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Unsaturated Polyester Resin: Kinetics of the Cross-Linking Reaction by Pulsed NMR

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Summary

Pulsed NMR at 20 MHz has been used to monitor the time course of the intermediate-final stage of the radical crosslinking reaction (cure of unsaturated polyester-styrene resins.) The measurement of Spin lattice relaxation time T_1 allowed us to follow the hardening process having as a parameter the loss of general mobility of the system at the molecular level.

The degree of cure as a function of time, the kinetic constant as well as the activation energy for the crosslinking reaction in isothermal conditions has been evaluated using the semiempirical kinetic equation proposed by Kamal and coworkers. The activation energy was estimated to be 13.6 Kcal per mole of double bonds in the components.

Introduction

Polyester resins of widespread technologycal applications are commonly prepared by mixing unsaturated polyesters and styrene in weight ratios to ensure a nearly complete reaction of polyester double bonds when the resin is crosslinked by means of radical processes (cure).

Typical polyesters are prepared by polycondensation of maleic and phtalic anhydrides and glycols. The polymers, thus obtained, contain fumarate residues, due to the occurrence of the cis-trans isomerization of the maleic residues. The latters finally can react with the added styrene monomer via a radical reaction, through which styrene units and/or styrene bridges link different polyester chains in various parts, thus giving rise to a three dimensional network.

In our laboratory the Spin-Lattice relaxation time T_1, (SLICHTER, 1980) of the time course of the curing process was measured in isothermal conditions at 20 MHz.

In fact pulsed NMR has been proven to be a useful technique in the recent past (LARSEN AND STRANGE, 1973 a, b, c) to characterize and to monitor the cure reaction of different type of resins.

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The results of these studies of the cure process suggest that pulsed NMR of the cure of unsaturated polyester resins would be informative, since it would enable to follow the loss of the mobility of the system during the hardening process due to the formation of a three dimensional network.

Particularly in the NMR experiments the size of the samples (1.0 cm Ø) is much more similar to that used in technologycal applications than with other techniques.

Moreover the time scale of samples preparation and of the NMR measurements causes a loss of experimental observations immediately after the mixing, however, the pulsed NMR technique gives the possibility to follow the kinetic of the process in its intermediate-final part.

Experimental

The resin under study is composed by an unsaturated polyester obtained by polycondensation from maleic-anhydryde (AM), phtalic anhydryde (AP) and propylene glycol (PG) in a molar ratio AM: AP: PG = 0.3:0.7:1.0 and Styrene 28% w/w.

MethylEtylKetonePeroxide as initiator (0.5% w/w) and Cobalt Octoate (0.05% w/w) as promoter were used.

Approximately 100 g of resin was initiated in a glass beker stirring vigorously for about 30 sec. An amount was transferred into a 10 mm tube (Ø ext) for the NMR measurements.

T_1 relaxation time was measured by the 180°-τ-90° pulse sequence with a waiting time of 10 sec as an average of ten sequences on a Bruker Minispec P-20 Instrument operating at 20 MHz. Magnetization was sampled by a window after 6-7 µsec after the second (90°) pulse in the PSD mode.

Temperature was held constant (±1°C) by a large flow of thermostatting liquid in the probe.

Measurements were performed every 15 minutes for 1 hour and every 30 minutes for 8-9 hours. The ultimate values were obtained after 24 hours from the initiation.

Results and Discussion

A plot of $\ln (M_\infty - M_\tau)$ vs. τ is reported in Fig. 1 at different elapsed time from the initiation of the radical reaction.

The plot shows a biexponential behaviour due to the presence in the sample of both a fast and a slow relaxing component.

The former disappears as the cure reaction proceeds. This suggests that there are separate behaviours of the protons of the sample from a mobility point of view. During the cure reaction the slow relaxing component changes its T_1 with time.

As expected T_1 reaches a minimum value and, after, increases asymptotically to a limiting value. This behaviour is strongly influenced by the temperature. The T_1 values observed as a function of time at different temperatures are reported in Fig. 2.

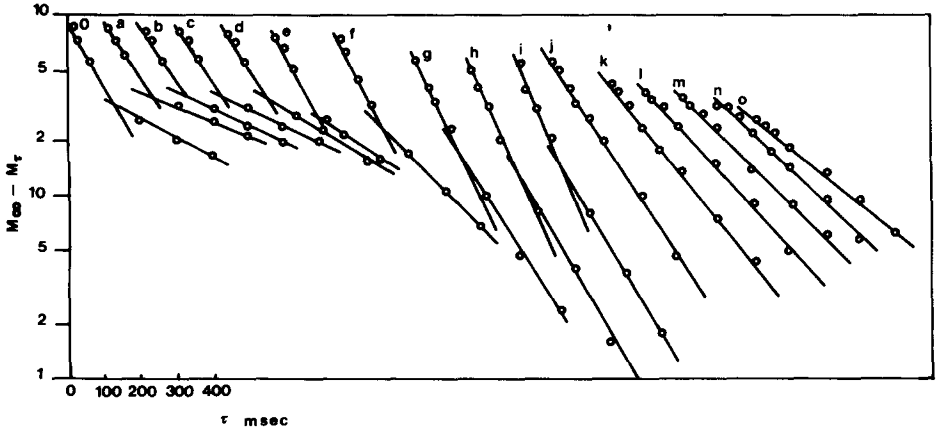

Fig. 1 - Longitudinal magnetization decay plot as a function of τ time in the 180°-τ-90° pulse sequence. Letters indicate different times of the cure reaction after initiation: 0)=t=o, a)t=15', b)t=30', c)t=45', d)t=1h, e)t=1.5h, f)t=2.0h, g)t=2.5h, i)t=3.0h, j)t=4.0h, k)t=5.0h, l)t=6.0h, m)t=7.0h, n)t=8.0h, o)t=24.0h. The values are reported only for the curve for t=0.

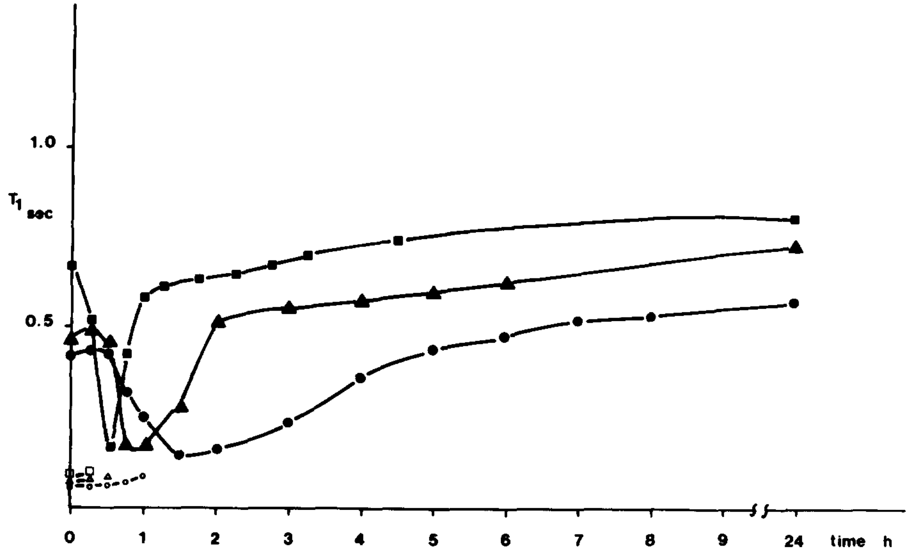

Fig. 2 - Spin-Lattice relaxation time T_1 during the cure reaction of the unsaturated polyester resin at 41, 51 and 64°C (●, ▲, ■ respectively). Open symbols refer to the fast relaxing component.

The T_1 variation with time should be attributed to the decrease of the general molecular mobility associated with the formation of the three dimensional network built up by the crosslinking reaction.

The result is noteworthy interesting because it describes the kinetic in the intermediate-final part of the process. Furthermore the observed quantity is the loss of general mobility, particularly important in such a system where a hardening occurs due to the crosslinking reaction.

Using the well-known dependence of the T_1 value on the correlation frequency of the molecular motion (BLOEMBERGEN et al., 1948, KUBO AND TOMITA, 1954) the frequency ν_C of the motions in the resin can be obtained during the time course of the radical process as reported in Fig. 3.

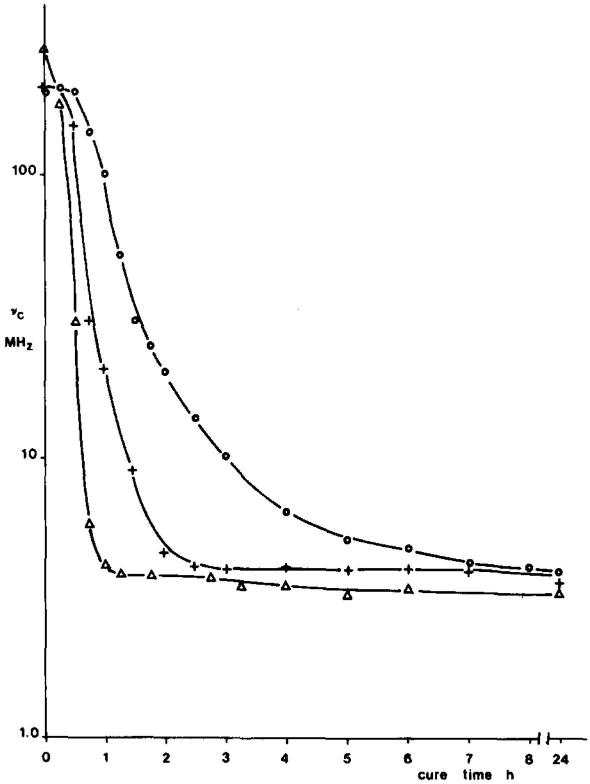

Fig. 3 - Correlation frequency ν_C of the general molecular motions obtained from the T_1 relaxation time of the slow relaxing component of Fig. 1 as a function of the cure time. Temperature 41(o), 51(+), 64(Δ)°C.

The ratio between the frequency of general molecular motions at time t and the final limiting value can be considered as a fractional loss of mobility representative of the degree of cure, α , during time. The values obtained are reported in Fig. 4.

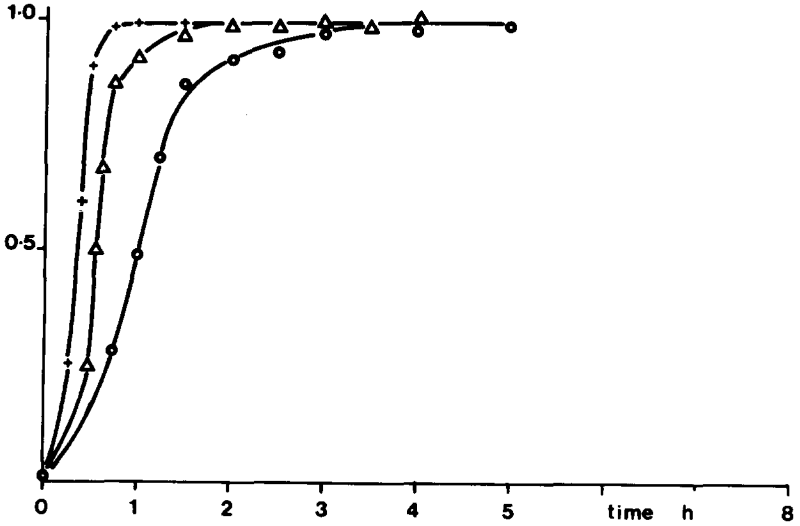

Fig. 4 - Fractional loss of mobility, α, during the cure reaction of the resin. Temperature °C 41(o), 51(Δ), 64(+).

The semiempirical kinetic expression for the autocatalytic isothermal cure process proposed by KAMAL et al. (1973 a, b) was proved to be in good agreement in such systems (PUSATCIOGLU et al., 1979):

$$(d\alpha/dt) = (K_1 + K_2\alpha^m)(1 - \alpha)^n .$$

Assuming that K_1 is very close to zero as found in several cases (CHANG DAE HAN and KWOK WAI LEM, 1983) the slope of α at $\alpha = 0.5$ can give directly the K_2 value:

$$(d\alpha/dt)_{\alpha=0.5} = K_2\ (0.5)^{m+n}$$

where m+n is generally assumed equal to 2 for the second order cure reaction.

Thus the kinetic constant for the crosslinking reaction can be obtained. The values are reported in Table I for the different temperatures.

TABLE I

Kinetic constants K_2 for the cure process of unsaturated polyester resin.

T°C	K_2 min^{-1} mol^{-1}
41	0.138
51	0.340
64	0.610

The activation energy obtained by the Arrhenius plot, shown in Fig. 5, resulted to be 13.6 ± 0.5 Kcal per mole of double bonds in the resin in the our experimental conditions.

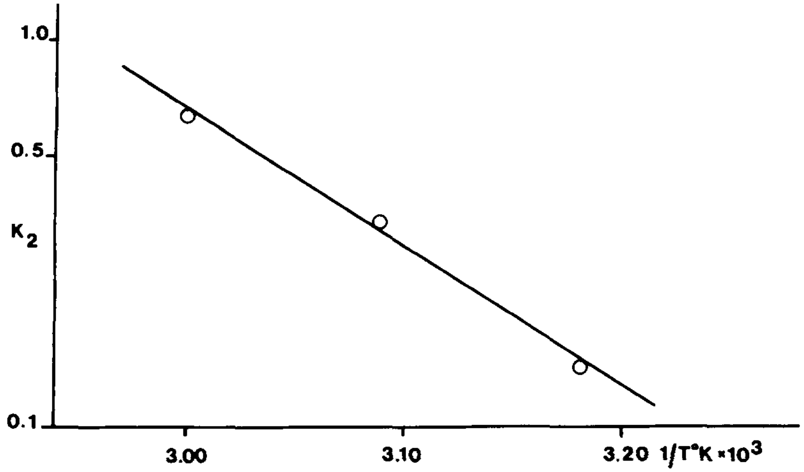

Fig. 5 - Arrhenius plot of the kinetic constant to evaluate the activation energy of the intermediate ultimate process of the cure reaction.

In conclusion pulsed NMR can be considered a valuable technique to characterize and study in detail the kinetic of crosslinking in such kind of resins. Further studied are in progress in order to investigate the effects on the kinetic constants and on the apparent activation energy of various additives like promoters, low profile agent and so on as well as of the presence of fillers and reinforcing agents.

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