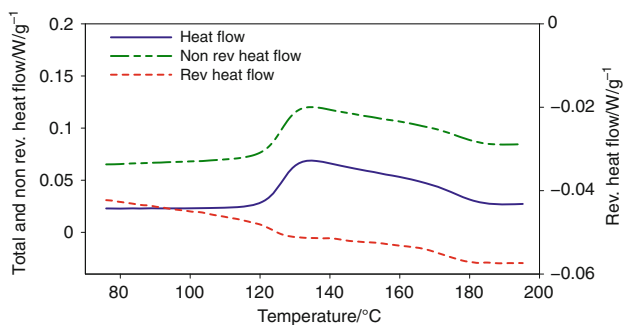| Pressure/bar	Heat of reaction/J g^{-1}	t_{vit}/min
1	402	41.8
5	405	35.27
35	424	35.02

Fig. 6 Reversing and non-reversing heat flows obtained in a modulated heating ramp

optimal bandwidth of the local linear Gaussian kernel regression estimate [27]. Figure 5 shows the smoothed Cp_{rev} derivative signal along with the corresponding unsmoothed data. The vitrification time, t_{vit}, was calculated from the minimum of the time derivative of Cp_{rev} according to a previously reported method [28]. The curing enthalpy was calculated from the total heat flow curve using a flat baseline. Vitrification times and cure enthalpies, obtained at different pressures, are shown in Table 2. Differences in t_{vit} are observed when increasing the pressure from 1 to 5 bar, but no important changes of t_{vit} were observed between 5 and 35 bar. The cure enthalpy is observed to increase when increasing the pressure at any level, although the increment from 1 to 5 bar produces a weak effect. It indicates that, also in isothermal conditions, the pressurized conditions produce a higher degree of curing than the obtained under atmospheric pressure.

Modulated and non-modulated linear heating

Figure 6 displays the total, reversing and non-reversing heat flows obtained in a modulated heating ramp test with a sample which was previously subjected to a quasi-isothermal curing. The glass transition change and the residual cure are clearly separated into the reversing and non-reversing curves. Two step changes can be observed on the reversing curve: the first one, about 124 °C, corresponds to the glass transition of the isothermally cured sample, at the beginning of the post-curing process, which is reflected on the non-reversing curve. The second step change, at about 175 °C, appears when the post-curing is almost completed, corresponding to the glass transition of the almost fully cured material. There are some small deviations from the

generally decreasing straight line of the reversing heat flow in between of the two step changes. The negative slope of the reversing signal in that region comes from the Cp increase of the sample with temperature. The slight deviations from linearity may be an indication of some vitrification and devitrification processes, which would result from the simultaneous changes of the crosslinking degree and temperature along time.

Table 3 shows the residual enthalpy, T_{gd} at the beginning and end of the post-curing process obtained in modulated ramps of the isothermally cured samples and T_g values of the fully cured samples, T_g^∞, obtained from the same samples in the last, non-modulated, ramp. The fact that T_{gd} at the end of the post-curing process is similar to T_g^∞ confirms that the T_{gd} corresponds to an almost fully cured system. The slightly higher values of some of the modulated measurements are due to the well-known frequency effect [29]. A slight decrease of T_{gd} and T_g^∞ is observed when increasing the pressure from 5 to 35 bar. It seems to contradict the enthalpy results, which indicate that a higher pressure results in a higher degree of curing. Accordingly, an increment of the T_{gd} would be expected. Although it falls out of the scope of this article and will be further investigated, it is likely that nitrogen can be dissolved in the uncured resin under pressure [30]. Thus, the dissolved nitrogen would alter the polymer network produced by the cure, resulting in a plasticizing effect.

Table 3 Residual enthalpy, T_{gd} at the beginning and end of the post-curing process obtained in modulated ramps of the isothermally cured samples and T_g^∞ values of fully cured samples obtained in non-modulated ramps

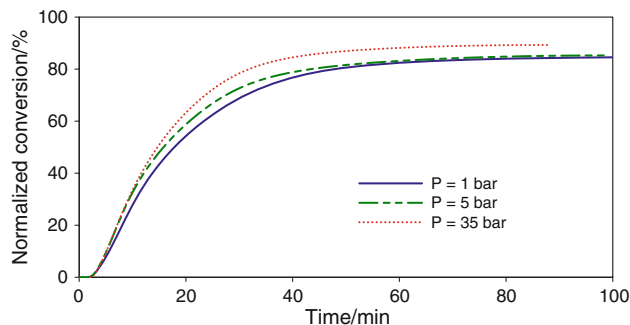| Pressure/bar	Residual enthalpy/J g^{-1}	T_{gd} at the beginning of post-curing/°C	T_{gd} at the end of post-curing/°C	T_g of fully cured samples/°C
1	46.89	124.7	168.4	166.6
5	50.33	124.4	168.1	169.1
35	51.06	122.8	162.1	160.7

Fig. 7 Conversion curves obtained in the quasi-isothermal tests

Figure 7 presents an overlay of the normalized conversion curves obtained in the quasi-isothermal tests. The normalization was performed with respect to the maximum of the sums obtained from the curing (isothermal experiments) and post-curing (ramp experiments) heats. In agreement with the heat of reaction values shown in Table 2, the isothermal conversion curves indicate that a higher degree of curing is obtained when applying an external pressure. Nevertheless, the increment from 1 to 5 bar produces a very slight effect. However, the slope of the curves indicates that a higher reaction rate is obtained with any pressure increment.

Conclusions

PDSC was successfully used in traditional (non-modulated) mode to evaluate the degree of curing at different pressures.

Quasi-isothermal temperature modulation was applied in a PDSC cell from which the vitrification time was obtained, from the time derivative peak of the Cp reversing, at different pressures.

TMPDSC allows for measuring the vitrification times in quasi-isothermal experiments under pressure and calculating the conversion at t_{vit}.

Modulated heating experiments, after the quasi-isothermal tests, provided for separation of the glass transition and residual cure effects.

The curing enthalpy, conversion, vitrification time and glass transition of the partially and fully cured thermoset resulted to be affected by the pressure.

The use of a pressure cell attached to a suitable TMDSC instrument allows to perform modulated DSC experiments at high pressures. This is a novelty that opens a wide range of possibilities, which may be of high interest for the aeronautic industry, where their composites are normally cured under pressure conditions.

An unexpected trend of the glass transition of the cured system with respect to the curing pressure was observed. That trend is explained as a possible plasticizing effect induced by the pressurized nitrogen atmosphere.

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