



Vinyl ester resin modified with silicone-based additives: III. Curing kinetics

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ABSTRACT

Silicone-based additives have been used as fire retardants for thermoplastics with the advantage of improving the processing and the impact resistance of the polymers. In this work the influence of these additives on the curing kinetics of a vinyl ester resin was studied. Three silicone-based additives were used to modify the properties of the vinyl ester resin. The principal differences between them are the functional groups inserted in the polydimethylsiloxane chains. The additives were dispersed in the resin containing a commonly used mixture of initiator and catalyst methylethylKetone peroxide and cobalt-II octanoate, respectively. For some reactional mixtures *N,N*-dimethylaniline (DMA) was used as promoter. Differential scanning calorimetry (DSC) was used to perform the non-isothermal cure of the non-modified resin and of the resins modified with the additives. Ozawa's, Kissinger's and Ozawa's isothermal methods were used to determine the kinetic parameters. For resin cured in absence of DMA the silicone-based additives act as retardants for the curing reaction, a typical diluent effect, while in presence of this promoter the reaction enthalpy as well as the reaction rate were improved. This effect was attributed to specific interactions and reactions between DMA and the silicone-based additives that changed the curing mechanism as well as controlled the phase segregation.

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1. Introduction

Vinyl ester resins are oligomers resulting from the reaction between bisphenol-A based epoxy oligomers and unsaturated carboxylic acids, such as acrylic or methacrylic acid, which provide unsaturated terminal sites [1–6]. The viscosity of the resulting product is controlled by the molar mass of the vinyl ester resin as well as the amount of styrene [7].

Vinyl ester resins can be converted to a crosslinked network through highly exothermic free-radical copolymerization between vinyl groups of styrene or another monomer and the end acrylic or methacrylic groups of the resin. The copolymerization as well as the extension of phase segregation are influenced by reaction conditions, such as temperature and concentration of the monomers and initiators, and determine the mechanical properties

and morphology of the cured products [1,8–13]. The curing conditions must be selected in order to result in a product with appropriate properties and also to provide appropriate economic value.

In order to guarantee a complete cure a proper balance among initiator, catalyst and promoter must be maintained [3]. Post-cure temperature and time also play important roles in controlling the properties of the cured resins. Generally, temperature is the most important factor determining the extent of the conversion, rather than the time of post-cure. Moreover, post-cure is often avoided by manufactures because of cost factors and since facilities are not available to post-cure above 80 °C. Since the monomer and initiator concentrations are established prior to curing, the curing reaction is more readily controlled by means of adjusting the curing time and temperature [1].

The curing process of unsaturated polyester resins presents an induction period followed by polymerization which may involve the initial formation of microgels due to the inherently spatially heterogeneous nature of free radical polymerization. Microgels have been defined as

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domains of high crosslinking density dispersed in an unreacted mixture of monomers and oligomers. The crosslinking density of such microgels does not contribute to the global network structure until they are incorporated into the gel phase. The formation of microgels is followed by their growth, coagulation into clusters and linking of the clusters to form the final morphology of the cured resin. The existence of microgels suggests that monomers are not consumed homogeneously throughout the resin [7].

Curing kinetics may be followed using several methods. Differential scanning calorimetry (DSC) is one of the most convenient methods to follow the kinetics of reactions. Vinyl ester resins react exothermally with monomers and the heat of reaction can be monitored as a function of time or temperature. Whether the experiments will be conducted in isothermal or under non-isothermal conditions depends on the characteristics of the reactions and the sensitivity of the technique and equipment used. In general, if isothermal methods are used it is impossible to work at very high temperatures since a fraction of the heat of reaction is lost during the stabilization time at the required temperature. At very low temperatures some of the heat is likewise lost, since it is below the sensitivity threshold of the appliance. Non-isothermal methods do not usually present these problems, but in some instances they are not equivalent to isothermal ones. The kinetic parameters can vary greatly according to the method used. The activation energy can not only vary with the method used to determine it but also with the degree of conversion, which indicates that no single kinetic model can be used for the whole of the curing process [14].

In general, the methods used to describe the kinetics of a process are based on measurement of the rate at which heat is generated or absorbed in an exothermic or an endothermic chemical reaction, respectively. More specifically stated, with the assumption that the heat generated by a chemical reaction is proportional to the extent of reaction or conversion, the kinetic parameters can be determined from the endothermic or exothermic peaks obtained from either isothermal or non-isothermal measurements [15]. A review of the methods used for kinetic studies of thermoset curing reactions has been presented by Yosefi et al. [16].

Ozawa introduced a method for estimating the kinetic parameters from non-isothermal measurements. This method assumes that the extent of reaction at the maximum of the exothermic peak in the DSC curves is constant and independent of the heating rate. The Ozawa method provides the activation energy, and it does not require any information about the curing mechanism [17].

The rate law for an isothermal cure is

$$\frac{d\alpha}{dt} = kf(\alpha) \quad (1)$$

where t is the time, α is the extent of conversion, k is the Arrhenius rate constant and $f(\alpha)$ is a function dependent on the conversion.

For non-isothermal experiments the expression $d\alpha/dt$ can also be written as

$$\frac{d\alpha}{dt} = \beta \left(\frac{d\alpha}{dT} \right) \quad (2)$$

where β is the heating rate used in the DSC experiments.

The combination of the Arrhenius equation [$k = k_0 \exp(-\frac{E_a}{RT})$] with Eq. (1) gives

$$\frac{d\alpha}{dt} = \left[k_0 \exp\left(-\frac{E_a}{RT}\right) \right] f(\alpha) \quad (3)$$

where k_0 is the frequency factor and E_a is the activation energy.

Combining Eqs. (2) and (3) the Eq. (4) can be obtained:

$$\beta \left(\frac{d\alpha}{dT} \right) = \left[k_0 \exp\left(-\frac{E_a}{RT}\right) \right] f(\alpha) \quad (4)$$

Rearranging and integrating Eq. (4),

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (5)$$

Applying Doyle's approximation at constant conversion, the Eq. (5) becomes

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{k_0}{\beta} \left(\frac{E_a}{R} \right) P\left(\frac{E_a}{RT} \right) \quad (6)$$

where $P(E_a/RT)$ is a function defined by Doyle.

Doyle's function is given by the equation:

$$\log P\left(\frac{E_a}{RT} \right) = -0.4567 \frac{E_a}{RT} - 2.315 \quad (7)$$

Applying the logarithm to Eq. (6) and combining with Eq. (7):

$$\log \beta = \log \left(\frac{k_0 E_a}{v(\alpha) R} \right) - 2.315 - 0.4567 \frac{E_a}{RT} \quad (8)$$

where $v(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$ = constant.

Eq. (8) is a linear relation between $\log \beta$ and the reciprocal of the temperature. The Ozawa method consists in determining the activation energy (E_a) and the constant ($\log k_0 E_a / v(\alpha) R$) from the slope and intercept of the $\log \beta$ versus $1/T$ curve, respectively, where T is the temperature corresponding to the maximum of the exothermic peak (T_{\max}) obtained at different heating rate.

Eq. (8) can be written as

$$\log \beta = k_0 - 0.4567 \frac{E_a}{RT} \quad (9)$$

where

$$k'_0 = \log \left(\frac{k_0 E_a}{v(\alpha) R} \right) - 2.315 \quad (10)$$

Kissinger [18] derived a useful expression for the frequency factor for n -th order reactions:

$$k'_0 = \frac{\beta \cdot E_a \exp\left(-\frac{E_a}{RT_{\max}}\right)}{RT_{\max}^2} \quad (11)$$

where T_{\max} is the temperature corresponding to the maximum of the DSC peak. This expression is true by definition for first-order reactions and reasonable to describe the n -th order epoxy curing reactions [19].

According to the literature [14], isoconversional methods give more consistent results than those obtained by other methods, since these results reveal changes in the

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