INFLUENCE OF FUNCTIONAL RUBBERS ON THE CURING PROCESS OF UNSATURATED POLYESTER RESINS

M. Avella, E. Martuscelli and M. G. Volpe

ISTITUTO DI RICERCHE SU TECNOLOGIA DEI POLIMERI E REOLOGIA DEL C.N.R. VIA TOIANO 6,800 72 ARCO FELICE, NAPOLI, ITALY

The influence of an elastomeric second-phase on the kinetics of the curing reaction and the gel-time of a standard unsaturated polyester resin, by using the isothermal and dynamic techniques of differential scanning calorimetry (DSC) and a thermocouple was investigated. In particular we examined two different rubbers (polybutadiene hydroxyl-terminated and polybutadiene isocyanate-terminated), that, in the presence of polyester resins, affect the overall curing reaction kinetics in two ways: the former reduces the rate of reaction whilst the latter increases it.

Unsaturated polyester resins, formed by a free radical reaction of an \( \alpha, \beta \) unsaturated acid in a polyester with a vinyl monomer, show poor properties when toughness and high impact strength are required [1].

It is known that the impact resistance of such resins can be improved by incorporating inclusions of liquid reactive rubbers in the resins [2]. These rubbers must be mixed with the base resin before the curing process and then made to precipitate in a second phase, during the cure, from the solution to give the rigid matrix the desired toughening action [3].

Of course, it is very important to know the influence of the rubber phase on the curing process of the polyester resins.

The cure of thermoset resins, in general, is the overall transformation from liquid to gel, to rubber, to glass that occurs as a result of a reaction of curing which produces a measurable exothermic effect [4, 5].

In this paper the results of studies on the curing kinetics and the gelation time of rubber-modified polyester resins are reported. In particular two sets of blends were investigated, consisting of the same unsaturated polyester matrix and two elastomers having the following terminal functional groups:

i) low molecular weight hydroxyl terminated polybutadiene;
ii) low molecular weight isocyanate terminated polybutadiene.

The two different terminal groups of the elastomer interact with the matrix in
different ways: the hydroxyl terminal groups do not react chemically with the functional groups present in the polyester, whereas the isocyanate terminal groups react with the terminal groups of the polyester matrix, in the usual temperature range used for the curing process. This different reactivity of the terminal groups of polybutadiene with the matrix strongly influences the kinetic parameter and the gel-time of the base resin.

Experimental

Materials

The uncured unsaturated starting polyester resin (code: PER), supplied by SNIAL-Colleferro-Roma, is constituted by a solution containing about 68% of a polyester prepolymer dissolved in a solution of a styrene monomer. The prepolymer is formed by the reaction of a mixture of phthalic and maleic anhydride with a saturated glycol, propylene glycol (mole ratios 0.7 : 0.3 : 1). The molecular structure of such a prepolymer may be schematically represented as follows:

\[
\begin{align*}
\text{HO} & \quad \Phi \quad \text{Cl} \quad \text{O} \quad \text{CH} \quad \text{CH}_2 \quad \text{O} \quad \text{C} \quad \Phi \quad \text{C} \\
\mid & \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \\
\text{O} & \quad \text{O} \quad \text{CH}_3 & \quad \text{O} & \quad \text{O} \\
\text{O} & \quad \text{CH} \quad \text{CH}_2 \quad \text{O} \quad \text{C} \quad \text{CH} = \text{CH} \quad \text{C} \quad \text{H}_n \quad \text{O} \quad \text{CHCH}_2 \quad \text{OH} \\
\mid & \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \quad \mid \\
\text{CH}_3 & \quad \mid \quad \text{O} & \quad \text{O} & \quad \text{CH}_3 \\
\end{align*}
\]

\(\Phi = \text{phenyl ring}\)

The acid number of the prepolymer was maintained around 40 ± 45 (this value represents the milligrams of KOH used for the titration of 1 g of resin). Methyl ethyl ketone peroxide (Butanox, 1 wt%) and Co-octoate (0.25 wt%) were used as catalyst and accelerator respectively (the first is available as 50 wt% solution in dimethyl-phthalate while the second was already present in the starting formulation, as naphthenate solution).

Hydroxyl terminated polybutadiene (HTPB) \(\text{Mn} = 1350\), supplied by Polysciences, was used as starting rubber. The molecular structure of HTPB was determined by analyzing the 270 \text{MHz} \text{^1H}–\text{NMR} \text{ spectrum in CDCl}_3 \text{ solution, using TMS as the internal standard. It was found that about 70% of the units are arranged in a 1.2 enchainment and 30% in a 1.4 cis/trans enchainment. The hydroxyl number was determined by the following procedure: first the hydroxyl end groups were quantitatively converted into isocyanate end groups, then an}