

Study of the curing process of a vinyl ester resin by means of TSR and DMTA

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Abstract

The curing reaction of a vinyl ester resin (VER), using methyl ethyl ketone peroxide (MEKP) as initiator and cobalt hexanoate (HxCo) as promoter has been studied by thermal scanning rheometry (TSR) and dynamic-mechanical thermal analysis (DMTA) under isothermal conditions. The gel time, which is defined by several criteria, has been utilized to determine the apparent activation energy (E_a) of the process. Furthermore, an empirical model has been used to predict the change of complex viscosity (η^*) with time, and assuming a first order kinetics, a new value for E_a is obtained independent of HxCo concentration. Finally, the vitrification time has been obtained from DMTA experiments. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Vinyl ester resin; Curing reaction; Gel time

1. Introduction

Vinyl ester resins (VER), introduced in the late 1960s, have made large strides in reinforced plastics applications. Originally developed for their high corrosion resistance performance, VER now find use in a wide range of applications due to their inherent physical and mechanical properties [1].

VERs are the addition product of an epoxy resin and an unsaturated carboxylic acid such as acrylic and methacrylic acid. There exists a great number of possible products depending on both the resin and the acid used, but the most utilized is that based on the Bisphenol A epoxy resin as it exhibits easy handling properties as well as good resistance to most chemical agents and due to its mechanical and thermal properties.

The crosslinking reaction of VERs proceeds by free-radical polymerization with organic peroxides and hydroperoxides as initiators, which are being generally used as accelerators for faster production of the free radicals. The rate of the polymerization reaction depends on the temperature and concentration of the monomer and initiator, which are established prior to curing.

Curing of these resins is difficult due to the change in physical properties during the cure process [2] and it has

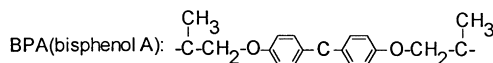
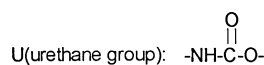
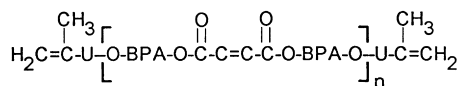
been characterized, as for every thermosetting system, by the gelation and vitrification processes.

The gel time is an important characteristic of the cure process of these materials as it conditions their processing. In this work we have studied the gelation process of a VER by means of thermal scanning rheometry (TSR) and dynamic-mechanical thermal analysis (DMTA); and some kinetic parameters for this process have been obtained.

2. Experimental

2.1. Materials

The VER used (ATLAC 580) was supplied by DSM RESINS España S.A. Their chemical structure is given as follows:



The technical characteristics of the VER ATLAC 580 are

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Table 1
Technical characteristics of VER ATLAC 580 (Supplied form: Liquid yellow-green)

Properties	ATLAC 580	Unit	Measurement method
Density at 25°C	1050	kg m ⁻³	BS 3532
Acid number	3–6	mg KOH g ⁻¹	ISO 2114
Viscosity at 25°C	400 ± 50	mPa s	Brookfield-LVT
Styrene content	47 ± 1	wt%	BS 2782

shown in Table 1. The resin is kept sealed at 4°C under nitrogen atmosphere to avoid any possible water condensation.

The polymerization goes through a free-radical polyaddition mechanism using methyl ethyl ketone peroxide (MEKP) as initiator which supplies the required free radicals, and cobalt hexanoate (HxCo) as promoter or accelerator which acts besides the initiator increasing the free radical production rate.

The experimental conditions are: MEKP (wt%): 1.0, 1.5, 2.0, 2.5 and 3.0; HxCo (wt%): 0.15, 0.30, 1.2 and 1.5.

2.2. Techniques

The techniques used in this work are TSR and DMTA. These techniques allow us to study the dynamic-mechanical properties of the VER during the cure process.

Thermal scanning rheometry: the TSR was designed and developed for monitoring the viscoelastic state of a wide range of materials and particularly the changes in the rheological properties with temperature or time [3]. The instrument may be used to track the change in viscoelastic properties of a thermoset right up to full cure or solidification.

The TSR uses a probe and a sample container that can be thrown away at the end of each experiment. The probe is connected via a spring of known force constant to a linear vibrator that is driven at constant amplitude and frequency (2 Hz). As the viscosity of the sample increases, the motion of the probe becomes progressively damped because of viscous drag. This change in amplitude and phase with respect to the drive motion is a function of the viscoelasticity of the material.

It is possible to change the spring used in order to vary the viscosity range; in our case a standard spring was used, which allows to measure viscosities from 1.0 to 300 000 Pa s.

The force generated on the probe due to the viscous drag is equal to the force F that acts on the spring, according to the equation:

$$F = \omega \eta^* C P^* = k(P_0 - P^*) \quad (1)$$

where η^* is the complex viscosity of the sample, P^* represents the complex motion of the probe when immersed in the sample, C represents a geometric factor related to the probe–material contact area, ω is the angular frequency that

is related with the oscillation frequency f ($\omega = 2\pi f$), P_0 is the maximum amplitude of the probe in the air and k is the force constant of the spring.

The complex motion is made up of the in-phase component (P') and the quadrature component (P''), and is given by the equation:

$$P^* = P' - iP'' \quad (2)$$

By combining Eqs. (1) and (2), the real dynamic viscosity η' and the imaginary viscosity η'' can be calculated from:

$$\eta' = \frac{P''P_0}{P'^2 + P''^2} \frac{k}{\omega C} \quad (3)$$

$$\eta'' = \left(1 - \frac{P'P_0}{P'^2 + P''^2}\right) \frac{k}{\omega C} \quad (4)$$

The shear storage modulus G' , the shear loss modulus G'' and the loss tangent $\tan \delta$ are given by:

$$\begin{aligned} G' &= 2\pi f \eta'' \\ G'' &= 2\pi f \eta' \Rightarrow \tan \delta = \frac{G''}{G'} = \frac{\eta'}{\eta''} \end{aligned} \quad (5)$$

The TSR is calibrated using a standard calibration fluid PL-Standard Silicone Fluid 01, the rheological properties of which are known for a set of temperatures. The calibration constants are introduced into the calibration file by the operator. The geometric factor C is calibrated every month while the maximum amplitude of the probe in the air, P_0 , is recalibrated for each experiment.

From thermorheometric studies the dynamic-mechanical properties of the VER system can be monitored with time until gel time. A complementary technique is needed to study the cure process after gelation.

Dynamic-mechanical thermal analysis: the dynamic-mechanical method assesses the structure and properties of solids and viscoelastic liquids via their dynamic and damping modulus. The method is highly sensitivity in detecting changes in internal molecular mobility [4]. The DMTA imposes a sinusoidal stress on a sample and determines the sample moduli G' , G'' and $\tan \delta$ as a function of temperature and/or frequency. Maximum loss in the scan is observed when the frequency of the motional process coincides with the impressed frequency. With increase in measurement frequency the loss process is found at higher temperatures, where the molecular motion is faster.

Liquid materials can be measured by the shear sandwich geometry. Here a disc or plate is affixed to the drive clamp and the sample is sandwiched between this and the studs mounted on the fixed clamps. The faces of this arrangement may be horizontal or vertical. It is recommended that the samples used are of equal dimensions (sample thickness = 1.5 mm and plate diameter = 12 mm).

A sample undergoing DMTA is subjected to a sinusoidal force of known magnitude and the resultant displacement in the sample is measured. The DMTA generates and controls the sinusoidal signal applied to the sample whilst monitoring

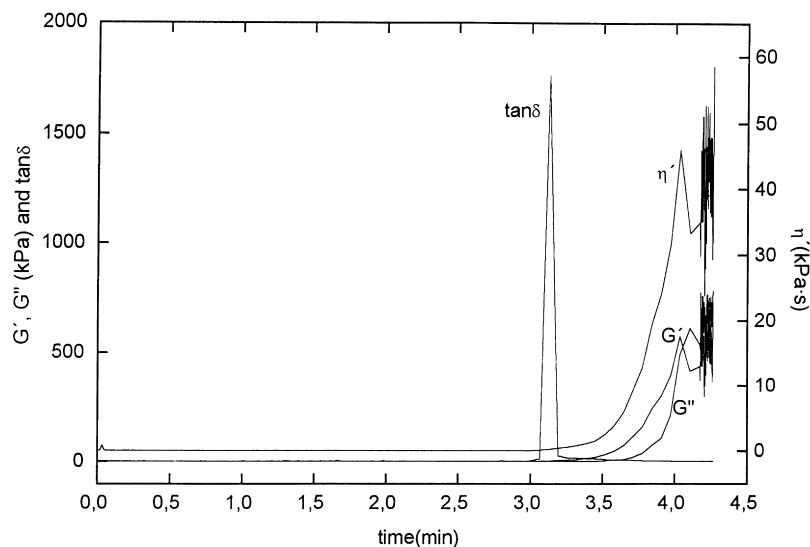


Fig. 1. Storage modulus (G'), loss modulus (G''), dynamic viscosity (η') and $\tan \delta$ versus time for the VER system from TSR.

the resultant displacement. It then analyses both signals to give results related to the dynamic behaviour of the sample.

The running conditions depend on the kind and geometry of the sample. In our work the conditions have been: isothermal temperature of 40°C , variable oscillation frequency of 2–20 Hz, displacement of $64\ \mu\text{m}$ and test time of about 2 h.

3. Results and discussion

Isothermal curing of a thermosetting resin is usually characterized by gelation and vitrification. Gelation corresponds to the incipient formation of an infinite network of cross-linked polymer molecules which occurs at a fixed extent of conversion as long as the reaction mechanism is not a function of temperature, and it is responsible for the transformation from a liquid to a rubbery state. Vitrification involves a transformation from a liquid or rubbery state to a glassy state as a result of an increase in molecular weight [5].

The cure of thermosetting resins is complicated by the interaction between the chemical kinetics and the changing physical properties. Near vitrification, the kinetics is affected by the local viscosity, which in turn is a function of the extent of reaction and temperature. Thus the cessation of reaction is not necessarily an indication that the reaction is complete, i.e. the reaction may have quenched due to vitrification.

3.1. Thermorheometric analysis

The gel time (t_g) is one of the most important kinetic characteristics of curing since it describes the attainment of a certain critical conversion responsible for the transition from the first to the second stage of the process [6]. The gel point is characterized by the appearance, in the reactive

system, of a macromolecule with an infinitely large molecular weight, $\bar{M}_w \rightarrow \infty$.

Generally, rheological and mechanical techniques are used to determine the gel time by means of extrapolation to infinite viscosity. The shear rate and vitrification affect the gel time determination. The dynamic-mechanical tests are the best methods for rheologic studies during polymerization. In the viscoelastic model [7]:

$$G^* = G' + iG'' \quad \tan \delta = G''/G' \quad (6)$$

where G' is the shear storage modulus, G'' the shear loss modulus and $\tan \delta$ the loss tangent.

In Fig. 1, three different regions are noticed. In the first region, the G' modulus is parallel to the time axis due to the low crosslinking. In the second region, this modulus increases exponentially versus time, where the gel time is reached. In the last region, the modulus increases more rapidly, where a great dispersion of the measurements is obtained indicating that the resin has been cured.

Tung and Dynes [8] proposed a correlation between the gel point and the intersection point of the curves of storage and loss modulus. In the liquid state the viscous properties are predominant, so $G'' > G'$ and $\tan \delta > 1$, whereas in the solid state the elastic properties are the predominant, $G'' < G'$ and $\tan \delta < 1$. Therefore, at gel point $G'' = G'$ and $\tan \delta = 1$. Winter and Chambon [9,10] proposed that G' and G'' curves are parallel or coincident in a narrow range of frequencies near the gel point. Harran and Landourd [11] determined gelation by means of the decrease in the rate of growth of G'' during the cure. The change in the slope between the two linear zones of $\log G''(t)$ is used to determine the gel point (independently of the experiment frequency).

Other authors have proposed different methods to determine the gel point during isothermal curing: White [12]

Table 2

Gel times (min) for the VER system cured at 50°C for all the criteria used (tg_1 , criterion of tangent line to G' curve; tg_2 and tg_3 , criteria of the viscosity (100 and 500 Pa s, respectively))

HxCo wt%	MEKP wt%	tg_1	tg_2	tg_3
0.15	1.0	39.4	42.3	45.9
	1.5	30.7	31.3	33.9
	2.0	19.5	21.3	23.6
	2.5	16.8	17.7	19.6
	3.0	14.6	16.2	18.2
0.30	1.0	39.7	39.9	41.6
	1.5	25.8	26.6	28.5
	2.0	21.3	21.1	23.6
	2.5	14.4	15.9	17.5
	3.0	13.0	14.1	15.6
0.50	1.0	33.1	34.7	36.6
	1.5	24.2	25.5	27.4
	2.0	18.4	19.1	20.9
	2.5	13.4	14.1	15.7
	3.0	10.9	11.9	13.2
1.20	1.0	23.5	25.6	27.3
	1.5	18.2	19.9	21.8
	2.0	13.3	14.3	15.9
	2.5	12.5	13.2	14.7
	3.0	9.92	10.8	12.0

correlated the gel point with the intersection between the two tangent lines at the beginning and at the end of the viscosity curve; Gillham [13] considered the gel point when the storage modulus G' is maximum; Willard [14] proposed the crossing point between the tangent line at G' curve and the base line ($G' = 0$); and Malkin and Kulichikhin [6] considered the gel point as that for which a maximum loss in the tangent is attained.

3.2. Gel time measurements

We have carried out TSR isothermal experiments at different temperatures (30, 40, 50, 60 and 80°C) and the

gel time has been determined according to the following criteria.

Criterion of the tangent line to G' curve: the gel time has been taken at the point corresponding to the crossing between the tangent drawn at G' , when G' reaches a fixed value, and the baseline ($G' = 0$).

Criterion of the viscosity: at this point the real dynamic viscosity η' reaches several determined values (100 and 500 Pa s).

Table 2 shows the gel time values obtained for the VER system at 50°C according to the above criteria.

The curing reaction of a VER is a free-radical polymerization among active chains and styrene molecules that act as the bridge between the resin chains. Depending on the amount of active chains and their generation rate, the cross-linking will be more or less fast and the gel time will be major or minor. In our system three variables have been found.

The gel time decreases when the cure temperature increases since an increase of temperature implies an increase in the mobility of the active chains, leading to a faster cure reaction;

The gel time decreases when the MEKP wt% increases due to the major amount of active chains generated and, consequently, a faster curing reaction occurs;

The gel time decreases when the HxCo wt% increases, due to a faster generation of the active chains.

However, the decrease in the gel time is higher when MEKP wt% increases than when HxCo wt% does. This can be explained by the total number of radicals determined by the MEKP wt%. A similar behaviour for vinyl ester and polyester resins has been reported by other authors [15–17].

Fig. 2 shows a linear relationship between $(tg_3)^{-1}$ and MEKP wt% for HxCo 0.3 wt%. For 30, 40 and 50°C, as is

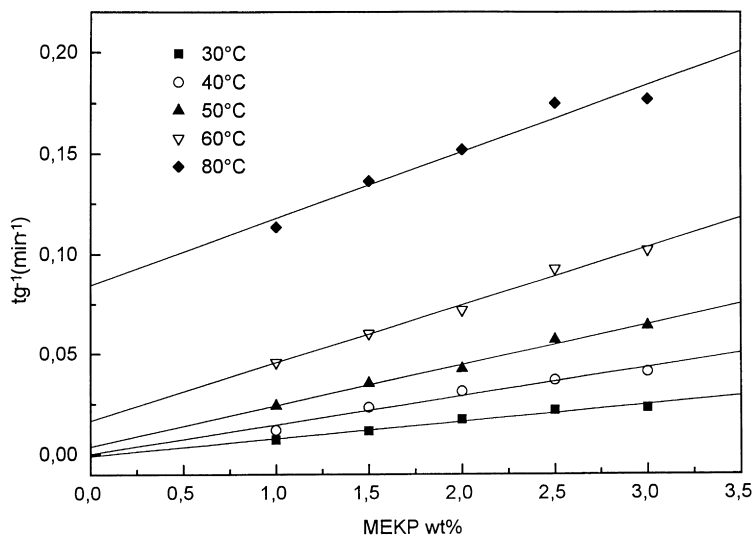


Fig. 2. Gel time–MEKP wt% dependence for isothermal experiments.

Table 3
Apparent Ea (kJ mol⁻¹) taking into account the different criteria (Ea₁: criterion of tangent line to G' curve; Ea₂ and Ea₃: criteria of the viscosity (100 and 500 Pa s, respectively))

MEKP wt%	HxCo wt%	Ea ₁	Ea ₂	Ea ₃	$\bar{E}a$
1.0	0.15	49.32	48.91	48.07	49.01
	0.30	50.16	49.74	50.16	
	0.50	50.16	50.16	50.16	
	1.20	48.49	48.49	44.31	
1.5	0.15	43.05	43.47	43.89	42.31
	0.30	42.64	42.64	43.05	
	0.50	42.22	41.72	42.64	
	1.20	40.38	40.59	41.42	
2.0	0.15	37.58	38.12	38.29	37.22
	0.30	36.20	36.49	37.70	
	0.50	37.20	37.49	38.82	
	1.20	35.45	36.20	37.16	
2.5	0.15	34.69	35.70	36.57	35.40
	0.30	35.36	35.36	36.74	
	0.50	33.98	34.65	36.11	
	1.20	34.49	34.94	36.16	
3.0	0.15	34.23	34.90	36.78	33.95
	0.30	33.15	34.48	35.86	
	0.50	33.77	34.48	35.74	
	1.20	30.18	31.35	32.44	

expected, when the MEKP wt% decreases the y-axis approaches zero as the tg approaches infinity. That is to say, the crosslinking process does not occur in the absence of an initiator. However, for 60 and 80°C the y-axis does not approach zero (1/tg ≠ 0), indicating that the crosslinking is initiated by a thermal process.

Apparent activation energy: the chemical conversion reached at the gel time is considered constant for a given system [18]. Therefore, the gel time can be related to the apparent kinetic constant (k') through the equation:

$$tg = ctelk' \tag{7}$$

Assuming that k' is related to the temperature by an Arrhenius relationship:

$$k' = k_0 \exp\left(\frac{-Ea}{RT}\right) \tag{8}$$

and replacing Eq. (8) in Eq. (7), it can be obtained:

$$\ln tg = cte' + \frac{Ea}{RT} \tag{9}$$

There is a linear relationship between ln(tg) and the inverse of temperature for isothermal cure reactions. From the slope of this plot, the apparent Ea can be obtained. Table 3 shows the values obtained for our system according to the different criteria used; some interesting facts are observed.

Ea values are similar independent of the criterion used for its calculation.

Ea does not vary with HxCo wt% for a fixed MEKP wt%. Ea decreases when MEKP wt% increases.

As Ea is a function of MEKP wt%, we have included an average Ea as well in Table 3.

Kinetic analysis through viscosity measurements: there are different methods for the quantitative treatment of the viscosity data obtained from thermosetting systems cured under isothermal conditions, most of them being based on the Williams–Landel–Ferry (WLF) equation [19–21].

Viscosity data can also be treated by fitting an empirical equation, where the temperature and the conversion dependency of the viscosity is separated into two independent terms:

$$\eta(T, \alpha) = \eta(T)\eta(\alpha) \tag{10}$$

Assuming that the reaction in the liquid state follows a first order kinetics until the gel time is reached, and taking into account that $\eta(\alpha)$ is related to the degree of entanglement and that for a fixed temperature $\eta(T) = \eta_0$, it can be

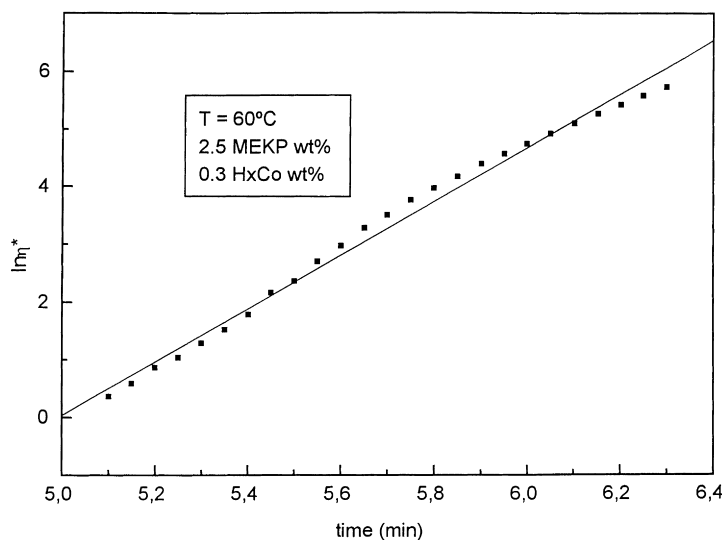


Fig. 3. Complex viscosity (η^*) dependence with time from TSR measurements.

Table 4
 k' (min^{-1}) values obtained for all MEKP wt% and curing temperatures

T ($^{\circ}\text{C}$)	MEKP wt%	0.3 wt% HxCo	0.5 wt% HxCo	1.2 wt% HxCo
30	1.0	0.351	0.373	0.396
	1.5	0.463	0.555	0.569
	2.0	0.782	0.799	0.803
	2.5	0.908	0.895	0.949
	3.0	1.06	1.02	1.25
40	1.0	0.507	0.588	0.706
	1.5	0.793	0.952	1.35
	2.0	1.15	1.44	1.62
	2.5	1.22	1.90	1.82
	3.0	1.47	2.32	2.47
50	1.0	1.25	1.28	1.35
	1.5	1.53	1.52	1.93
	2.0	1.67	2.06	2.55
	2.5	2.38	2.88	3.24
	3.0	3.00	3.46	3.68
60	1.0	2.03	1.91	2.53
	1.5	2.75	2.50	3.18
	2.0	3.67	3.45	4.51
	2.5	4.61	4.41	5.95
80	3.0	5.00	5.71	7.15
	1.0	4.46	–	–
	1.5	7.53	–	–
	2.0	8.46	–	–
2.5	11.4	–	–	
3.0	14.1	–	–	

written:

$$\ln \eta = \ln \eta_0 + k't \quad (11)$$

where η is the viscosity as a function of the temperature and the conversion, η_0 is the viscosity at $t = 0$ and k' is an apparent kinetic constant.

The complex viscosity dependency with time $\eta^*(t)$ is obtained from TSR measurements. Then, plotting $\ln \eta^*$ versus time according to Eq. (11), a linear plot is observed

Table 5
 Global kinetic constants k ($\text{min}^{-1} \text{wt}\%^{-1}$)

T ($^{\circ}\text{C}$)	0.3 gwt% HxCo	0.5 wt% HxCo	1.2 wt% HxCo
30	0.358	0.360	0.399
40	0.509	0.738	0.797
50	0.970	1.12	1.27
60	1.78	1.81	2.34
80	4.61	–	–

Table 6
 Vitrification times (min) for all frequencies from DMTA measurements

MEKP wt%	HxCo wt%	2 Hz	3 Hz	5 Hz	10 Hz	20 Hz
1.0	0.15	112	111	109	106	103
	0.30	102	101	100	97.4	–
	0.50	92.6	–	–	87.8	–
	1.20	96.7	–	–	90.9	–
1.5	0.15	84.5	83.7	82.9	82.0	77.2
	0.30	72.7	71.9	71.1	70.2	69.4
	0.50	64.2	63.5	62.8	62.1	–
	1.20	54.4	–	–	52.2	–
2.0	0.15	64.7	64.0	63.3	62.6	58.6
	0.30	55.3	54.5	53.7	52.9	52.0
	0.50	55.2	54.5	53.9	53.2	–
	1.20	49.8	–	–	46.3	–
2.5	0.15	58.4	57.5	56.5	53.5	49.9
	0.30	47.2	46.4	45.5	44.7	43.9
	0.50	44.3	43.6	42.9	42.2	–
	1.20	43.0	–	–	40.2	–
3.0	0.15	49.8	48.9	47.9	47.0	46.1
	0.30	49.7	48.7	47.8	46.8	43.1
	0.50	40.6	–	–	38.4	–
	1.20	33.2	–	–	32.3	–

for each experiment (see Fig. 3) from which the value for the apparent kinetic constant can be obtained (Table 4). It can be observed that k' depends on MEKP wt% for each cure temperature and Fig. 4 shows that it can be written as:

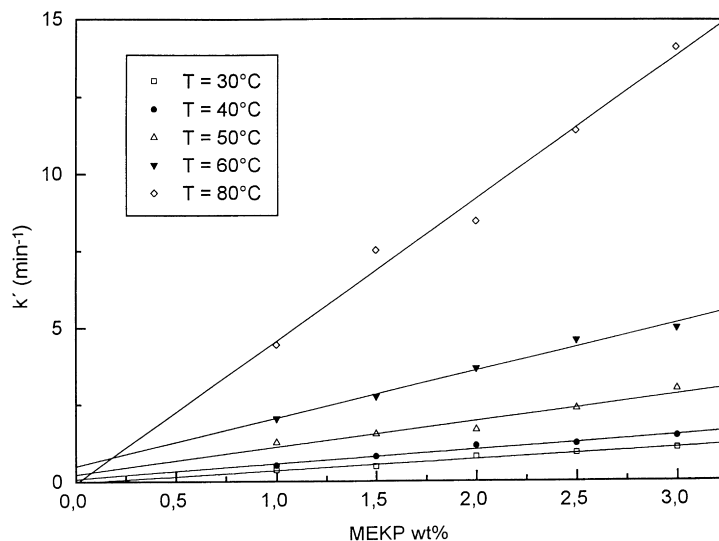


Fig. 4. Determination of the global kinetic constant (k).

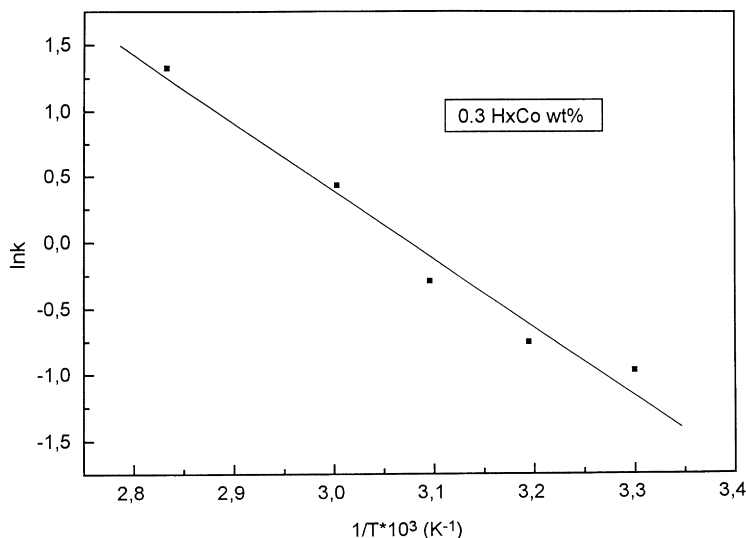


Fig. 5. Determination of the E_a through viscosity measurements from TSR.

$$k' = k[\text{initiator}] = k[\text{MEKP}] \quad (12)$$

where exists a linear dependence, the slope being the global kinetic constant k (Table 5). A slow dependence on HxCo wt% is noted, and assuming an Arrhenius relationship for k (Fig. 5), a global E_a was calculated for each HxCo wt%:

- 0.3 wt% HxCo $\Rightarrow E_a = 46.4 \text{ kJ mol}^{-1}$;
- 0.5 wt% HxCo $\Rightarrow E_a = 43.9 \text{ kJ mol}^{-1}$;
- 1.2 wt% HxCo $\Rightarrow E_a = 48.1 \text{ kJ mol}^{-1}$.

These values allow us to conclude that the E_a is not a function of the promoter concentration, as has been already observed from the gel time studies. The average E_a for the crosslinking process of the VER can be calculated as $E_a = 46.0 \text{ kJ mol}^{-1}$

3.3. Dynamic-mechanical analysis

The aim of this study is to study the rheological properties of our VER system. Fig. 6 shows a DMTA isothermal experiment in which three zones can be distinguished.

Gelation zone: gel time is assumed as the time at which a maximum in $\tan \delta$ curve occurs, corresponding to the maximum difference between the storage and the loss modulus, i.e. the moment at which the resin begins to crosslink generating the maximum difference between the elastic and the viscous behaviour.

Vitrification zone: vitrification time is identified as the second maximum in $\tan \delta$ curve. In this zone, either the storage or the loss modulus increases, giving the material in this interval a viscoelastic behaviour.

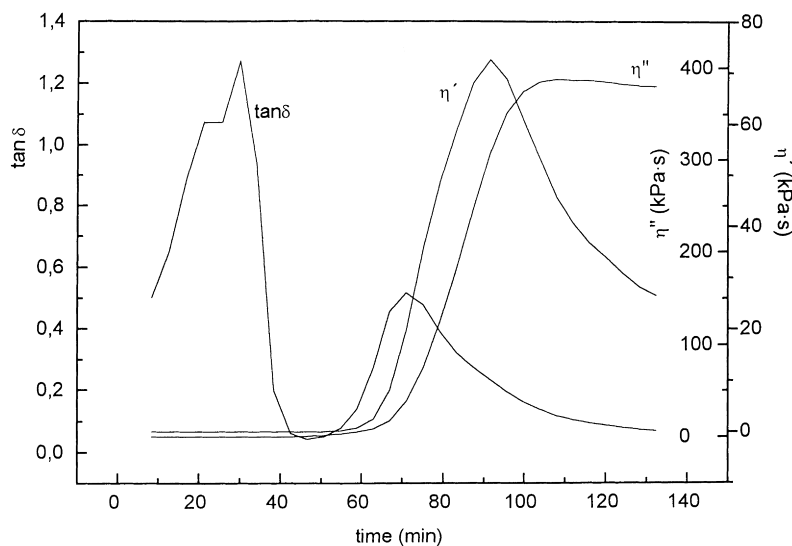


Fig. 6. Storage modulus (G'), loss modulus (G'') and $\tan \delta$ versus time for the VER system from DMTA.

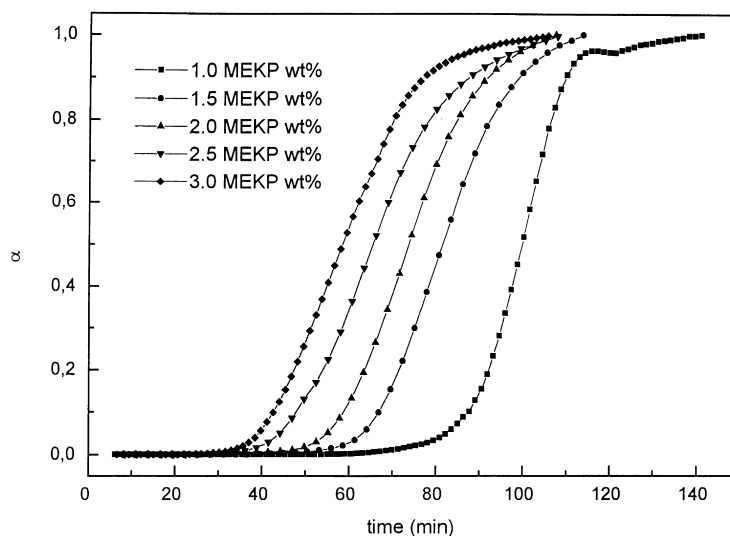


Fig. 7. Conversion versus time from DMTA experiments for all MEKP wt% (at HxCo 0.5 wt%).

A third zone where the material is highly crosslinked and has lost its capacity to dissipate energy. Therefore, η' decreases while η'' remains constant.

Table 6 shows the vitrification times obtained at several frequencies; it can be observed that the vitrification time decreases when either initiator or promoter concentration increases, due to increase in the amount of free radicals in the system and increase in their generation rate, respectively. The vitrification time decreases, while the frequency increases due to the displacement of moduli and $\tan \delta$ to lower time values.

3.4. Determination of the conversion

Defining the extent of reaction up to the end of the gelation process as:

$$\alpha = \frac{G_t^* - G_0^*}{G_\infty^* - G_0^*} \quad (13)$$

where G_t^* , G_0^* and G_∞^* are the values of the modulus at time t , at $t = 0$ (uncured resin), and at the end of the gelation process, respectively, it can be observed that initially the conversion is low since the number of active centres and the density of crosslinking are very small. Later the conversion grows very quickly, and at the end when the number of crosslinkings is high, the conversion stops.

Fig. 7 shows the influence of MEKP wt% on conversion at fixed HxCo wt%; as it can be observed for small values of MEKP wt% the conversion holds a long time in minimum values before it begins to increase. With respect to the HxCo wt%, its influence on conversion is small, as has been already noted for the other properties studied.

4. Conclusions

TSR and DMTA have been revealed as adequate techniques to describe the curing process of a VER. TSR allows to obtain in a simple manner one of the most characteristic parameters of the cure process, gel time, which determines when the resin becomes physically unprocessable.

The gel time value depends on the criterion used for its determination, this fact reveals that the gelation process occurs during a period of time. However, the E_a values determined from different criteria is the same. It has been observed that E_a values determined from gel time depend on MEKP wt% probably due to the fact that this treatment does not consider the full gelation process. Therefore we can determine the E_a values by means of the viscosity values available from TSR measurements; the value obtained is independent of both the initiator and promoter concentration.

Dynamic-mechanical analysis has allowed us to obtain the vitrification times at several frequencies as a function of MEKP and HxCo wt%.

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