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CURING OF PREPREG BASED BISMALEIMIDE THERMOSET COMPOSITE (HEXTOOL M61): DSC, DMA AND COUPLING DMA /IMPEDANCE SPECTROSCOPY CHARACTERIZATIONS

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In this study, differential scanning calorimetry (DSC) was used at different heating rates (0.5, 1, 3, 5, 10 and 15 °C/min) to study the cure kinetics of prepreg Carbon Fibre-Sheet Moulding Compound (bismaleimide resin (M61) /carbon fibre (AS4)), especially designed to produce resin transfer moulding tools with complex shapes and high tolerance. Activation energy and pre-exponential factor were calculated and compared for both model free kinetics and n-th order model reaction. The activation energy and the pre-exponential factor varied in the range 73.48- 146.39 kJ/mol and 4.64×10^{6} *-* 2.78×10^{14} s^{-1}*, respectively, and the average order of reaction for the prepreg M61 was equal to 1.2. Dynamical mechanical analysis (DMA) characterization was performed in the range from -100 to 190 °C at the heating rate 0.5 °C/min and the dwell at 190 °C for 2 hours as a function of cure time. It was found that the glass transition and the gelation temperatures* T_{g0} *and* T_{gel}*, respectively, are equal to 4.1 °C and 175 °C. On the other hand, impedance spectroscopy (IMPS) and dynamic mechanical analysis are employed simultaneously, to investigate progress of the curing reaction of thermoset composite (HexTool M61) at different heating rates (0.5 and 1 °C/min) from ambient temperature to 190 °C, and the dwell at 190 °C for 4 hours. The results obtained from the coupled methods (DMA and IMSP) show a good agreement.*

Keywords: Characterizations, DSC, Impedance spectroscopy, DMA, Cure process, HexTool M61

1. Introduction

Carbon fibre reinforced polymers are important materials for advanced structural applications due to their high specific stiffness and high specific strength [1]. Especially bismaleimide (BMI) resin-based composites which are characterized by excellent mechanical and thermal properties, high chemical, corrosion resistance, low shrinkage on curing and good processability, are preferred as construction materials of space-crafts [2] and more recently as

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composite mould for resin transfer moulding [3]. Cure process of BMI based prepreg (fibrous material preimpregnated with a particular resin) requires accurate technique for characterization. There are a number of techniques used to investigate thermosetting polymer curing [4, 5], such as differential scanning calorimetry (DSC), dynamical mechanical analysis (DMA), dynamical electrical analysis (DEA) (for insulating materials and optical fibres) [6-9]. The cured bismaleimide system gives a three-dimensional macromolecular network synthesized by polyaddition. The final morphology of this three-dimensional network, which determines the properties of the material, depends on this transformation. During the thermoset resin cure, there is an interaction between the chemical kinetics and the changing physical properties, which may involve an incomplete degree of conversion of the system. Two phenomena may appear during the reaction according to the cure temperature: gelation and/or vitrification. Gelation is the liquid to rubber transition, which occurs when the system reaches a certain degree of conversion corresponding to the occurrence of an infinite network. Vitrification is rubber to glass transition, which occurs when the glass transition of the reactive system increases to the temperature of cure [8]. For an optimization of the manufacture of thermosetting based composite parts, a better understanding of mutual influence of chemical and mechanical history on the material process and final properties will therefore be of great use [10-11].

In CF-SMC (Carbon Fibre-Sheet Moulding Compound) the electrical conductivity exists due to conductive fibre to fibre contacts as the volume fraction of these industrial composites is always above the percolation rate [12-17]. During curing the contact rate is modified due to different processes that occur such as thermal expansion, chemical shrinking of the matrix, waviness of the fibre, so the measurement of electrical conductivity appears to be a valuable technique for providing information about cure state even for in situ cure monitoring techniques in the case of large CF-SMC part [17]. Indeed, this method uses one part of the material system itself that is carbon fibres as sensors and needs non-intrusive electrodes mounted on the surface of the part to follow the cure mechanism. The electrical conductivity measurements were performed at the same time as the DMA technique.

Dynamical mechanical analysis (DMA) provides convenient and sensitive determination of thermo-mechanical properties of polymers as a function of frequency and temperature. It consists in either applying a sinusoidal stress (force) to a material and measuring the strain (displacement) or applying a strain and measuring the stress. Strain and stress are lagged by phase angle δ due to the viscoelastic characteristics of the polymers. From the stress and strain measurements the complex modulus can be deduced $M^* = M' + jM''$ where $M'$is the storage modulus and $M''$is the loss modulus. The loss factor is the ratio of loss modulus to storage modulus, $tan\delta = {M''}/{M'}$ where δ is the phase angle shift between stress and strain. The modulus can be either tensile (E*) or shear modulus (G*) depending on the loading. While gelation process, cannot be detected by DSC, due to its polymerization degree independence, both gelation and vitrification can be determined during cure using material viscoelastic measurements [18-20]. As far as we know there is no report related to the application of coupled Impedance Spectroscopy with DMA to investigate the curing of composite.

In this work, the cure behavior of a Carbon Fibre-BMI SMC prepreg was analysed using techniques DSC and DMA. Also, simultaneously, both Impedance Spectroscopy and dynamic mechanical analysis (DMA) are employed to investigate progress of the curing reaction of thermoset composite (HexTool M61) at different heating rates (0.5 and 1 °C/min).

2. Materials and procedures

2.1. Materials

CF-SMC prepreg used in this study are made from Bismaleimide (BMI copolymerized with 2,2'-diallyl bisphenol A) resin (BMI – M61) and hygroscopic carbon fibres and was supplied by Hexcel Composites (HexTool®). The prepreg is composed of short strips (8 mm x 50 mm) of chopped prepreg unidirectional tape that are randomly oriented to form a quasi-isotropic non-woven material. The nominal fibre volume of the prepreg is about 53% and the thickness of the prepreg material is about 1.3 mm. This high fibre volume fraction results in the formation of a strongly connected electrical network. This compound is mainly used for mould manufacturing.

2.2. Procedure

DSC measurements were performed in dynamical mode, using a heat flow DSC from Mettler Toledo (STAR 01). Sample weights ranged from 18-20 mg. The scans were performed for the following heating rates: 0.5, 1, 3, 5, 10 and 15 °C/min in the temperature range from -50 °C to 400 °C. Five samples for each heating rate were scanned. The experiments were carried out under air atmosphere. Both n-th order reaction models and model free kinetics methods are explored in this paper. The rates expressed by the most existing methods (Table 1) were developed by assuming a n-th order reaction (see eq. (1)) [4] and for model free kinetics, the phenomenological kinetics of cure can be described by the equation (2) [5, 23]:

$$\frac{d\alpha}{dt} = A exp(-E_a/RT)(1-\alpha)^n \tag{1}$$

$$d\alpha/dt = k(T)f(\alpha) = A exp\,(-E_a/RT)f(\alpha) \tag{2}$$

The equations summarized in Table 1 are used for the determination of the kinetics parameters by plotting $\ln(q/T^2)$ versus $1/T_p$, $\ln(q)$ versus $1/T_p$, $\ln(d\alpha/dt)_{\alpha i}$ versus $1/T_{\alpha i}$, $\ln(q)$ versus $1/T$, $\ln(q/T^2)$ versus $1/T_\alpha$ and $\ln(q)_\alpha$ versus $1/T_\alpha$ using

Kissinger, Ozawa, Frideman, Ozawa, Flynn and Wall, Vyazovkin and Isoconversional models, respectively.

In the above equations α is the conversion degree of chemical reaction, n is the order of the reaction, k is the rate constant, A is the pre-exponential factor, $E\alpha$ is the activation energy, $f(\alpha)$ is the reaction model, q is the heating rate, T_p is the temperature for the rate maximum of reaction, $T_{\alpha i}$ is the temperature of selected conversion degree at each heating rate, $E_{\alpha,\alpha}$ is the activation energy for dependence on degree of cure with temperature, and R is the gas constant.

Table 1

The n-th order reaction and model free kinetics method equations

Kissinger [21]	$\ln(q/T_p^2) = \ln(AR/E_a) - E_a/RT_p$ (3)
Ozawa [4]	$\ln(q) = \text{Constant} - 1.052\left(\frac{E_\alpha}{RT_p}\right)$ (4)
Borchardt, Daniels [4]	$\ln(d\alpha/dt) = lnA - E_a/RT + n\, ln(1-\alpha)$ (5)
Model free kinetics (MFK) methods	
Friedman [22]	$\ln(d\alpha/dt)_{\alpha i} = \ln\big(A_\alpha f(\alpha)\big) - E_{a,\alpha}/RT_{\alpha i}$ (6)
Ozawa, Flynn, Wall [23]	$\ln(q) = \ln(AE_a/R) - G(\alpha) - 5.3305 - 1.052\, E_a/RT$ (7)
Vyazovkin [24]	$E_{\alpha,\alpha} = -R\left[\frac{d(\ln(q/T_\alpha^2))}{d(1/T_\alpha)}\right]$ (8)
Isoconversional [25]	$E_{\alpha,\alpha} = -R\left[\frac{d(\ln(q)_\alpha)}{d(1/T_\alpha)}\right]$ (9)

Dynamic mechanical tests were performed using DMA50 0.1 dB Metravib on a rectangular bar in tension/compression mode at controlled alternating displacement (±10 µm). The prepreg samples are about 55 mm long and 16 mm width. The temperature range was from -100°C (or 23°C in the case of simultaneous measurements of complex modulus and conductivity) to 190°C with a heating rate of 1°C/min and the frequency was varied from 0.1 to 10 Hz. The electrical measurements were performed using impedance analyser Solartron 1260 and Z60W software. Two electrodes are introduced in parallel in the sample. The distance between the electrodes is 16 mm. Electrodes are connected to impedance spectroscopy apparatus. Measurements were carried out for each test at a voltage of 0.5 V and a frequency of 1 kHz to ensure a quasi-DC resistance value (ohmic behavior of the carbon fibre network). In order to monitor the crosslinking at the same time by the collecting electrical and dynamical mechanical analysis (DMA) measurements, a modification was made within the DMA furnace; it consists in a fixed plate of resistant material at high temperature used to attach the cables of the spectroscopic impedance, as shown in the apparatus used for the experiment (Fig. 1).

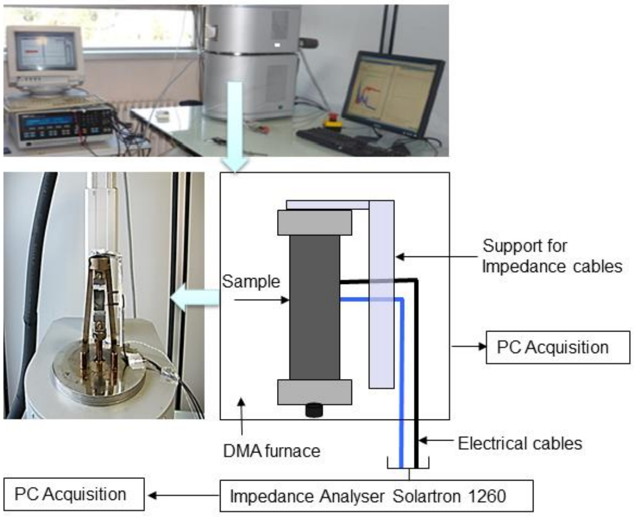

Fig. 1. Scheme and photography of experimental (for both DMA and Electrical conductivity) device used to monitor curing of the composite material

3. Results and discussions

3.1. Differential scanning calorimetry

Fig. 2 shows the DSC curves recorded at 0.5, 1, 3, 5, 10 and 15 °C/min. All DSC curves show a single peak.

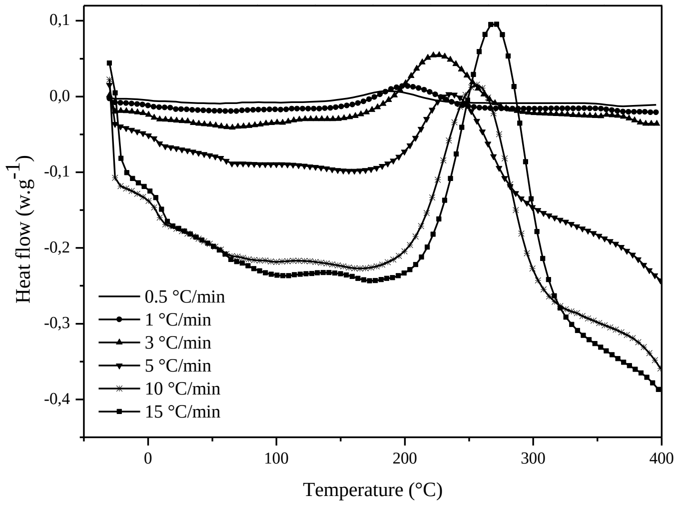

Fig. 2. DSC curves at different heating rates

The initial curing temperature, T_i, the peak exothermic temperature, T_p, the conversion, α_p, and temperature of complete cure, T_{end}, were calculated from DSC curves. The heat of reaction was estimated by drawing a spline line connecting the base line before and after the exothermic peak and integrating the enclosed area. The heat of reaction, ΔH_r, values varies over the range 95-103 J/g with a mean value of 98.33 J/g for the prepreg HexTool M61. Table 2 summarized curing characteristics of the HexTool M61. Fig. 3 shows the fractional conversion for dynamic cure at different heating rates.

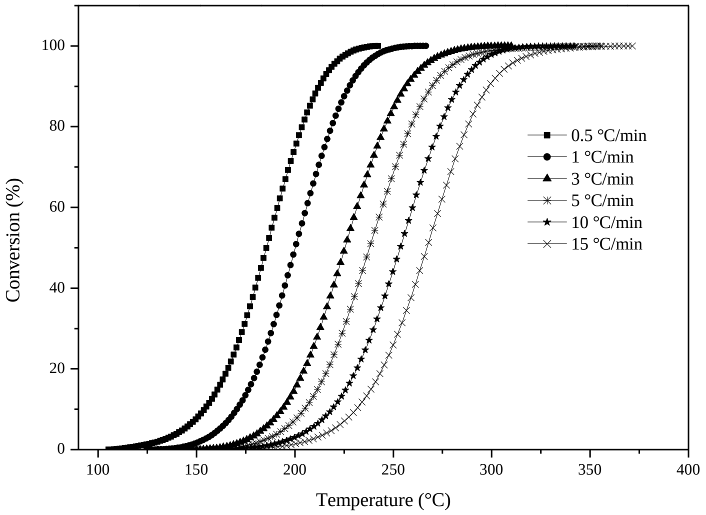

Fig. 3. Plot of the conversion degree vs. temperature

Table 2

Curing characteristics of the HexTool M61 evaluated from DSC curves

q (°C/min)	**ΔH_r (J/g)**	**T_p (°C)**	**α_p**	**T_i (°C)**	**T_{end} (°C)**
0.5	103 ± 2	186.2 ± 1	51.3 %	105.3 ± 1	243.2 ± 1
1	97 ± 2	199.6 ± 1	48.9 %	124.8 ± 1	267.0 ± 1
3	97 ± 2	224.7 ± 1	48.7 %	141.5 ± 1	310.0 ± 1
5	95 ± 2	238.0 ± 1	51.1 %	148.9 ± 1	356.8 ± 1
10	101 ± 2	256.5 ± 1	54.7 %	151.5 ± 1	341.7 ± 1
15	97 ± 2	270.6 ± 1	55.5 %	161.9 ± 1	371.6 ± 1

Mathematical software MATLAB is used to solve (for A, Ea and n) a multilinear linear regression equation (5) with $\ln(d\alpha/dt)$, $1/T$ and $\ln(1-\alpha)$ as variables. Results are shown in Table 3. The activation energy for the prepreg HexTool M61 varied in the range 73.48-146.39 kJ/mol and the order of reaction found was in the range of 0.82-1.43 with the average value n= 1.2.

Table 3

Kinetic parameters of the HexTool M61curing reaction obtained from equation (5)

q (°C/min)	Ea (kJ/mol)	ln A (s^{-1})	n
0.5	73.48 ± 3.45	15.35 ± 0.98	0.82±0.04
1	105.90 ± 3.23	24.03 ± 0.88	1.12 ± 0.03
3	100.64 ± 8.63	21.92 ± 2.23	0.98 ± 0.08
5	96.90 ± 8.51	21.15 ± 2.16	1.25 ± 0.08
10	146.39 ± 7.60	33.26 ± 1.90	1.42 ± 0.07
15	131.82 ± 6.32	29.36 ± 1.54	1.43 ± 0.06

The order n is observed to be equal to 1 with slight variations under lowest heating rate ($q \leq 3$ °C/min). At great heating rate ($q \geq 5$ °C/min), the order of reaction increases with the increase of the heating rate. Probably, elevated heating rate favours a larger number of chemical groups to react.

Figs. 4 and 5 show plotting $\ln(q/T_P^2)$ and $\ln(q)$ both versus $1/T_P$ respectively. Pre-exponential factor according to Kissinger model is calculated from intercept of the Kissinger plot.

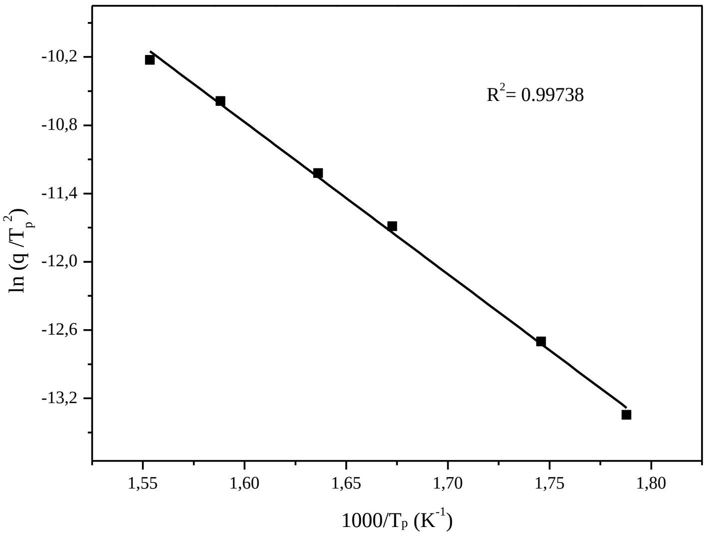

Fig. 4. Plot of the Kissinger equation heating rate *vs. 1/Tp*

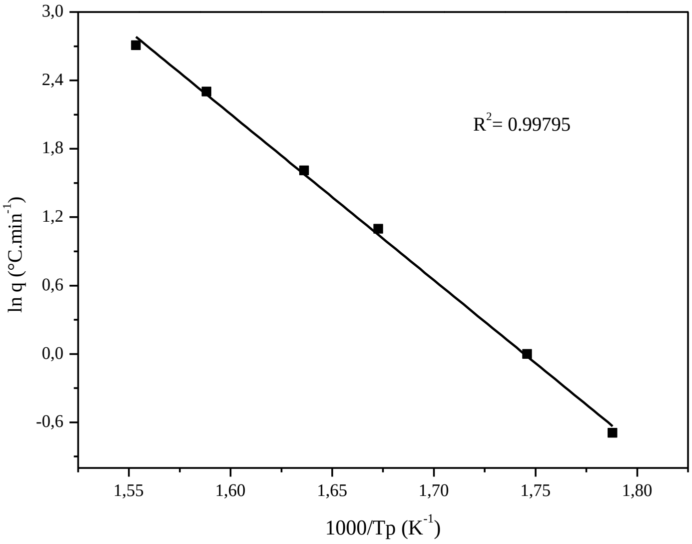

Fig. 5. Plot of the Ozawa equation heating rate vs. *1/Tp*

Table 4

Kinetics parameters according to Kissinger and Ozawa models

Methods	**Activation Energy (kJ/mol)**	**ln A (s^{-1})**	**Regression coefficient R^2**
Kissinger	111.11 ± 2,55	13.20	0.99738
Ozawa	121.07 ± 2,45	-	0.99795

Figs. 6, 7 and 8 show plotting ln(q), ln($d\alpha/dt$) and ln(q/T^2) all versus 1/T, respectively. Values of activation energy obtained from slope of curves are summarised in the following Table (Table 5).

Table 5

Activation energy according to model free kinetics

Methods	**Range of activation energy (kJ/mol)**	**Regression coefficient R^2**
Friedman	(77.75 - 85.48) ± 2.50	0.99914 - 0.9939
Ozawa, Flynn and Wall	(76.83 - 87.16) ± 3.35	0.99620 - 0.9999
Vyazovkin	(73.12 - 82.96) ± 3.19	0.99640 - 0.99589
Isoconversional	(80.824 - 91.689) ± 3.5	0.99687 - 0.9965

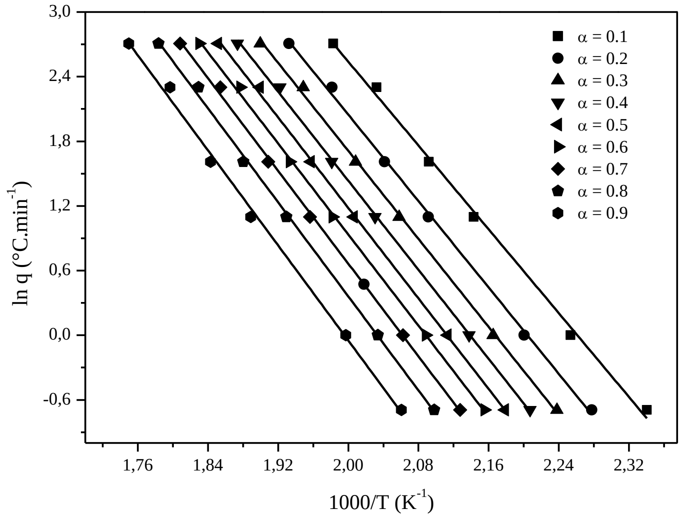

Fig. 6. Relationship between ln*(q)* and *1/T*

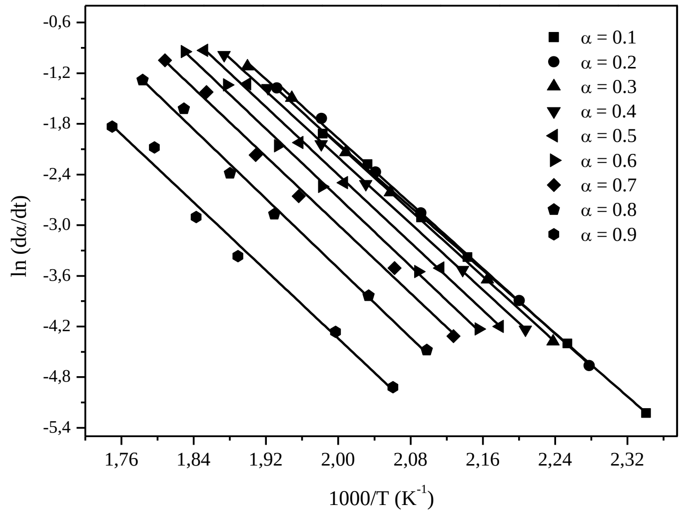

Fig. 7. Relationship between ln(*dα/dt*) and *1/T* according to Friedman model

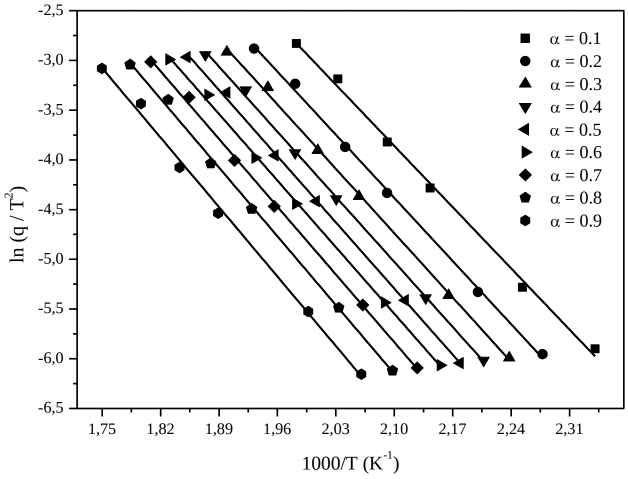

Fig. 8. Relationships between ln(q/T^2) and $1/T$ according to Vyazovkin model

Fig. 9 shows the change in the activation energy as a function of conversion.

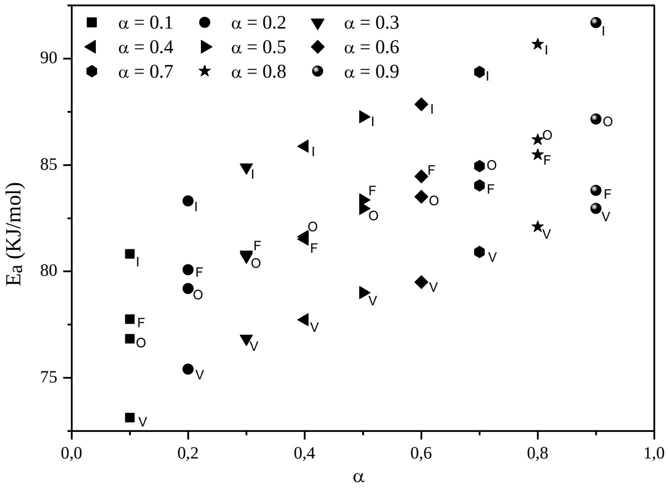

Fig. 9. Comparison of energy activation versus conversion for Model-Free Kinetics: Isoconversional (I), Friedman (F), Ozawa-Flynn-Wall (O), and Vyazovkin (V)

The value of activation energy is proportional to the conversion. Activation energies values of Friedman (F) and Ozawa-Flynn-Wall (O) models are between those of Vyazovkin (V) and isoconversional (I) models. The lowest values are assigned to the Vyazovkin model, while the highest values are obtained for the Isoconversional model. For a conversion of $\alpha \leq 0.3$, the Ea values for

Ozawa-Flynn-wall model are relatively lower than that of Friedman model. The reverse is observed when a conversion of $\alpha \leq 0.7$.

3.2. Dynamical mechanical analysis

Fig. 10 shows the storage modulus E' and $\tan\delta$ versus temperature and time during the curing of the prepreg. The stepwise temperature cure cycle has one isothermal processes. First, the temperature is raised from -20 to 190 °C at 0.5 °C.min^{-1} and then held at 190 °C for about 2 hours.

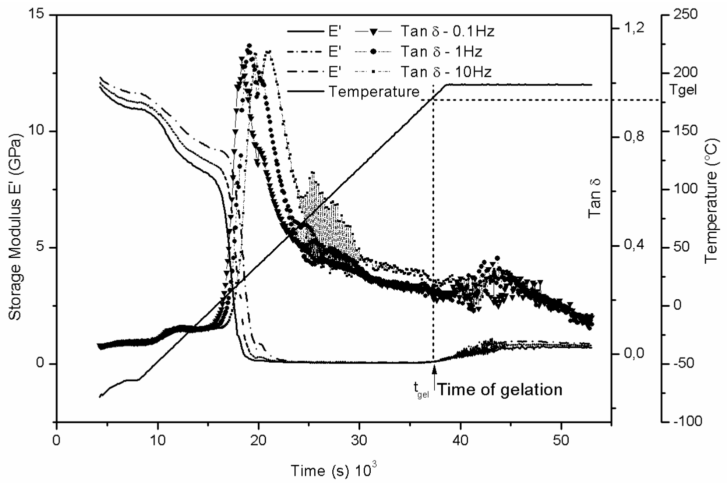

Fig. 10. Storage modulus E' and tan δ both versus time during cured prepeg M61 at 0.5 °C/min

Significant drop in storage modulus E' occurs from 4.1 °C and lasts till 40 °C at 1 Hz as the temperature increases. This decrease is associated with a peak of tan δ and a maximum takes place at the inflexion point of the modulus curve (15°C at 1 Hz). This relaxation process is associated with the α-relaxation of the uncured matrix (zero conversion) associated to the glass transition (Tg_0). The complex modulus is practically constant, the resin flow became negligible, voids are trapped, and chemical shrinkage of the resin occurs. In the case of composite system, the gelation point can be determined by the onset of the increase in the storage modulus E'. The onset of the further rapid increase of the modulus can be attributed to the threshold of network formation and can be assimilated to the time to gelation.

3.3. Coupling dynamical mechanical analysis and impedance spectroscopy at the same time

Figs. 11 and 12 show the evolution of the storage modulus E’ and the real impedance Z’ data plotted versus time during cure of the CF-SMC prepreg at different heating rate 0.5 and 1 °C/min, respectively.

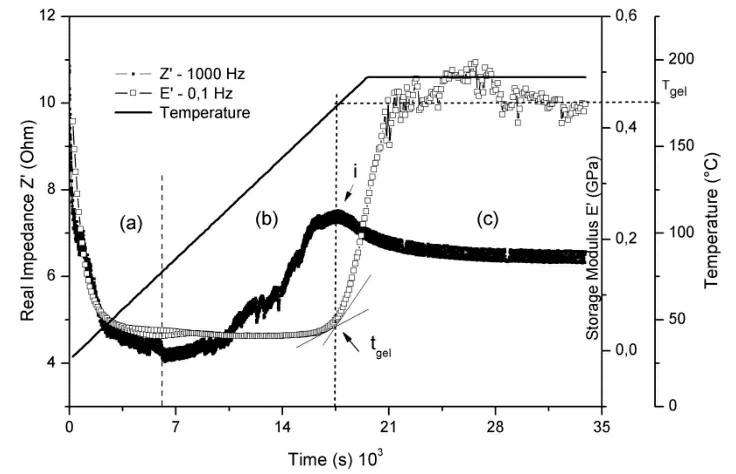

Fig. 11. Storage modulus E’ and real impedance Z’ versus time at 0.5 °C/min

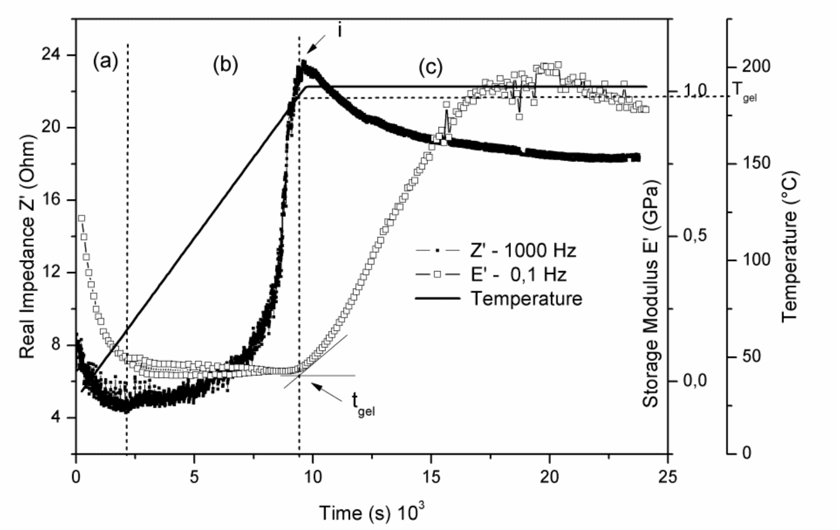

Fig. 12. Storage modulus E’ and real impedance Z’ versus time at 1 °C/min

Figures almost look the same, distinguished by three areas: (a), (b) and (c).

(a): After heating, the real modulus E’ of the prepreg decreases significantly related to the resin viscosity decrease. The decrease of real impedance Z’ as the temperature increases is dominated by the lowered viscosity bringing the fibres closer and leading to formation of new percolation paths due to slight waviness of the fibres [14, 17, 26].

(b): The increase of the real impedance Z’ is due to the decrease in the number of contacts between fibres due to other processes that are in competition with resin flow and tend to move away the reinforcement from each other: thermal expansion, void occurrence and rearrangements; additionally, wet air pockets entrapped during lay-up, and solvents in prepreg tend to expand or volatilise during heating thus causing voids to form [17, 27] mostly between plies that can growth by coalescence of surrounding voids. During this stage the storage modulus is practically constant.

(c): The peak (i) is related to the onset of gelation: the resin flow became negligible, voids are trapped, and chemical shrinkage of the resin occurs. The gel point can be determined by the onset of the increase in the storage modulus E'. The onset of the further rapid increase of the modulus can be attributed to the threshold of network formation and can be assimilated to the time to gelation. The end of reaction at high level of degree of conversion is characterized by the constant values of storage modulus E' and the real impedance Z'.

As expected, Figs. 11 and 12 shows that, at high heating rate, the peak (i) of the gelation moves to the left and its temperature T_{gel} increases. As can be seen in Figs. 10 and 11, the values of T_{gel} provided by the sample characterizing only by DMA and the sample characterized simultaneously by DMA and electrical measurements are in good agreement.

4. Conclusions

The kinetic parameters of prepreg bismaleimide composite HexTool M61 were evaluated. The activation energy varied in the range 73.48-146.39 kJ/mol, and the average order of reaction found for the prepreg HexTool M61 was equal to 1.2. The glass transition and the gelation temperatures, T_{g0} and T_{gel}, are equal to 4.1 °C and 175 °C, respectively. The agreement between DMA and IMPS data is quite good. This agreement in gelation data indicates the validity of the *in situ* electrical impedance spectroscopy measurements using carbon fibre for monitoring the polymerization reaction advancement. DMA coupled with impedance spectroscopy can be a great tool to enrich the method investigation of chemical and physical properties that take place during the curing of thermoset composites.

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