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KINETIC STUDY OF THE CURE REACTION OF UNSATURATED POLYESTER RESINS

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The kinetics of the cure reaction of standard unsaturated polyester resin was investigated by utilizing the isothermal and dynamic techniques of differential scanning calorimetry (DSC). The kinetic parameters and heat of the copolymerization reaction were determined. A method is proposed for optimization of the curing and postcuring of a polyester resin composite.

Unsaturated polyester resins are currently the thermoset polymer family most commonly used as matrices for glass-fibre reinforced composites. This is due to the fact that they have good mechanical properties, convenient curing cycles and lower costs as compared with other thermoset resins available on the market. To optimize costs, the composite industry has to reduce the time of the production cycle compatibly with the high quality of the material that must be obtained.

In order to improve productivity and at the same time to cut down production costs, efforts are usually directed at reducing the time of the overall cure reaction. The choice of the curing cycle is arrived at in a rather empirical way on the basis of the reactivity curves supplied by the resin producers and of the existing know-how of the moulder.

The choice of the standard curing and postcuring cycle must be such as to have in time dimensionally large enough manufactured components; this fact is very important, for instance, in the case of components used as coachwork-panels that must be coupled with other structures. At the same time the degree of polymerization must be such as to confer mechanical properties on the manufactured components. Moreover, other properties, such as water absorption or monomer transfer have to be optimized. In our case, just as in the food industry, these properties are quite fundamental.

In this paper we propose a method to determine a priori the shortest curing and postcuring cycle such that the fixed requisites of composite manufactured components are still fully met.

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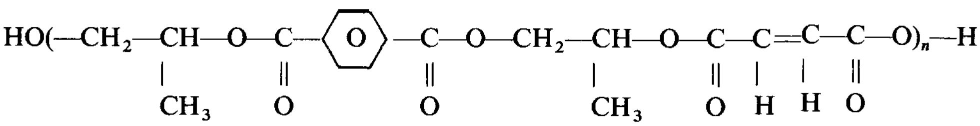
Experimental

Materials

The base polyester resin (Mn = 1250) used in the present work was prepared by using phthalic anhydride, maleic anhydride and propylene glycol in a mole ratio of 0.7 : 0.3 : 1.0. The acid number of the resin was maintained at around 40–45 for all the syntheses. The acid number is the number of miligrams of KOH used for titration of 1 g of resin. The molecular structure of the repeating unit of the base unsaturated polyester is as follows:



Styrene monomer was used as crosslinking agent. The styrene content was around 30–32% by weight. Two different catalyst systems were used:

1) 0.3% of cobalt octoate at 6% (w/w) in dibutyl phthalate and 1% of methyl ethyl ketone peroxide.

2) Benzoyl peroxide 1% (w/w).

The resins obtained with the first and second catalytic systems will be denoted samples *A* and *B*, respectively.

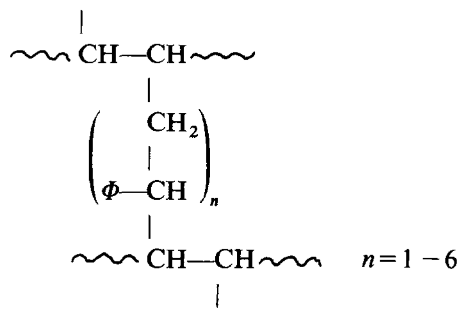
Calorimetric measurements

A Mettler TA–3000 apparatus, equipped with a control and programming unit (microprocessor TC10) and a calorimetric cell DSC–30 that allows temperature scans from $-170°$ to $600°$ was used to determine the heat related to the curing and postcuring processes and the kinetics of the overall reaction.

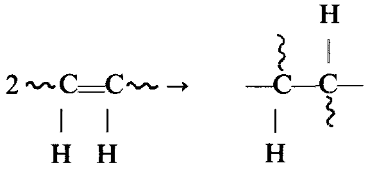
Results and discussion

The curing process of an unsaturated polyester resin is an exothermic free radical reaction characterized by the fact that a reactive diluent (styrene) is capable, in the presence of suitable catalysts, of acting as crosslinking agent by reacting with the unsaturated double bonds of the α, β acid residues present along the repeating unit of the polyester chains [1, 3]. The overall heat of the curing process is the resultant of the following reactions:

i) Propagation of the free radical crosslinking of the styrene monomer with active double bonds of the unsaturated polyester according to the following scheme:



ii) Homopolymerization of the maleic double bonds of the unsaturated polyester according to the following pathway:



iii) Decomposition of the peroxide initiator. If compared with these reactions, homopolymer formation from reactive diluent can be considered negligible. In fact, it is reported in the literature that even at high concentrations of styrene no polystyrene forms during curing [4, 5].

The heat related to reaction (iii) is also comparatively negligible. Thus, the heat generated during the cure reaction can reasonably be assumed proportional to the number of reactive double bonds present in the polyester.

The overall heat of reaction (Q_T) determined from the areas of the DSC exothermic peaks obtained by heating the reaction mixture from 20° to 230° (see Fig. 1) is 350 J/g for sample *A*.

No residual heat is generated during a second heating cycle. The exotherm of reaction shows to peaks, probably related to the crosslink process and to homopolymerization of the maleic double bonds (first and second peak, respectively).

Two similar peaks have been found by Malescot and Jasse [6] in the case of polyesteramides.

The total heat of cure Q_T as a function of the scan rate (v_s), is reported in Table 1 for sample *A*. From the data in Table 1 it emerges that the total heat of cure slightly increases with v_s.

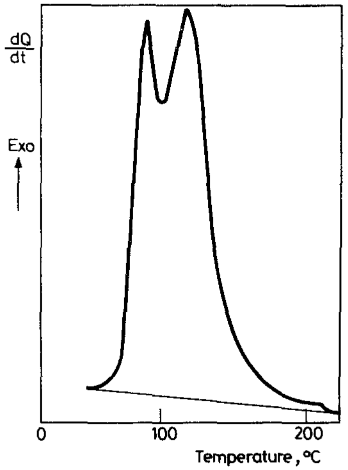


Fig. 1 Experimental curve of curing reaction obtained in dynamic scan from 25°C to 230°C for sample *A*

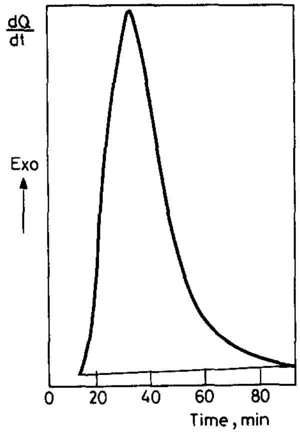


Fig. 2 Experimental curve of curing reaction obtained in an isothermal scan (T = 25°C) for sample *A*

Table 1

V_s, deg/min	Q_T, J/g
5	320
10	313
15	330
20	350
30	357

Table 2

Sample	T, °C	Q_P^T, J/g	Q_R, J/g	$Q_T = Q_P^T + Q_R$, J/g
A	25	188	160	~350
	40	260	90	
B	80	175	125	300
	90	200	100	

These findings are consistent with those reported by several investigators [2, 7, 8]. The amount of heat generated when the process of cure is performed isothermally at 25° ($Q_p^{25^\circ}$) (see Fig. 2) is 188 J/g for sample *A*, indicating that under such conditions the system undergoes a partial curing process. As shown in Table 2, the heat generated during an isothermal process of curing (Q_P^T) increases with the temperature (at 40° Q_P^T rises to 260 J/g for sample A). It should be pointed out that Q_T cannot be measured in a single isothermal run. This behaviour can be attributed to the reaction that becomes highly diffusion-controlled at advanced stages of cure and a very long time is required to reach completion under isothermal conditions [7]. Sample B present the same behaviour, for in this case the benzoyl peroxide is active at a higher temperature (Q_P^T = 175 J/g at 80° and 200 J/g at 90°).

The residual heat of the isothermal cure process (Q_R) is determined from the area of the DSC exotherm of reaction obtained by heating the sample from isothermal temperature to 230°.

As shown in Table 2, Q_R decreases with the increase of the isothermal temperature at which the isothermal process occurs; nevertheless, the total heat $Q_T = Q_P^T + Q_R$ seems to be constant for a given reacting system (Q_T = 350 J/g for sample A and 300 J/g for sample B). These results suggest that the value of Q_T is not influenced by the thermal history of the curing mixture.

Assuming that the curing reaction follows kinetics of n-th order and that the temperature-dependence of the kinetic rate constant k is consistent with the Arrhenius law, then for a given temperature the following equations may be written:

$$\alpha = \frac{d\alpha}{dt} = k(1-\alpha)^n \tag{1}$$

$$k = k_{\infty} \exp(-Ea/RT) \tag{2}$$

where α is the degree of the cure reaction, $\dot{\alpha}$ is the rate of reaction, n is the order of the reaction, k_∞ is the kinetic constant at $T = \infty$, Ea is the activation energy and R is the gas constant.

By combining Eqs (1) and (2), Eq. (3) is obtained:

$$\dot{\alpha} = k_\infty \exp(-Ea/RT)(1-\alpha)^n \tag{3}$$

The degree of conversion at constant T as a function of time may easily be calculated from the DSC exotherm, as shown in Fig. 3. The DSC exotherm, obtained in a thermal scan, allows the determination of the two basic parameters required to solve Eqs (1) and (2). First, the reaction rate $\dot{\alpha}$ is obtained by determining the ratio between the peak height at time t and the overall peak area at temperature T. Secondly, the degree of conversion α at time t is easily obtained from the ratio between the partial area ΔH_t and the total area ΔH_{tot} at temperature T.

If we know $\dot{\alpha}$ and α, then it is possible, by means of Eq. (1), to obtain k for any given temperature. By plotting ln k against $1/T$, the activation energy of the overall

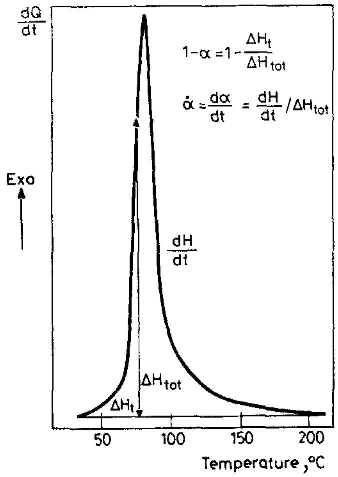
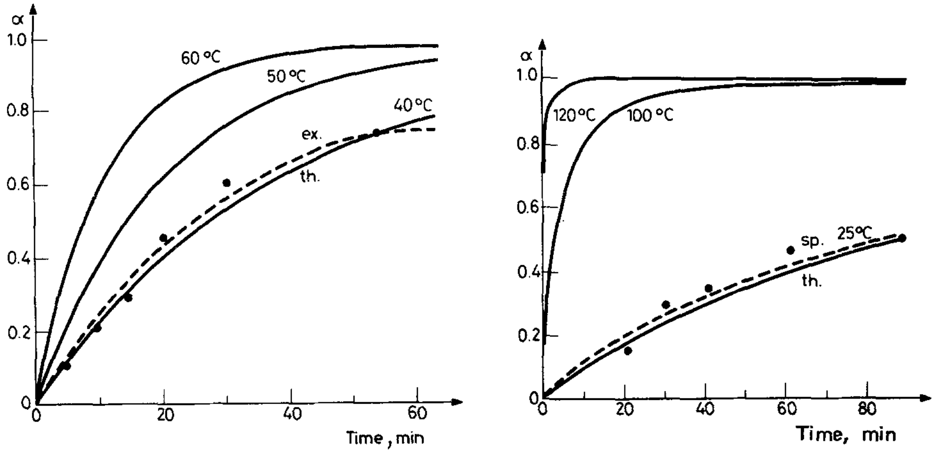


Fig. 3 Example of curing reaction exotherm for a standard polyester resin



Figs. 4–5. Reaction conversion curves *vs.* time at different temperatures

cure process may be obtained together with k_∞ and n. From the known values of k_∞, Ea and n for every temperature, a theoretical curve of α *vs.* time can be drawn.

Table 3 gives the values of the kinetic parameters found for samples *A* and *B* by using the proposed kinetic model of Eq. (3). Moreover, the values of α calculated as a function time, relative to sample *A* for several temperatures, are shown in Figs 4 and 5.

The same figures also give the α curves obtained by means of experimental isothermal DSC (dashed lines) for two temperatures (25° and 40°); the comparison shows a fairly good agreement between the trends of the experimental and theoretical curves. Thus, the curing and postcuring cycles for the polyester resin composite can be optimized by simply applying the theory, once the minimum reaction conversion degree has been defined.

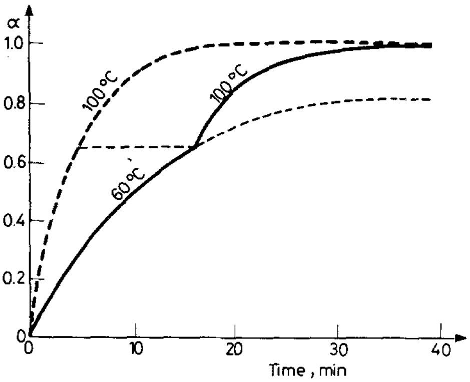


Fig. 6 Example of application of the method of graphic presentation of expected time of curing and postcuring with given temperature

Table 3

Sample	QT, J/g	Ea, kJ/mol	$\ln k_\infty$	n
A	350	50.6	11.6	1.5
B	300	118.7	33.5	1.7

Figure 6 shows an example of the use of *vs.* time curves for a typical polyester resin. In this case we wanted to determine the minimum curing and postcuring cycle of polyester resin which is to be moulded at 60° and postcured at 100°.

We knew that the maximum reaction degree for the manipulation and for drawing the material from the mould is $\alpha = 0.65$ and that the final reaction degree must be 0.99.

In Fig. 6 the plot of α as a function of time t is constructed for the above-described thermal history, using the isothermal curve at 60° up to $\alpha = 0.65$ and shifting along the abscissa the isothermal curve at 100° from point $\alpha = 0.65$ up to $\alpha = 0.99$.

In other words, 16 minutes after the beginning of the reaction, the resin attains a value of $\alpha = 0.65$. At this point let us suppose that the temperature is brought to 100°. 39 minutes after the beginning of the reaction, the resin attains a polymerization degree of 99% and thus we can assert that the composite is sufficiently cured.

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Zusammenfassung — Die Kinetik der Aushärtung eines ungesättigten Standardpolyesterharzes wurde mittels isothermer und dynamischer DSC untersucht. Kinetische Parameter und die Reaktionswärmen der Kopolymerisation wurden bestimmt. Eine Methode zur Optimierung der Aushärtung und Nachhärtung von Polyesterharzverbundstoffen wird vorgeschlagen.

Резюме — С помощью изотермической и динамической дифференциальной сканирующей калориметрии исследована кинетика реакции вулканизации стандартной ненасыщенной полиэфирной резины. Определены теплоты и кинетические параметры реакции кополимеризации. Предложен оптимальный метод отверждения и последующей вулканизации полиэфирной резиновой смеси.