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Effect of carbon nanofibers on the cure kinetics of unsaturated polyester resin: thermal and chemorheological modelling

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Abstract

We report the study of the effects of carbon nanofibers (CNFs) on the cure kinetics and on the chemorheology of unsaturated polyester resins (UP). Two main experimental techniques were utilized: differential scanning calorimetry and rheometry. Isothermal and dynamic tests were performed on the neat polyester resin and on two nanocomposite systems, with 0.5 and 1.0 wt% of CNFs. Furthermore, a TGA study of the selected systems at different isothermal temperatures was performed to evaluate the styrene consumption and related loss rate during the curing process. Subsequently, a phenomenological model (autocatalytic approach) was applied to the experimental data, both in isothermal and dynamic conditions. In the case of dynamic curing, the evidence of multiple peaks in the heat flow curves was studied through the deconvolution of the overall reaction thermogram in single reaction steps. An empirical rheological model coupled with the reaction kinetics was successfully applied to simulate the viscosity changes of the UP matrix. Experimental and modelling results demonstrate the presence of a delay effect of the CNFs on the cure of the UP resin matrix.

Keywords: A. Nano composites, B. Curing, D. Differential scanning calorimetry (DSC), D. Rheology, cure kinetics.

1 Introduction

The cure reaction of thermosetting resins is particularly relevant due to the wide use of these polymers in a large number of industrial processes and applications. Thorough knowledge of the dynamics of the chemical reactions involved in the curing of thermosets can lead to the optimization of their processes in terms of processing time, costs and final properties of the materials produced. Moreover, following the important role of thermosetting polymers as matrices of composites and nanocomposites, this topic acquires particular relevance due to the complex chemorheological effects of the interaction of the matrices with the reinforcing phase. While the modelling of the chemorheological behaviour of thermosetting polymers and matrices of composite materials has been extensively reported in scientific literature [1-3], the same does not apply to nanocomposites. In this sense, the modelling of cure kinetics is important because it represents a very powerful tool in analyzing how the introduction of nanocomposite matrices in traditional fiber composites can affect the processing condition and curing time. In fact, if the cure reaction is delayed by the presence of nanoparticles, it represents additional efforts and costs for processing optimization in large-scale production.

Of all the thermosetting polymers, unsaturated polyester resins play an important role because of their versatility in properties, flexibility in processing and low cost.

Therefore, the kinetics and monitoring of an UP resin cure have been intensively studied in the last twenty-five years [1-7]. The cure reaction of UP resins follows a free radical reaction mechanism, which is quite complex, involving initiation, propagation and termination. Due to the rapid build-up of a crosslinked network, copolymerization leads to the early formation of microgels, even at conversion levels as low as 3-4% [1-3]. Another parameter to take into account is the use of styrene as solvent and reactive material, which is normally subjected to evaporation, being a highly volatile component

of the reactive system. In fact, a significant loss of styrene can occur during processing when the resin is still completely liquid, as well as during the exothermic polymerization.

Since the discovery of the great potential for breakthrough properties that nano-sized particles have on polymers, the interest in thermoset curing shifted to the study of the role of nanoparticles in the cure reaction of thermoset-based nanocomposites. Many researchers have paid attention to this topic, demonstrating that no simple and univocal cure behaviour trend can be encountered when nanoparticles are mixed with a thermoset [8-11]. In particular, most of the studies were performed on epoxy systems, whereas according to our investigation, less attention has been focused on polyester-based nanocomposites. In particular, some studies have focused on the effects of the introduction of nanoclays [12-17] and POSS [18-19] on the curing kinetics of UP nanocomposites. In particular, Zhou et al. [17] found a delaying effect of modified montmorillonite nanoplatelets on the curing reaction of polyester matrices.

Very limited information is instead available on the effect of carbon-based nanofillers on the cure reaction of UP resins, although the employment of this kind of fillers in an UP matrix has great potential on modifying the electrical, thermal and mechanical behaviour of the unfilled systems [20-31].

Among the different techniques which can be used to study the cure kinetics of a thermosetting polymer [32-35], DSC and rheometry are two of the main approaches commonly employed. Differential scanning calorimetry (DSC) is based on the assumption that the heat produced during cure is proportional to the extent of reaction. Although it gives little or no information on the chemistry associated to the reaction, it is one of the most popular techniques for cure monitoring because of its simplicity and relative rapidity. Chemorheology follows the curing process by monitoring the viscoelastic behaviour of the reacting systems, which is directly related to the change in

molecular weight from the liquid state to an infinite molecular network (gelation) and eventually to a glassy state (vitrification).

In this research, the two aforementioned approaches are used to study the cure process of an UP resin filled with vapour-grown carbon nanofibers. Then, a phenomenological model is used to obtain the kinetic parameters of the cure process adopting a mathematical approach previously proposed for fibre reinforced UP matrices [3]. The kinetic model is then combined with an empirical rheological model proposed by Castro and Macosko for polyurethane systems [36] and successfully applied to describe the chemorheology of unsaturated polyester systems by Kenny and coworkers [3].

2 Material and Methods

The resin employed in this study was a low-viscosity orthophthalic unsaturated polyester resin supplied by Cray Valley, its commercial name being Enydyne I 68835 (41% styrene content, see table 1). Carbon nanofibers, produced by Grupo Antolín (Spain) and named GANF, were employed as a nanofiller. GANFs are helical ribbon carbon nanofibers, which consist of a continuous graphene sheet rolled up along the fiber axis [37]. As claimed by the manufacturer, they have very small diameters (20-80 nm), high aspect ratio (>100) and highly graphitic structure (graphitization degree about 70%). They are provided without any chemical functionalization. For this study, they were employed as supplied by the manufacturer, with two different contents, namely 0.5 and 1 wt%.

The dispersion process of the CNFs inside the polyester resin consisted of several steps. The accurately selected ratios of CNF:resin (0.5:99.5 and 1.0:99.0) were weighed and put in a vial which was connected to a high-shear mechanical stirrer. The vial was hermetically sealed, in order to hamper the strong styrene evaporation which is favoured by the heating of the mixture. This is due to the high shear stresses produced by the mixing itself, and causes a significant chemical change to the global reactive system and

a change in the ratio of the resin to nanofibers. After 30 minutes of mechanical stirring the nanocomposite mixture was placed in an ultrasound bath for 1 hour to improve the homogeneity of the dispersion and to degas the mixture.

After the mixing procedure, the styrene content of the nanocomposite blends was evaluated, making it possible to calculate the amount of styrene evaporated during mechanical stirring. This calculation consisted of several steps (UNI EN ISO 3251). The nanocomposite mixture was diluted with acetone in a ratio of 1 mg mixture to 3 ml acetone and evenly dissolved. The obtained blend was put in an oven at 110°C for one hour and then removed, allowed to cool down to room temperature and weighed. The residual mass consisted of the polyester monomer and the carbon nanofibers (when present), whereas the lost part of the mass consisted of styrene and acetone. In this way, the styrene content of the mixture after the process can be easily calculated by the following equation:

$$\%_{styrene} = \left(1 - \frac{m_2 - m_{CNF}}{m_1 - m_{CNF}} \right) \cdot 100 \quad (1)$$

where m_2 is the residual mass after baking, m_1 is the initial mass of the nanocomposite mixture and m_{CNF} is the amount of CNFs in the weighed mixture, as calculated by $m_{CNF} = m_1 \cdot [\%_{CNFs} / (100 - \%_{CNFs})]$.

The styrene content in the neat resin as supplied by the manufacturer was also evaluated and compared with the content in the nanocomposite mixtures in order to calculate the exact amount of styrene needed for the same amount of styrene in the neat resin and in the nanocomposite blends. The styrene added has a purity which is more than 99% and was purchased from Sigma Aldrich. It was mixed with the blends by means of magnetic stirring for 1 hour. During this mixing phase, the vessel with the blends was sealed in order to avoid further styrene evaporation. After this process, the styrene content was evaluated again, to verify that the new styrene content was the same as the pristine resin.

The cure reaction of the resin was activated by means of butanone peroxide, supplied by Sigma Aldrich, at the recommended percentage of 1.5 wt%, and accelerated by 0.15 wt % of cobalt octoate (6%). The accelerator, cobalt octoate, was added before the mixing process, while the initiator was added just before the preparation of the specimens for testing. Both the peroxide and the cobalt octoate weight were considered part of the resin when establishing the ratio of the resin to CNF, that is the ratio CNF:UP was actually CNF:(UP+Peroxide+Co).

DSC tests were performed with a DSC Mettler Toledo, model 822e, and rheology tests with an ARES N2 Rheometric Scientific rheometer. Isothermal and dynamic scans were performed at various temperatures and scan rates for both DSC and rheology measurements. In particular, the isothermal tests were performed at 25 – 40 – 55 °C, and the dynamic tests were performed at 3 – 5 – 10 °C/min. In all cases, the cure reaction occurred during testing, and the changes in heat flow and viscosity with time were monitored. Rheological tests were conducted with the parallel plate geometry (plate diameter 25 mm) with a gap of about 1 mm. They were performed in dynamic mode, setting the strain at 0.15%, and with an oscillation frequency of 1 Hz. In this study the viscosity was studied only at a single frequency because the dependence on the frequency was already investigated [20] and it was not part of this paper. Each test was repeated at least five times in order to minimize errors.

In a further analysis, we monitored the loss of weight of the three reactive systems in order to study the evaporation of volatile components during network formation. To achieve this, a Seiko model Exstar 6300 thermogravimetric analyzer was utilized. The tested isothermal curing temperatures were the same as in the other techniques (i.e. 25-40-55°C).

A morphological investigation on the blends was carried out by means of microscopy. In particular, an optical microscope (Nikon Epiphot 300 reflection microscope) was employed to study the homogeneity of the dispersion in the liquid state, whereas a transmission electron microscope (Philips EM 208 TEM) was used for the investigation of the dispersion in the fully cured materials. Although optical microscopy can not give highly magnified images to observe single nanofibers and therefore to thoroughly investigate the degree of dispersion, it can be useful in checking the homogeneity of the bulk distribution during curing. Moreover, it is important to verify the presence of aggregates as a consequence of the re-agglomeration tendency of CNFs during the gelation process. This characterization was carried out using a hot stage Mettler Toledo mod. FP82.

3 Results and discussion

Figure 1 shows the results of the morphological investigation for the 0.5%-CNF nanocomposite. In particular, figures 1a and 1b show the optical micrographs of the liquid mixture for the isothermal cure at 40°C at the beginning of the cure reaction and at the gel point, respectively. It is possible to observe that slight re-agglomeration is actually present during the gelation process. Nonetheless, this phenomenon is not strong enough to significantly compromise a fully cured nanocomposite with an even dispersion of CNFs. In fact, as a result of the TEM analysis (an example thereof is shown in figure 1c), the cured nanocomposites were characterized by a dispersion which is quite uniform. Similar micrographs were obtained for the 1%-CNF nanocomposite and for the other temperatures and are not reported in this paper.

Figure 1

Table 1

Styrene content [%]		
Neat polyester	41.04 ± 0.55	
	<i>after mixing</i>	<i>after addition</i>
0.5% CNFs	36.58 ± 0.43	40.73 ± 0.36
1% CNFs	39.55 ± 0.07	40.68 ± 0.43

The variation in the styrene content in the nanocomposites, due to styrene evaporation during the mixing process, was evaluated and the results are shown in table 1. It is possible to observe that only a little styrene evaporation occurs as a consequence of the mechanical stirring process. Moreover, this evaporation is more pronounced at 0.5 wt%

because the lower viscosity of the mixture (due to a low content of CNFs) allows a greater amount of styrene to evaporate. In order to confirm this, we evaluated the styrene content in the neat polyester previously subjected to the same processing condition as the nanocomposites. After the mixing process, the neat polyester has a styrene content of 35.08% (not reported in table 1), which is lower than the values obtained for the nanocomposites, confirming that by increasing the CNF content, styrene evaporation is reduced.

This result concurs with those obtained in the TGA analyses performed at all the temperatures studied in this work. As an example, figure 2 shows the weight loss curves of the reacting systems during isothermal cure at $T = 25^{\circ}\text{C}$. These plotted curves were normalized to the effective content of the styrene present in the mixture before curing. Analogous curves were obtained at the other temperatures and are not reported in this paper. Assuming that the styrene is the only diffusing material that causes mass loss in the UPs, the unfilled system shows the highest styrene loss rate before the gel point, while the CNFs filled system shows a decrease in the styrene consumption with respect to the neat system. This result, obtained during both the mixing phase and cure reaction can be explained by the fact that carbon nanofibers tend to increase the viscosity of the resin [20] and hamper styrene evaporation. The elbow transition observed in the curves from short time loss (linear slope) and long time loss can be associated to the vitrification of the systems so, after this point, any evaporation phenomenon is hindered. The second column of table 1 reports the styrene content after it was added to compensate the amount evaporated during the mixing process. It is possible to see that the systems in which the cure kinetics has been analyzed, have the same styrene content as the neat polyester.

Figure 2

3.1 Curing kinetics

Once the correct styrene content was set in all the nanocomposite blends, an analysis of the cure kinetics was performed. Figure 3 reports the heat flow curves for the three selected systems at the same heating rate (10°C/min) and for the 0.5% CNFs at different heating rates. It should be pointed out that in dynamic scans there is always a double reaction peak with a shoulder that is more visible as the scan rate increases. Double reaction peaks or peaks with shoulders are often detected in DSC traces during non-isothermal curing of UP resins [38]. Kubota [39] and Avella [40] confirmed that polyester homopolymerization was a cause of the highest temperature exothermic reaction in the DSC curves of the UP resin crosslinking. At higher temperatures, polyester coils possess enough energy to override steric hindrances and polyester homopolymerization becomes notable. Hence, as mentioned above, the first peak can be associated to the styrene polymerization coupled with the crosslinking reaction between styrene and polyester molecules, which, from activation energy measurements, is much easier than the homopolymerization of polyester itself. Lowering the heating rate of the test, the third exothermic reaction is less visible or disappears because at lower rates all the polyester chains are able to react with the styrene monomers. An increasing rate

does not permit the styrene-polyester reaction to take place fully and so, at higher temperatures, the unreacted polyester chains can react with each other. Based on these considerations, we can assign the first double exothermic peak to the styrene–polyester copolymerization and styrene homopolymerization, while the single exothermic reaction at higher temperatures, referred above as the third peak, was due to polyester homopolymerization.

Figure 3

In figures 4a and 4b, DSC thermograms of isothermal tests are reported. Figure 4a shows the isothermal tests of the three systems at $T=40^{\circ}\text{C}$, whereas figure 4b shows the isothermal thermograms of 0.5% CNF-loaded nanocomposites, performed at different temperatures. In tables 2 and 3, all the reaction characteristics of the calorimetric

experiments have been summarized. In particular, the temperature at which there is a peak in the heat flow (T_{peak}) and the total heat produced during dynamic cure (ΔH_{dyn}) have been reported for the dynamic scans (table 2) (all the values of the heat flow were normalized to the net amount of resin in the nanocomposite mixtures).

Figure 4

Table 2

	ΔH_{dyn} [J/g]			T_{peak} [°C]		
	3°C/min	5°C/min	10°C/min	3°C/min	5°C/min	10°C/min
Neat Polyester	287.4 ± 8.4	269.3 ± 3.1	239.9 ± 1.6	68.7 ± 0.6	77.5 ± 1.0	93.3 ± 2.3
0.5% CNFs	273.1 ± 11.2	265.1 ± 15.4	233.9 ± 48.2	70.6 ± 4.8	86.9 ± 7.6	94.6 ± 6.9
1.0% CNFs	239.6 ± 4.4	225.5 ± 32.4	187.5 ± 14.5	86.9 ± 4.9	94.5 ± 2.6	103.8 ± 1.1

The parameters associated with isothermal tests (table 3) are the time at which the heat flow curve reaches a maximum (t_{peak}), the induction time (t_{ind}) calculated as the intersection between the horizontal right baseline and the heat flow curve, the heat related to isothermal curing (ΔH_{iso}) and the maximum degree of cure obtained in the final stage (α_{max}). The degree of cure α is calculated as the ratio between the amount of heat generated, H_t at time t and the total heat of reaction H_{TOT} , which is calculated in dynamic scans:

$$\alpha(t) = \frac{H_t}{H_T} = \frac{1}{H_{\text{dyn}}} \int_0^t \left(\frac{dH}{dt} \right) dt \quad (2)$$

Table 3

	ΔH_{iso} [J/g]			α_{max} [-]		
	25°C	40°C	55°C	25°C	40°C	55°C
Neat Polyester	185.2 ± 18.5	196.2 ± 17.8	213.9 ± 4.7	0.66 ± 0.06	0.74 ± 0.06	0.90 ± 0.02
0.5% CNFs	172.0 ± 30.4	192.9 ± 11.0	205.6 ± 23.6	0.63 ± 0.10	0.75 ± 0.05	0.83 ± 0.13
1.0% CNFs	166.4 ± 4.6	179.0 ± 7.8	200.2 ± 31.9	0.69 ± 0.02	0.80 ± 0.11	0.92 ± 0.07
	t_{peak} [min]			t_{ind} [min]		
	25°C	40°C	55°C	25°C	40°C	55°C
Neat Polyester	72.2 ± 10.5	21.7 ± 10.7	9.9 ± 2.3	19.2 ± 1.5	8.3 ± 3.6	1.9 ± 0.2
0.5% CNFs	85.6 ± 24.5	28.4 ± 0.5	12.1 ± 4.9	46.7 ± 7.4	10.7 ± 0.8	2.5 ± 0.5
1.0% CNFs	112.9 ± 24.3	40.6 ± 9.5	16.4 ± 2.1	59.8 ± 22.0	14.7 ± 0.5	4.3 ± 1.6

In figure 5, the trend of the degree of conversion was plotted as a function of temperature and time for dynamic (a) and isothermal (b) tests respectively, for the 0.5%-loaded system. Similar plots were obtained for the other systems. As expected, the onset temperature of the cure reaction in dynamic tests increases with the heating rate while an incomplete resin cure is obtained in isothermal tests, with the maximum value of conversion increasing with the cure temperature. A linear dependence of the final degree of reaction on the isothermal curing temperature was found (figure 6), which is analogous to the trend found by Kenny and co-workers [3] for unsaturated polyester systems. No significant difference between the three systems was found with respect to

the final degree of reaction and just one linear equation was sufficient for the interpolation of the data.

Based on an overall analysis of the DSC results, it is possible to make the following comments. The heat of reaction evolution in both dynamic and isothermal tests is delayed when CNFs are present in the blend and this delay depends on the nanofiber content. In fact, in both dynamic and isothermal tests, there is a shift in the exothermal peak toward higher temperatures and longer times, as shown in figures 3a and 4a respectively. Even t_{peak} and t_{ind} are shifted to higher values when increasing the CNF content. On the other hand, the maximum degree of reaction is not affected by the presence of the nanofibers.

Figure 5

Figure 6

This delay, which does not produce a variation in the maximum extent of reaction, has been also observed in UP-carbon nanotube nanocomposites [41] while opposite results were reported on the curing of epoxy matrices, where an acceleration effect of the addition of carbon nanotubes has been reported [10]. It should be considered here the different nanofiber-matrix interactions expected in both cases. While for epoxy resins, the main interaction is represented by a strong non-covalent interaction of the amine hardener with the aromatic wall [10], in unsaturated polyesters, the free radicals scavenging activity of the carbon-based fillers can be considered as the main mechanism. As widely reported in the case of carbon nanotubes [42-45], untreated CNFs can be capable of entrapping the free-radicals generated by the initiator within their aromatic walls due to their huge surface area. As a result, the styrene can not react fully with the polyester molecules and is forced to self-polymerize. This consideration is also supported by our DSC results in figure 3a. In this figure, in fact, it is possible to see that the second and third peak, which are assigned to the self-polymerization of styrene and polyester respectively, are much more pronounced for the filled systems.

As already mentioned, the model adopted for the cure kinetics was the one proposed by Kenny et al. [3], where an incomplete cure reaction due to vitrification in the final conversion is considered:

$$\frac{d\alpha}{dt} = K\alpha^m(\alpha_{\max} - \alpha)^n \quad (3)$$

where K is a kinetic rate constant and $m + n$ is the overall reaction order. The kinetic parameters for all the three systems at the different isothermal temperatures are reported in table 4. This model successfully predicts the chemical progress of the cure reaction with time. As an example, model and experimental data for the isothermal tests of the UP+0.5% CNF system are well compared in figure 7.

Table 4

	Neat Polyester			0.5% CNFs			1% CNFs		
	25°C	40°C	55°C	25°C	40°C	55°C	25°C	40°C	55°C
K (*10⁻³)	1.47	3.14	3.72	0.94	2.13	3.67	0.53	1.18	2.10
m	0.50	0.51	0.53	0.60	0.62	0.67	0.66	0.52	0.57
n	1.31	1.55	1.55	1.60	1.47	1.53	1.26	1.28	1.42
m + n	1.80	2.06	2.08	2.20	2.09	2.20	1.91	1.80	1.99

The delaying effects of the CNFs are mainly reflected on the rate constant K which decreases with the amount of carbon nanofibres. The overall order of reaction $m+n$, is close to 2 as typically reported for phenomenological models of thermosets curing [1, 3, 46] and remains practically constant with negligible changes with the CNFs content.

Figure 7

The apparent activation energy and the pre-exponential factor can be obtained from the reaction constant K at the different temperatures assuming an Arrhenius equation:

$$\ln K = \ln K_o - E_a / RT \quad (4)$$

The activation energies were then calculated from the plot of $\ln(K)$ vs $(1/T)$ obtained in isothermal tests (figure 8). The obtained values are reported as an insert in figure 8. The common trend is, as previously noted, that the cure reaction is delayed in temperature and time, upon increasing the CNF content (evidence of the delay is given by an increasing E_a value).

Figure 8

Whereas the isothermal traces are constituted by a single peak which can be correctly evaluated applying the kinetic model, dynamic cure is based on three different reaction peaks clearly visible in the heat flow curves (figure 3) and they need to be separated by a deconvolution process (in order to separate the three contributions to the total reaction pathway and to identify the individual kinetic steps). A model which properly fits the dynamic experimental was considered and the hypothesis was that each reaction obeys a rate law such as:

$$\frac{d\alpha}{dt} = K\alpha^m(1-\alpha)^n \quad (5)$$

supposing that every reaction was going to take place fully and the final conversion was

1. The overall expression for the reaction rate can be written as:

$$\begin{aligned} \left(\frac{d\alpha}{dt} \right)_{TOT} &= \left(\frac{d\alpha}{dt} \right)_1 + \left(\frac{d\alpha}{dt} \right)_2 + \left(\frac{d\alpha}{dt} \right)_3 = \\ &= AK_1\alpha^{m_1}(1-\alpha)^{n_1} + BK_2\alpha^{m_2}(1-\alpha)^{n_2} + CK_3\alpha^{m_3}(1-\alpha)^{n_3} \end{aligned} \quad (6)$$

where A , B and C are the fractions of three different reactions.

Figure 9

The calculations were performed as follows. First of all, the derivative of the overall extent of reaction curves $(d\alpha/dt)_{TOT}$ were separated in three different sub-reactions.

Each peak was integrated in time domain in order to obtain the extent of reaction of each single reaction and to evaluate the fraction coefficients A , B and C . The maximum degree of reaction of each sub-reaction was then normalized to 1 and equation (5) was applied. As an example, figure 9 reports the overall reaction rate predicted by the model as a sum of the three reaction rates, for the 10°C/min-dynamic test of neat polyester.

Table 5 reports all the calculated parameters. As it is possible to observe, the overall reaction rates $(m+n)$ for the three separated peaks in all the different systems do not significantly vary, confirming the effectiveness of the approach of a linear combination of the chosen kinetic equation. With respect to the k values, we should analyze the three systems separately: it is clearly visible that the most important reaction, that is the first

one in all the systems (fraction A is the highest), representing the copolymerization of the styrene with the polyester monomer, is also the reaction with the highest constant rate. This indicates that this reaction is the most thermally favoured. If we observe how the k_i values vary from the neat system to the CNF charged systems, we note that the value for the second peak increases when increasing the CNF content in filled systems, indicating that the styrene homopolymerization reaction becomes more relevant. Regarding the third peak, assigned to the polyester homopolymerization, we can assert that no clear tendency for the importance of the reaction was detected from dynamic DSC tests.

It should be noticed that, since the curing process of a polyester resin is represented by several competing reactions with very different kinetics and activation energies, when the processing conditions change (as in the case of isothermal and dynamic processes) also the contribution of the individual reactions changes, leading to completely different reactions paths. For this reason it is highly difficult that the same kinetic equation and parameters can fit the experimental data collected. Then, the best possible approach is to have the same equation with different parameters that are able to describe the reaction in isothermal conditions (at different temperatures) and in dynamic conditions (at different heating rates).

3.2 Chemorheology

As already stated, the curing process was also investigated by monitoring the viscoelastic behaviour of the liquid reactive system during the chemical reaction, i.e. using rheological measurements. In fact, in this way it is possible to observe the temperature at which viscosity starts to grow, which means that the hardening stage has begun and to check how fast this stage takes place. In this case, both dynamic and isothermal tests were also performed under the same condition as the DSC tests. Basically, viscosity in temperature and time domains were plotted and analyzed. The

plot of $\tan\delta$ as a function of time during isothermal tests was exploited to estimate the gel time, calculated as the minimum peak of the curve [3]. As an example, figure 10 reports a typical plot of the results for the isothermal test. Table 6 reports the gel times for all the studied materials and temperatures. It is possible to observe that these data can be correlated with heat flow peaks in isothermal DSC analysis.

Table 5

3°C/min	Neat Polyester			0.5%CNFs			1%CNFs		
	A = 0.800; B = 0.061; C= 0.130			A = 0.756; B = 0.112; C = 0.117			A = 0.882; B = 0.040; C = 0.086		
	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak
k_i (*10 ⁻³)	5.16	0.62	0.33	4.12	0.96	0.34	3.39	0.18	0.45
m_i	0.77	0.74	0.79	0.77	0.74	0.79	0.77	0.78	0.72
n_i	0.86	0.89	0.82	0.86	0.89	0.84	0.85	0.81	0.92

5°C/min	Neat Polyester			0.5%CNFs			1%CNFs		
	A = 0.837; B = 0.110; C = 0.042			A = 0.858 B = 0.078; C = 0.069			A = 0.819; B = 0.072; C = 0.042		
	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak
k_i (*10 ⁻³)	7.15	1.11	0.28	6.07	0.82	0.22	5.81	1.24	0.18
m_i	0.78	0.77	0.78	0.78	0.76	0.77	0.79	0.75	0.76
n_i	0.85	0.86	0.83	0.85	0.87	0.77	0.84	0.88	0.73

10°C/min	Neat Polyester			0.5%CNFs			1%CNFs		
	A = 0.896; B = 0.097; C = 0.012			A = 0.868; B = 0.055; C = 0.086			A = 0.841; B = 0.069; C = 0.092		
	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak
k_i (*10 ⁻³)	11.13	2.39	0.28	9.74	2.42	1.09	9.88	3.53	1.25
m_i	0.79	0.76	0.76	0.79	0.70	0.78	0.78	0.68	0.78
n_i	0.84	0.87	0.85	0.85	0.93	0.84	0.85	0.95	0.85

Figure 10

Table 6

	Gel Times [min]			25°C	α_{gel} [-]	
	25°C	40°C	55°C		40°C	55°C
Neat Polyester	79.5 ± 4.0	20.1 ± 2.3	8.7 ± 0.7	0.23 ± 0.02	0.24 ± 0.03	0.26 ± 0.03
0.5% CNFs	88.1 ± 13.5	26.7 ± 4.8	11.2 ± 0.5	0.23 ± 0.03	0.23 ± 0.05	0.30 ± 0.07
1% CNFs	118.5 ± 12.5	39.2 ± 1.2	16.0 ± 3.9	0.22 ± 0.03	0.23 ± 0.04	0.32 ± 0.07

Figure 11 represents the trend of the viscosity in the temperature domain during the 5°C/min –dynamic scan for the three systems studied, whereas figure 12 shows the viscosity in the time domain during isothermal tests at 40°C. As already encountered in the DSC tests, it is possible to observe the same general delay in the reaction rate in the nanocomposites in comparison to the neat matrix, and, in particular, the higher the nanofiber content, the more the delay effect is pronounced. It should be noted that the level of scatter in the viscosity profiles before gelation is due to the fact that the torque values produced by the resin flow are below the sensibility of the transducer. Nonetheless, for the present study, the viscosity of the reactive system is relevant only close to the gel point.

Figure 11

Figure 12

The relationship between viscosity and the degree of reaction in the interval before the gel point during isothermal cure, was described by using the empirical model developed by Castro and Makosco [36] and previously adopted for UP matrices for fiber reinforced composites [3]:

$$\eta = K_{\eta} e^{\frac{E_{\eta}}{RT}} \left(\frac{\alpha_{gel}}{\alpha_{gel} - \alpha} \right)^{A+B\alpha} \quad (7)$$

where K_{η} is a pre-exponential factor, E_{η} is the activation energy A and B are constants and α_{gel} represents the extent of reaction at the gel point. This equation was successfully applied to our experimental data. Table 7 reports all the parameters and in figure 13 experimental and modelling results are well compared for the three systems studied for the isothermal cure at 40°C. Similarly, good results were obtained for all the temperatures analyzed. The A and B parameters are related to the rate of the variation of the viscosity as a consequence of the gelation. As a result of this modelling, it is possible to notice that they both decrease (B in modulus) when increasing the CNF content, giving further confirmation of the delay of the hardening process.

Table 7

	Cure Temperature							
	25°C		40°C		55°C			
	A	B	A	B	A	B	K [Pa-s]	E [KJ/mol]
Neat Polyester	7.0	-22.2	13.2	-44.0	10.6	-24.0	3.4 x 10 ⁻¹⁴	84.8
0.5% CNFs	4.8	-10.9	10.4	-35.8	9.3	-19.8	5.0 x 10 ⁻¹⁶	96.2
1% CNFs	3.9	-9.5	9.7	-33.8	8.2	-12.6	4.0 x 10 ⁻¹⁶	98.3

Figure 13

4 Conclusions

The cure kinetics of a CNF-filled UP resin was studied by means of thermal and chemorheological analyses. Both the DSC and rheology results have shown that the addition of carbon nanofibers to a UP resin produces a delay in the cure reaction, consisting of a shift in the exothermal reaction peak toward higher times and temperature in isothermal and dynamic tests, respectively. In rheological tests, the delay is clearly visible from the shift in the sharp increase in viscosity due to gelation.

However, the final degree of reaction of the UP resin is not affected by the presence of CNFs.

Phenomenological models that have already been effectively applied to UP resins for composite materials, were here utilized to successfully predict the thermal and rheological behaviour of the CNF-UP system. The kinetic parameters of the models

adopted, which were calculated from experimental data, confirmed that the reaction rate is delayed when CNFs are added to the system. This conclusion is supported by considering that the main effect of CNFs on the unsaturated polyester resin during the curing process is represented by the free radicals scavenging activity of the carbon-based fillers. So, untreated CNFs are capable of entrapping the free-radicals generated by the initiator through an interaction with their aromatic walls and taking advantage of the huge surface area offered by this interaction.

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Figure captions

Figure 1: Optical micrographs before curing (a) and after the gel point (b), TEM image (c) of 0.5%-CNF fully cured nanocomposite.

Figure 2 : Weight loss curves for isothermal curing at 25°C for the three systems.

Figure 3 : DSC thermogram of 10°C/min dynamic scans for the studied systems (a) and 0.5% CNFs system at different heating rates (b) .

Figure 4 : Isothermal DSC thermograms of different systems at T=40°C (a) and of 0.5%-CNFs at different temperatures (b) .

Figure 5: Degree of cure of the 0.5%-CNFs during dynamic scans at different scan rates (a) and mean values obtained for isothermal tests at different cure temperatures (b).

Figure 6: Fitting of the experimental final degree of reaction vs isothermal temperature

Figure 7: Comparison of experimental data and model for isothermal tests for the UP + 0.5% CNFs system.

Figure 8: Calculation of the apparent activation energies.

Figure 9: The calculated da/dt versus time curve (—) , and the experimental data (Δ).

The three simulated peaks are drawn too.

Figure 10: Typical rheological outcome, for a isothermal test at 25°C, of the neat resin.

Figure 11: Evolution of the viscosity during dynamic tests at 5°C/min for the neat polyester, the 0.5% and the 1% CNF nanocomposites.

Figure 12: Evolution of the viscosity during isothermal tests at 40°C for the neat polyester, 0.5% and 1% CNF nanocomposites.

Figure 13: Curves of relative viscosity versus time for the three studied systems: experimental data and model prediction.

Table captions

Table 1: Styrene content in all the systems analyzed, before and after the addition.

Table 2: DSC results for dynamic tests.

Table 3: DSC results for isothermal tests

Table 4: Kinetic parameter of isothermal cure.

Table 5: Kinetic parameters of dynamic tests.

Table 6: Gel times and degree of reaction at the gel point as calculated by rheological tests.

Table 7: Kinetic parameters of the rheological model.

Highlights

We study the effect of CNFs on the cure kinetics of unsaturated polyester resin.

A kinetic model was applied to DSC and rheological results.

A delaying effect on the cure was observed when CNFs are added to the matrix.

Scavenging activity of CNFs on the free radicals causes the delaying effect.

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Table 1: Styrene content in all the systems analyzed, before and after the addition.

Styrene content [%]		
Neat polyester	41.04 ± 0.55	
	<i>after mixing</i>	<i>after adding</i>
0.5% CNFs	36.58 ± 0.43	40.73 ± 0.36
1% CNFs	39.55 ± 0.07	40.68 ± 0.43

Table 2: DSC results for dynamic tests.

	ΔH_{dyn} [J/g]			T_{peak} [°C]		
	3°C/min	5°C/min	10°C/min	3°C/min	5°C/min	10°C/min
Neat Polyester	287.4 ± 8.4	269.3 ± 3.1	239.9 ± 1.6	68.7 ± 0.6	77.5 ± 1.0	93.3 ± 2.3
0.5% CNFs	273.1 ± 11.2	265.1 ± 15.4	233.9 ± 48.2	70.6 ± 4.8	86.9 ± 7.6	94.6 ± 6.9
1.0% CNFs	239.6 ± 4.4	225.5 ± 32.4	187.5 ± 14.5	86.9 ± 4.9	94.5 ± 2.6	103.8 ± 1.1

Table 3: DSC results for isothermal tests

	ΔH_{iso} [J/g]			α_{max} [-]		
	25°C	40°C	55°C	25°C	40°C	55°C
Neat Polyester	185.2 ± 18.5	196.2 ± 17.8	213.9 ± 4.7	0.66 ± 0.06	0.74 ± 0.06	0.90 ± 0.02
0.5% CNFs	172.0 ± 30.4	192.9 ± 11.0	205.6 ± 23.6	0.63 ± 0.10	0.75 ± 0.05	0.83 ± 0.13
1.0% CNFs	166.4 ± 4.6	179.0 ± 7.8	200.2 ± 31.9	0.69 ± 0.02	0.80 ± 0.11	0.92 ± 0.07
	t_{peak} [min]			t_{ind} [min]		
	25°C	40°C	55°C	25°C	40°C	55°C
Neat Polyester	72.2 ± 10.5	21.7 ± 10.7	9.9 ± 2.3	19.2 ± 1.5	8.3 ± 3.6	1.9 ± 0.2
0.5% CNFs	85.6 ± 24.5	28.4 ± 0.5	12.1 ± 4.9	46.7 ± 7.4	10.7 ± 0.8	2.5 ± 0.5
1.0% CNFs	112.9 ± 24.3	40.6 ± 9.5	16.4 ± 2.1	59.8 ± 22.0	14.7 ± 0.5	4.3 ± 1.6

Table 4: Kinetic parameter of isothermal cure.

	Neat Polyester			0.5% CNFs			1% CNFs		
	25°C	40°C	55°C	25°C	40°C	55°C	25°C	40°C	55°C
K (*10⁻³)	1.47	3.14	3.72	0.94	2.13	3.67	0.53	1.18	2.10
m	0.50	0.51	0.53	0.60	0.62	0.67	0.66	0.52	0.57
n	1.31	1.55	1.55	1.60	1.47	1.53	1.26	1.28	1.42
m + n	1.80	2.06	2.08	2.20	2.09	2.20	1.91	1.80	1.99

Table 5: Kinetic parameters of dynamic tests.

3°C/min	Neat Polyester			0.5%CNFs			1%CNFs		
	A = 0.800; B = 0.061; C = 0.130			A = 0.756; B = 0.112; C = 0.117			A = 0.882; B = 0.040; C = 0.086		
	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak
$k_i (*10^{-3})$	5.16	0.62	0.33	4.12	0.96	0.34	3.39	0.18	0.45
m_i	0.77	0.74	0.79	0.77	0.74	0.79	0.77	0.78	0.72
n_i	0.86	0.89	0.82	0.86	0.89	0.84	0.85	0.81	0.92

5°C/min	Neat Polyester			0.5%CNFs			1%CNFs		
	A = 0.837; B = 0.110; C = 0.042			A = 0.858 B = 0.078; C = 0.069			A = 0.819; B = 0.072; C = 0.042		
	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak
$k_i (*10^{-3})$	7.15	1.11	0.28	6.07	0.82	0.22	5.81	1.24	0.18
m_i	0.78	0.77	0.78	0.78	0.76	0.77	0.79	0.75	0.76
n_i	0.85	0.86	0.83	0.85	0.87	0.77	0.84	0.88	0.73

10°C/min	Neat Polyester			0.5%CNFs			1%CNFs		
	A = 0.896; B = 0.097; C = 0.012			A = 0.868; B = 0.055; C = 0.086			A = 0.841; B = 0.069; C = 0.092		
	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak	1 st Peak	2 nd Peak	3 rd Peak
$k_i (*10^{-3})$	11.13	2.39	0.28	9.74	2.42	1.09	9.88	3.53	1.25
m_i	0.79	0.76	0.76	0.79	0.70	0.78	0.78	0.68	0.78
n_i	0.84	0.87	0.85	0.85	0.93	0.84	0.85	0.95	0.85

Table 6: Gel times as calculated by rheological tests.

	Gel Times [min]			α_{gel} [-]		
	25°C	40°C	55°C	25°C	40°C	55°C
Neat Polyester	79.5 ± 4.0	20.1 ± 2.3	8.7 ± 0.7	0.23 ± 0.02	0.24 ± 0.03	0.26 ± 0.03
0.5% CNFs	88.1 ± 13.5	26.7 ± 4.8	11.2 ± 0.5	0.23 ± 0.03	0.23 ± 0.05	0.30 ± 0.07
1% CNFs	118.5 ± 12.5	39.2 ± 1.2	16.0 ± 3.9	0.22 ± 0.03	0.23 ± 0.04	0.32 ± 0.07

Tab. 7: Kinetic parameters of the rheological model.

	Cure Temperature							
	25°C		40°C		55°C			
	A	B	A	B	A	B	K [Pa-s]	E [KJ/mol]
Neat Polyester	7.0	-22.2	13.2	-44.0	10.6	-24.0	3.4×10^{-14}	84.8
0.5% CNFs	4.8	-10.9	10.4	-35.8	9.3	-19.8	5.0×10^{-16}	96.2
1% CNFs	3.9	-9.5	9.7	-33.8	8.2	-12.6	4.0×10^{-16}	98.3

Figure2

(a)

(b)

(a)

(b)

Figure6

Figure7

Figure8

Figure9

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Figure10

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Figure11

Figure12

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Figure13