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Effect of CTBN rubber inclusions on the curing kinetic of DGEBA–DGEBF epoxy resin

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Abstract

The curing kinetics of an epoxy resin matrix, based on diglycil ether of bisphenol A and F (DGEBA–DGEBF), associated with an anhydride hardener, at different carboxyl-terminated copolymer of butadiene and acrylonitrile liquid rubber (CTBN) concentration (0–10 phr) are studied using a differential scanning calorimetry (DSC) and a stress-controlled rheometer in isothermal and dynamic conditions. The aim of this work is to correlate the presence of the rubber phase with the transition phenomena that occur during the curing process. The CTBN rubber induces a catalytic effect on the polymerization of the pure resin clearly observed by a significant enhancement of the curing rate. Calorimetric and rheological analysis also evidences that gelation and vitrification times take place not punctually but in a wide range of time. Rheological data show that the presence of rubbery phase induces a higher rate of gel formation during the early stages of the reactions, confirming the calorimetric results. Finally the results are compared with theoretical models evidencing a good fitting between experimental and predictive data.

Keywords: Curing; Epoxy; Rubber; Chemo-rheology; Pultrusion

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1. Introduction

The epoxy resins are widely utilized as high performance thermosetting resins for pultruded profilates. Among various composite-manufacturing techniques, pultrusion is recognized as a very high potential process: it combines simplicity, low cost and capability of fabrication of constant cross-section composite parts. In the pultrusion process continuous fibre is pulled through a resin bath into a heated die. Inside the die, the resin cures and solidifies into a laminate with the same cross-sectional profile of the die. A puller continuously draws fibres through the die, and a travelling cut-off saw cuts the profiles into desired lengths. A schematic of the process is given elsewhere [1].

But manufactured articles are characterised by a quite low toughness. Thus the development of polymer matrix composites is limited in several industrial applications; consequently, the toughness should be increased without pre-judging the other useful properties of rigid network polymers. A method often used for toughening epoxies is the addiction of elastomers into the polymeric matrix.

With small rubber amount (10–15%), the dispersed phase bonded with the epoxy matrix act as dissipation centre of mechanical energy by cavitation and shear yielding, inducing the increase of crack grow resistance and finally excellent fracture properties [2].

The increase of the fracture resistance does not involve a meaningful reduction of the mechanical properties of the modified epoxy resins [3].

However to optimise the curing process and to define carefully the property–structure relation, the knowledge of physical and kinetic curing mechanisms of the resin is

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Nomenclature

$A(T)$	shift factor
A_i	calorimetric pre-exponential or frequency factor
A_η	rheological pre-exponential constant
E_a	cure activation energy
E_{ki}	activation energy related at calorimetric reaction rate
E_η	rheological activation energy
G''	loss modulus
G'	storage modulus
$k_i(T)$	calorimetric specific reaction rate
m	calorimetric kinetic exponent
n_1	calorimetric kinetic exponent
n_2	calorimetric kinetic exponent
R	universal gas constant
T	absolute temperature
$\tan\delta$	loss tangent
T_g	glass transition temperature
H_T	total heat reaction
α	conversion of reaction
α_d	conversion at onset of diffusion-controlled kinetics
α_g	conversion at gel
α_P	the maximum degree of conversion
μ_0	viscosity at $t = 0$

necessary [4,5]; an accurate definition of the process is than possible [5,6].

In fact during the cure of the resin on the die a high number of chemical reactions and physical state transformations (as the gelation or vitrification) occur, so the cross-linking process gives rise to a complex kinetic behaviour. As the resin passes through the heated die, during the curing process, the viscosity initially decreases due to melting and then it increases exponentially until the gelation takes place [7].

Therefore, the knowledge of rheological and curing behaviour of the resin systems is particularly necessary to have a correct control of the process mechanism and a subsequently engineering design.

The viscosity is important to have an accurate characterization of the process conditions and to visualize also the gelation, vitrification transition state. Moreover, the rheological analysis is indispensable to find out the relation between conversion and viscosity for the process simulation.

For thermosetting systems in industrial application, it is important to establish relations of transition phenomena (i.e. gelation, vitrification, and/or phase separation) to reaction time at different cure temperatures so that desired properties can be controlled. When these transitions proceed, the thermosetting system decreases its workability.

Another aspect, to be considered during the curing process, is the effect that the rubber addiction has on the rheo-kinetic properties of the resin. This factor is also relevant for industrial applications in the thermosetting composite field.

Currently, the rheological and DSC techniques are generally adopted to study the cure and the viscosity variation during processing of thermoset resins [8–10].

In this work we analyse the effect of thermal treatment on the curing kinetics of an epoxy resin, blend of DGEBA (60–70%) and DGEBF (30–40%) optimised for pultrusion process cured with an anhydride hardener, using the rheological and DSC techniques. To identify relations among the transition state, the temperature and the time of cure, a time-temperature-transformation (TTT) diagram is proposed for all the resin studied. The experimental data are compared with kinetic and rheological models. The effect of the rubber content on the chemo-rheological properties and the physical transformations are also studied.

2. Experimental procedure

The epoxy monomer used was a blend of diglycil ether of bisphenol-A (DGEBA) and F (DGEBF) (Epikote 235, supplied by Shell Chemicals). An anhydride was used as curing agent, methyl-tetrahydrophtalic anhydride (MTHPA) (Epiclon B-570, supplied by Shell Chemicals). The elastomer used was a carboxyl-terminated copolymer of butadiene and acrylonitrile, CTBN (Nippon Zenon 1300 × 13), added at different percentages (from 0 to 10 phr). A DY 070 supplied by Ciba-Geigy was used as catalyst.

The CTBN rubber was previously dissolved in acetone and subsequently mixed into a flask with the monomer. The contents were stirred on a 50 °C heated hot plate until clear. When the acetone used for the dilution was evaporated the hardener and the catalyst was added under magnetic stirring at room temperature until a homogeneous mixture is obtained. The mixture has been let rest up when the beads, trapped in the resin consequent to the stirring, are removed.

A differential scanning calorimeter, TA Instruments, model 2920, was used to monitor the cure kinetics. Resin samples of approximately 10–20 mg were used in sealed pans for all experiments. At first the experiments was performed in temperature ramp mode with scanning temperature of 5 °C/min ranging from room temperature to 200 °C. This test was used to define the total heat reaction associated at the full conversion of the resin. Further information of the curing kinetics was obtained executing isothermal curing tests at different temperatures for all blends investigated.

The isothermal scanning temperatures were selected in 10 °C increments between the starting peak temperature and the maximum peak temperature obtained by dynamic tests. The curves, obtained with the long-time isothermal scanning, were used to determine the degree and the curing rate using the traditional procedure of the reaction heat [11,12].

The rheological properties during curing were measured by a parallel plate SR5, a stress-controlled rheometer supplied by Rheometric Scientific. A liquid resin volume of about 0.5–1.0 cm^3 was placed on an aluminium plate of 25 mm of diameter, which will be thrown away at the end of the each experiment. To have a direct relation with the calorimetric data, dynamic tests at 5 °C/min from room temperature to 250 °C and isothermal tests at the same curing temperatures, analysed by DSC, were conduced. The experiments were carried out with stress of 1000 Pa at 1 Hz frequency.

In the present study four criteria for gelation were applied to the dynamic mechanical data. Some workers [13] have indicate that for many systems the gel point is not equal to calculated value at $G' = G''$ or $\tan\delta$ peak [14]. When the gelation occurs the viscosity exponentially increases to infinity. However, it is difficult to detect the "infinity" viscosity. Another method to identify the gel point is to locate the time at which the viscosity reaches a value of 10^3 or 10^4 Pa s [15]. In the present work the rheological gelation time was located at 10^3 viscosity value.

Another procedure is the criterion of the tangent line to the G' curve; the gel time is detected by the crossover between the tangent line at G' when this curve reaches a value close to 100 kPa s and the baseline $G' = 0$ [16].

About vitrification no accepted criterion has been defined [17]; the vitrification time has been determined according to two different criteria [18]:

Criterion of maximum $\tan\delta$ peak at 1Hz; criterion corresponding to the maximum G'' peak at 1 Hz.

3. Results and discussion

3.1. Calorimetric analysis

In Fig. 1 the trace of the dynamic tests at the DSC, conduced from 30 to 250 °C with a heating rate of 5 °C/min, is showed for all investigated systems.

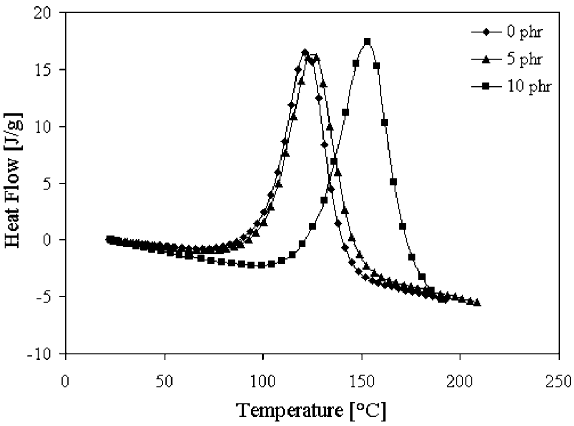

Fig. 1. Dynamic scan of all systems run at 5 °C/min.

From the above-reported results we can observe that the maximum temperature of the exothermic peak for the pure epoxy resin is about 30 °C greater than rubber modified ones.

The total reaction heat values (obtained by integration of the area between this peak and the baseline), H_T, are in the range of 342–349 J/g; this fact shows that it is independent from rubber content. Moreover this confirms that the presence of CTBN rubber not induces significant modifications on the final reaction state.

Typical plots of conversion vs time, at different temperatures, are showed in Fig. 2. The sigmoidal shape of these plots is observed, similarly to other epoxy matrices [4,19].

Curing kinetics of all systems leading to thermosetting networks involve several competing reactions. At the beginning cross-linking bonds form large molecules with high molecular weight. After, during the curing process, the free volume in the molecular arrangement decrease, resulting in the reduction of the mobility and inducing an increase of the resin viscosity. At this point the gelation takes place, so the reaction becomes diffusion

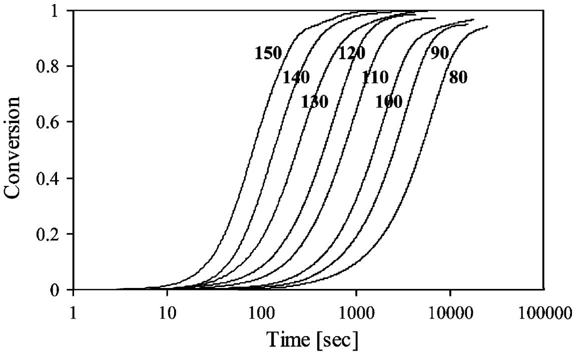

Fig. 2. Conversion vs time for the 0 phr system at different cure temperatures.

controlled; this phenomenon also influences its rate and mechanism.

Thus the complete conversion is not allowed and only some segmental movements, caused by structural relaxation processes, can take place.

Depending on the curing temperature, the curve shapes are very similar, suggesting a limiting conversion degree from which it is possible to extrapolate the final value.

The reaction rate and the final conversion increase with increasing curing temperatures, indicating that vitrification is reached progressively at higher conversion when higher reaction temperatures are used. The vitrification occurs when the glass transition temperature, T_g, reaches the cure temperature, due to the increase of the cross-linking density at the progressively higher conversion.

In order to observe the effect of CTBN rubber into the epoxy resin, in Fig. 3 a comparison of the cure kinetics, at the reference temperatures of 80 and 120 °C and at different rubber amount, is reported. The presence of the CTBN rubber induces faster curing process than the unmodified resin. The final conversion increase with higher CTBN content, too.

Wise et al. [20] have reported that the use of the CTBN rubber modifiers induces a high reactivity of the end groups with the epoxide ring, which will results in shorter curing times.

This behaviour brings to more perfect network structure. The increasing reaction rate of the epoxy-modified resins is due to the interaction between the carboxyl-terminated groups of the CTBN rubber and the epoxide rings of the monomer. So it is possible to draw that the CTBN carboxyl groups induce a catalytic effect on the curing process.

With reference to Fig. 3, we can observe that the differences between the neat epoxy and the rubber modified epoxy resins are amplified at the lower temperature (80 °C). This behaviour can be explained considering that temperature enhance the rate of the all-curing reaction masking the effect of the other factors and induces uncertainties in the determination of reaction heat in the initial time interval [21].

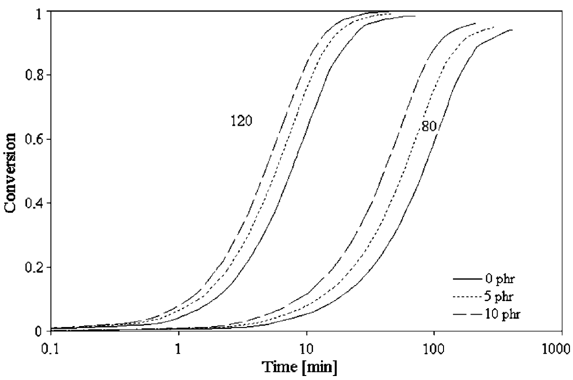

Fig. 3. Conversion vs time for isothermal cure at 120 and 80 °C of all systems.

Table 1
Activation energy for 0 phr, 5 phr and 10 phr system obtained by calorimetric data

Sample (phr)	Activation energy (kJ/mol)
0	73.2
5	70.1
10	62.1

The conversion vs log(time) curves at different temperatures can be overlapped, by simply translation of each curve along the log(time) axis with respect to an arbitrary reference temperature curve, employing a shift factor,

$$A(T) = \ln(t_{\text{ref}}) - \ln(t_{\text{T}}) \tag{1}$$

This parameter can be used to calculate the cure activation energy through the relationship:

$$\begin{aligned} A(T) &= \ln(t_{\text{ref}}) - \ln(t_{\text{T}}) = \ln k(T) - \ln k(T_{\text{ref}}) \\ &= -\frac{E}{RT} + \frac{E}{RT_{\text{ref}}} \end{aligned} \tag{2}$$

The relationship between the shift factor and the inverse of the absolute temperature (K) is linear. From the slope of this relationship, the cure activation energy (E_a) is obtained [22].

In Table 1 the dependency of activation energy by rubber amount is observed; the activation energy decreases with the rubber content increase. Moreover a reduced energy is necessary to promote the molecular mobility and to enhance the curing reaction. The activation energy values are compatible with the results reported in literature [11,23].

3.2. Chemical kinetic model

The data, obtained by DSC analysis, in the present paper are fitted by the mathematical model proposed by Chen and Macosko [24]:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^{n1}; \quad \alpha < \alpha_d \tag{3}$$

$$\frac{d\alpha}{dt} = k_3(\alpha_P - \alpha)^{n2}; \quad \alpha > \alpha_d \tag{4}$$

α_d is determined from reaction rate vs conversion graph (a change in slope indicates the onset of diffusion controlled kinetics) [25].

Table 2
Order of reaction and kinetic parameters for 0 phr system

Temperature (°C)	Autocatalytic parameters				Diffusive parameters	
	m	n_1	k_1	k_2	n_2	k_3
80	0.38	0.877	6E-05	0.00014	0.94	0.00024
90	0.36	0.962	0.00007	0.00036	0.99	0.00053
100	0.4	1.115	0.00009	0.00072	1.55	0.0019
110	0.38	1.121	0.00016	0.00151	1.4	0.0036
120	0.44	1.206	0.0002	0.00169	–	–
130	0.46	1.511	0.00025	0.00701	–	–
140	0.5	1.534	0.00028	0.01468	–	–
150	0.48	1.5	0.0004	0.02342	–	–

$k_i(T)s$ can be expressed by the Arrhenius relationship [12]

$$k_i = A_i e^{-(E_{ki}/RT)} \quad i = 1\text{–}3 \qquad (5)$$

With this model it is possible to take into account that the process is diffusion controlled when the conversion increase and the T_g approaches the reaction temperature. So the decrease to zero of the reaction rate before reaching full conversion is obtained.

A multiple regression technique is used to perform the analysis of the isothermal test and to obtain the kinetic parameters.

Table 2 show the value of reaction orders and the kinetics constants for the 0 phr system.

We can observe that k_1 values are lower than k_2 ones which affect the reaction more strongly. At the same time the kinetic constant values increase with increasing temperature. The overall reaction order, $m + n_1$, is in the range 1.25–2 (greater reaction order is attained at high temperature). Similar consideration can be draw for other systems.

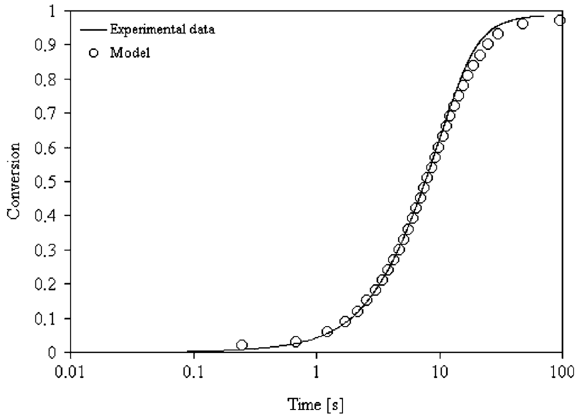

Fig. 4. Comparison between experimental and model values for degree of cure as a function of the cure time at 120 °C for the 0 phr system.

Table 3
Cure reaction activation energies system

		E_{K1}	E_{K2}	E_{K3}
E (kJ/mol)	0 phr	36, 44	91, 44	111, 12
E (kJ/mol)	5 phr	46, 19	88, 70	114, 60
E (kJ/mol)	10 phr	77, 28	74, 71	96, 94

By integration of Eqs. (3) and (4) it is possible to draw the conversion vs time and by this way we can know how the cure reaction progresses during the process. In Fig. 4 the trace of isothermal test at the reference temperature of 120 °C for the 0 phr epoxy resin is reported; the experimental data agree very well with the theoretical prediction, showing a good sensibility of the mathematical model.

Table 3 shows the activation energy associated to k_1, k_2 and k_3 for all analysed systems. E_{k1} increase with increasing rubber content; on the other hand it is possible to notice a reduction of E_{k2} with increasing rubber amount.

This fact implies that the rubber phase induces catalytic effect during the second part of the curing process.

3.3. Rheological analysis

Fig. 5 shows the variation, on isothermal curing treatment at 80 °C, of elastic and loss modulus vs time for the mixture containing 5 wt.% CTBN rubber.

At the beginning we identify a zone where the G' modulus is quite constant at varying times, the system is liquid and the stiffness is low.

Then, both G' and G'' increase as cross-linking reactions progress to have a crossover G'/G''; at this point the system presents both an elastic and viscous behaviour, storing a similar amount of the energy dissipated. In this zone the gelation state occurs.

The isothermal curve shapes are similar to the other ones obtained by dynamic measurements.

In Fig. 6 the viscosity vs time at different temperatures for unfilled resin is reported. A similar behaviour was found for all analysed systems. At the increase of the

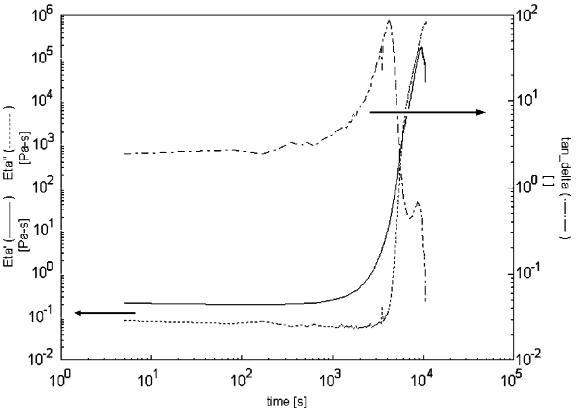

Fig. 5. G', G'' and $\tan\delta$ for the 5 phr system measured at the curing temperature of 80 °C.

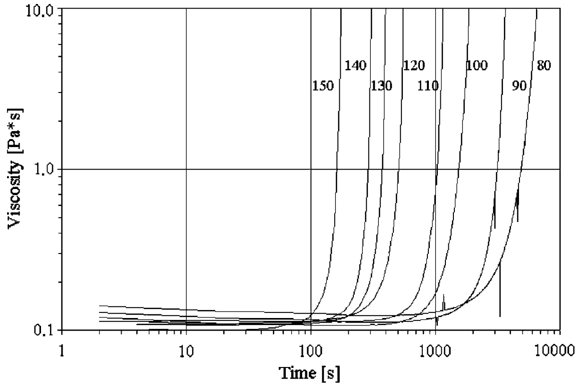

Fig. 6. Changes in viscosity for the 0 phr resin in the range 80–150 °C.

temperature we can observe two effects: the reduction of the initial viscosity, η_0, and the curves are shifted on the left, because the reaction is thermally accelerated, and consequently the decrease of the gel time is evidenced.

The gelation transformation induces, at the same time, various chemical and physical phenomena. The resin viscosity increases and the cross-linking densification advances; the curing reaction proceeds until vitrification or the transformation of the rubbery network into a glass solid takes place.

During curing, a correct thermal treatment is necessary to have the optimisation of process conditions. At the beginning a finest viscosity value is necessary; in this way a good fibre wetting is obtained; after, during the polymerisation the viscosity exponentially increase, and the resin flow is reduced. A premature gelation (and then vitrification) can leave to irregular resin distribution in the composite laminates, obtaining imperfections as voids or poor adhesion fibre matrix into the final hand-manufactured article. On the other hand, a slow reaction rate induces expensive production costs.

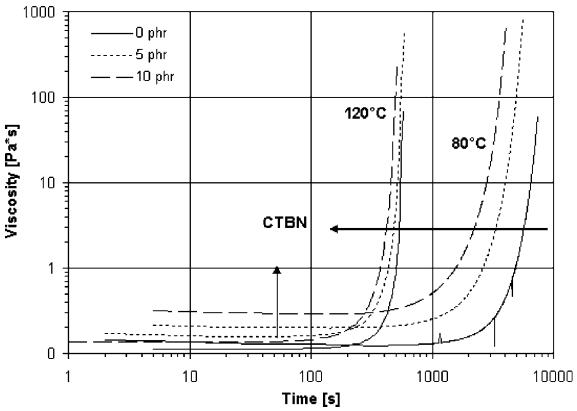

Fig. 7. Changes in viscosity with increasing rubber amount at the reference temperatures of 80 and 120 °C.

In Fig. 7 a comparison of the viscosity vs time at different rubber amounts is reported, at the reference temperatures of 80 and 120 °C.

The presence of the CTBN rubber into the epoxy matrix induces a slight increase of the viscosity of ungelled resin; this influences negatively the wetting resin. On the other hand, the polymerisation rate increases proportionally with the rubber content. The moderate difficulties encountered in the wetting phase (due at the increase of viscosity for the modified epoxy resin) are balanced by the considerable optimisation of curing and flow of the resin and generally of process conditions.

The results, about the vitrification and gelation times for 0 phr system, are showed in Table 4.

For all studied systems the gel and vitrification times vary depending on the criterion selected. This fact can be explained considering that these processes take place in a wide interval of time and not in punctual moments.

The gel time decreases with increasing cure temperature at a fixed CTBN rubber amount. This means that at higher temperatures the molecular mobility increases and the chemical interactions between the molecules are favourites; therefore the curing reaction occurs rapidly. At a fixed temperature, the gel time decrease with the increase of CTBN rubber contents. The presence of rubbery phase induces a higher rate of gel formation during the early stages of reactions, confirming the calorimetric results. Similar consideration can be obtained for the vitrification.

In order to characterize these transformations as a function of temperature and time, a TTT diagram is developed [26]. The TTT diagram for the neat epoxy is proposed in Fig. 8. The gel and the vitrification times reported are obtained by average of the all criterions used in this work.

The behaviour of the resin depends by cure temperature. It is evident that the gelation and vitrification are transformation processes that extend over a large part of

Table 4
Gelation e vitrification for the 0 phr system

Temperature (°C)	Gelation (s)			Vitrification (s)		
	G'/G''	max tanδ	$\mu' = 10^3$ Pas	tan G'	tan δ peak	max G''
80	8705	6620	8480	9090	12470	13145
90	4083	3655	4073	4168	4585	4659
100	2045	1850	2750	2187	3710	3755
110	1670	1130	1595	1750	2090	2330
120	560	530	1325	623	1670	1745
130	395	380	560	441	1265	1325
140	304	289	394	329	–	–
150	170	170	275	196	–	–

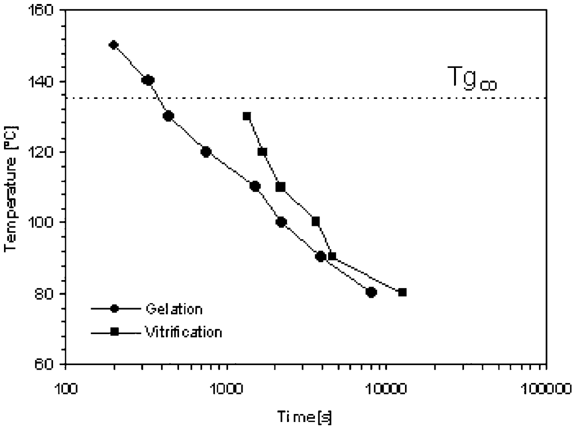

Fig. 8. Times to gelation and vitrification for 0 phr system.

the cure. The vitrification times do not show noticeably the characteristic minimum.

The influence of the rubber content into the epoxy matrix on the cross-linking process and on the thermal properties of the cured mixture is also analysed in Fig. 9 where the gelation times for different rubber contents and different temperatures are showed. A rubber increase induces a reduction of gel time (evidenced graphically by the curves translation on the left).

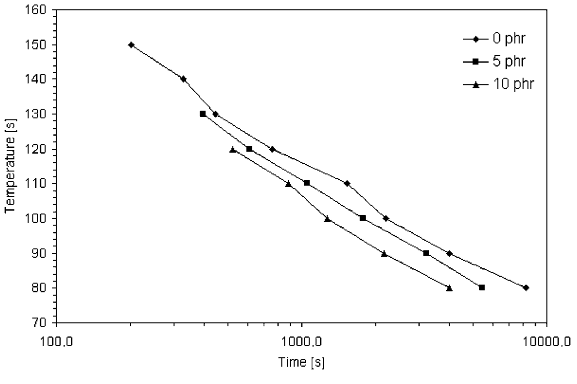

Fig. 9. Time to gelation for all systems.

Table 5
Activation energy for 0, 5 and 10 phr system obtained by rheological data

Sample	Activation energy (kJ/mol)
0 phr	65.5
5 phr	57.3
10 phr	57.7

The apparent activation energies are obtained from the slope of the logarithmic plot $\log t_g$ vs the reciprocal absolute temperature (K) [9] and are presented in Table 5.

These values are suitable between 57.7 kJ/mol for the 10 phr resin and 65.5 kJ/mol for the neat epoxy. The activation energies are slightly inferior at data obtained in DSC analysis.

This can be explained considering that on the DSC analysis small differences in sample volume can induce considerable uncertainty in the comparison of the results [9]. Other researchers [27] have found that the gel time obtained by rheological analysis is higher than kinetic one. This effect is clear when the difference between the masses of samples is higher.

3.4. Rheological model

The data are fitted with an empirical chemo-rheological model proposed by Castro and Macosko [28]. With this model the resin viscosity to temperature and degree of cure or time at a specific temperature are relate.

$$\eta(\alpha, T) = \eta_0 \left(\frac{\alpha_g}{\alpha_g - \alpha} \right)^{f(\alpha)} \tag{6}$$

$f(\alpha) = A + B\alpha$. The initial viscosity term, μ_0 is expressed in terms of temperature by an Arrhenius type expression,

$$\eta_0 = A_\eta e^{(E_\eta/RT)} \tag{7}$$

Table 6
The Castro–Makosko parameters at various temperatures for the 0 phr system

T (°C)	80	90	100	110	120	130	140	150
α_{gel}	0.76	0.73	0.65	0.84	0.62	0.72	0.83	0.81
η_0	0.12	0.11	0.11	0.11	0.11	0.10	0.10	0.09
A	−0.15	−0.40	−0.15	−0.50	−0.10	−0.36	−0.10	−0.31
B	2.72	2	2.86	1.86	1.62	1.2	0.45	0.85

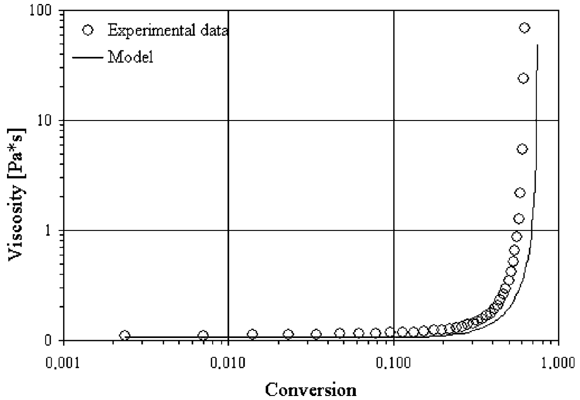

Fig. 10. Viscosity vs conversion in isothermal test at 120 °C for 0 phr resin.

The DSC and rheological data are analysed simultaneously at a common temperature to fit the viscosity data with the model; the obtained rheological parameters for the 0 phr system are reported in the Table 6.

In the Fig. 10 the results, obtained by experimental representative test compared with mathematical model, are showed. It is interesting to notice that the experimental data are very well interpolated by the theoretical model.

4. Conclusions

The addiction of carboxyl terminated butadiene–acrylonitrile rubber to the epoxy resin show an increase of the curing rate, due at a catalytic effect of the CTBN carboxyl end groups on the cure process. We also notice the activation energy decreases with increasing rubber amount, which confirms the previously considerations.

Rheological analysis, in comparison with the kinetic results, is used to determine the gelation and vitrification points at different temperatures, giving rice to a TTT diagram for all systems. The gel and vitrification time decrease with the temperature and the rubber amount, in agreement with the calorimetric results. The knowledge of these properties give us useful information to develop an appropriate predictive model to simulate the process condition in a pultrusion line.

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