Determination of a Kinetic Model for the Polyaddition of Bisphenol A with an Epoxide Liquid Resin

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Abstract: Solid epoxy resins are produced at Vantico SA by catalyzed reactions of a low-molecular weight liquid resin (RBL) with bisphenol A (BPA). These reactions lead to solid epoxy resins, which are used in surface coatings or adhesives. The chain lengthening step (advancement reaction) is based on the reaction of the epoxy functional group with the phenolic hydroxyl group leading to the formation of a secondary hydroxyl group. These secondary hydroxyl groups can also react with epoxy groups to form branched molecules. This paper presents a kinetic model describing the transformation of BPA with a RBL up to complete conversion of BPA. The polymerization kinetics is investigated by isothermal measurements for temperatures between 180 and 210°C and for different initial concentrations of BPA. A reaction scheme describing both the advancement and the branching reactions has been developed. For modeling the branching rate, a detailed diffusional and semi-empirical model has been adapted and modified in order to fit the experimental results.

Keywords: Advancement reaction · Branching reaction · Epoxy resin · Kinetic model · Polyaddition reactions

1. Introduction

Epoxy resins are characterized by a three-membered ring known as the epoxy group. The capability of this ring to react with a variety of substrates imparts versatility to the resins. Epoxy resins were first offered commercially in 1946 and are used in protective coatings, constructions and adhesives for the most part. High chemical corrosion resistance, good mechanical and thermal properties, flexibility are some of the characteristics of these materials [1][2].

One of the methods for the synthesis of high molecular weight polyhydroxy ethers based on bisphenol A (BPA) is the base catalyzed polyaddition of an epoxy liquid resin (RBL) with bisphenol A in the melt (Scheme 1). Conventional solid epoxy resi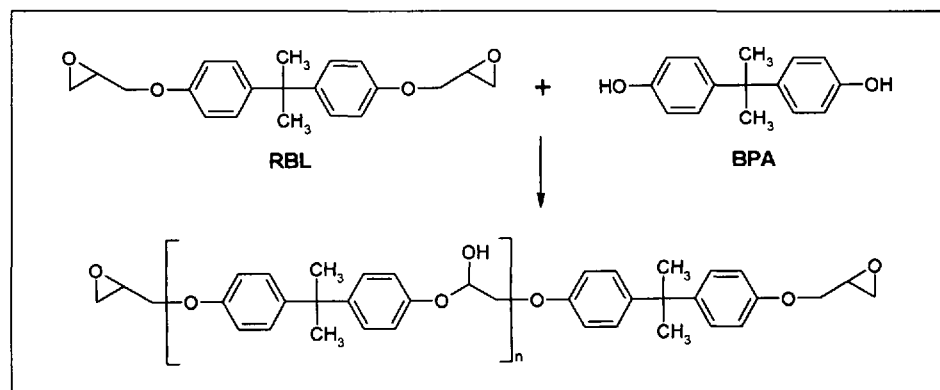ns are usually prepared with an excess of RBL and have n < 20 [3]. Different initial molar ratios of RBL and BPA characterize the type of the solid epoxy resins and thus the final viscosity of the melt. The lower is the molar ratio the higher is the melt viscosity. The product quality depends on the final concentration in epoxy and on the melt viscosity.

The peculiar feature of this polyaddition reaction is the possibility of further addition of an epoxy to a secondary hydroxyl group to form branched molecules (Scheme 2). The extent of the branching reaction is catalyst and temperature dependent [4].

2. Experimental

2.1. *Sample Preparation*

From a number of kinetic runs with different conditions of temperature, catalyst concentration and initial molar ratios between epoxy and phenolic groups, pure monomer Dgeba (diglycidyl ether of bisphenol A) has been used. The isothermal kinetic studies of polyaddition were carried out in a Mettler RC1 colorimeter at 180, 190, 200 and 210°C. The molar ratio R has been varied from 2.04, 1.57, 1.42 and 1.22 respectively corresponding to

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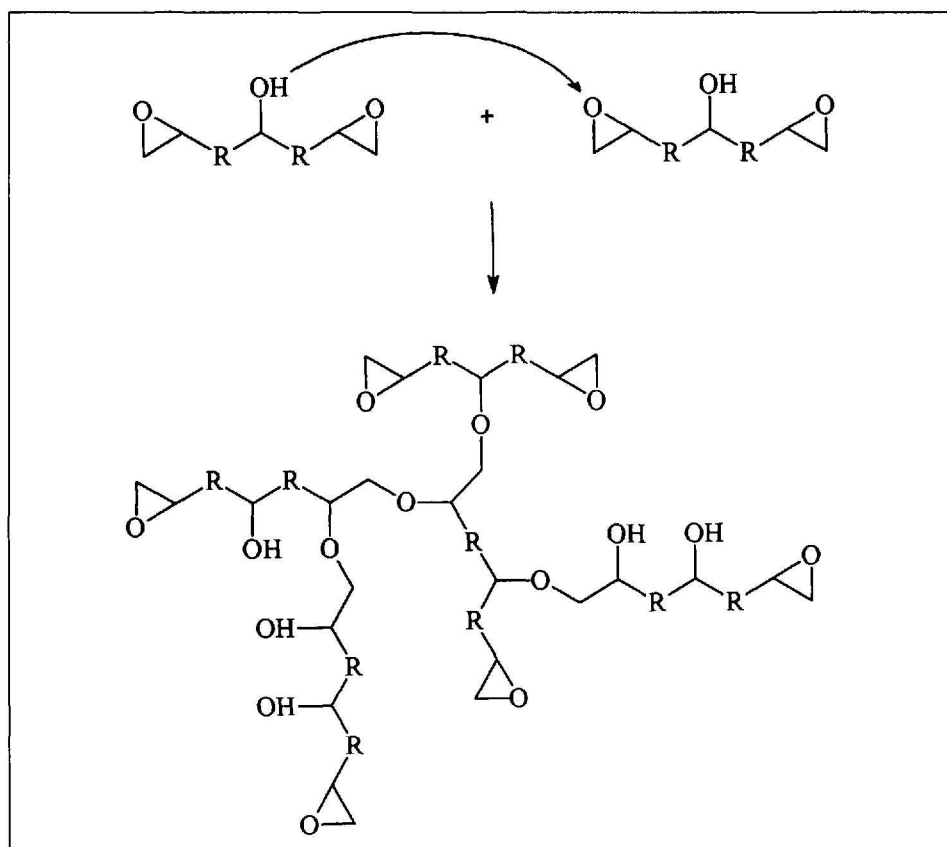Email: thierry.meyer@epfl.ch
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Scheme 1. Polyaddition reaction of a RBL with BPA.

Scheme 2. Branching lengthening step reaction.

type 2, 4, 5 and 7 solid resins. The reaction mixture was brought to the desired reaction temperature. Then, the solution of catalyst was injected corresponding to time zero. At specific times samples were taken from the calorimeter, quenched to room temperature and analyzed [2][5].

2.2. Analyses of Samples

The content of epoxy groups in the solid epoxy resin was determined by direct potentiometric titration (716 DMS Titrino, Metrohm, Switzerland). The samples were dissolved in chloroform and tetraethylammonium bromide/acetic acid, and the solutions were titrated with 0.1N perchloric acid.

2.3. Viscometry

The viscosities REL analyses were investigated with a I.C.I Cone & Plate Viscometer Visco-plot 256 (Epprecht Instruments + Control, Switzerland). 100 mg of solid resin was melted on a heated plate. Then, the cone was dropped in the melted resin and set in rotational motion. The torque resistance provides the viscosity value.

3. Theoretical

3.1. Kinetic Modeling

It is reasonable to divide the advancement reaction rate in two components: linear advancement and branching. The variation of the kinetic rate constant k_{br} has been correlated to the increase of the melt viscosity based on a modified diffusional semi-empirical model proposed by Chiu [6].

3.2. Kinetic Equation

The advancement rate is proportional to the concentration of epoxy C_{Ep}, the phenolic concentration C_{OHp} to the nth power and the concentration of catalyst.

$$-R_{ad} = k_{ad,\infty} \exp\left(\frac{-E_{ad}}{RT}\right) C_{cat} C_{Ep} C_{OHp}^n \quad (1)$$

For the branching reaction a direct proportionality to the concentration of epoxy and the concentration of secondary hydroxyl groups C_{OHs} is proposed (Eqn. 2).

$$-R_{br} = k_{br} \exp\left(\frac{-E_{br}}{RT}\right) C_{Ep} C_{OHs}$$

$$\text{with } C_{OHs} = C_{OHp,0} - C_{OHp} \quad (2)$$

The theoretical epoxy value, characterizing the type of solid resin, is defined as:

$$C_{Epth} = C_{Ep,0} - C_{OHp,0} \quad (3)$$

The empirical diffusion model for the branching rate constant k_{br} is expressed by:

$$\frac{1}{k_{br}} = \frac{1}{k_{br,\infty}} + \frac{C_{Ep} K_{diff} \eta_{red}}{T}$$

$$\eta_{red} = \frac{\eta}{\eta_{C_{Epth}}} \quad (4)$$

Finally, the kinetic equations for the consumption of epoxy and phenolic groups can be expressed by:

$$-\frac{dC_{Ep}}{dt} = k_{ad,\infty} \exp\left(\frac{-E_{ad}}{RT}\right) C_{cat} C_{Ep} C_{OHp}^n + \frac{k_{br,\infty} T}{T + k_{br,\infty} K_{diff} C_{Ep} \eta_{red}} \exp\left(\frac{-E_{br}}{RT}\right) C_{Ep} C_{OHs}$$

$$-\frac{dC_{OHp}}{dt} = k_{ad,\infty} \exp\left(\frac{-E_{ad}}{RT}\right) C_{cat} C_{Ep} C_{OHp}^n \quad (5)$$

4. Results and Discussion

The model has been integrated with an explicit Runge-Kutta (4,5) and the optimization of kinetic parameters is run by the simplex search method of Lagarias [7] using Matlab®, software [8]. The graphical results provided by the optimization are represented in the Fig.

As shown, the kinetic model based on a semi-empirical diffusional assumption for the branching rate well describes the experimental measurements. The observation of the rate constants for both reactions shows that the epoxy groups are preferentially consumed by the phenolic groups ($k_{ad} \approx 13 k_{br}$).

The branching rate on the plateau is quite constant whatever the resin types. This situation shows that the decrease of the branching rate is not only due to the variation of the melt viscosity but also by the steric hindrance which prevent chemical reactions between reactive species. The introduction of the reduced viscosity permits the effect of the viscosity to be minimized and can be defined as a parameter describing both the variations of the melt viscosity and the steric hindrance, which cannot be quantified.

The important error characteristic of the parameter n (Table) could be explained by the difference in reactivity between phenolic groups attached on a long polymerized chain or on a short one. The kinetic model has been developed by as-suming that phenolic reactivity is identical whatever the length of the polymerized chain.

Table: Kinetic parameters provided by the Matlab®, optimization

k_{ad} [IS unit]*	E_{ad} [J mol^{-1}]	k_{br0} [IS unit]	E_{br} [J mol^{-1}]	n [-]	K_{diff} [K s]
$2.2 \times 10^9 \pm 10^4$	79634 ± 10	$4.6 \times 10^7 \pm 10^3$	81336 ± 30	0.19 ± 0.3	0.113 ± 0.02

5. Concluding Remarks

The proposed kinetic model of the advancement and branching reactions describes the experimental observation in the industrially important temperature range of 160 to 210 °C and catalyst concentrations. This kinetic model has been implemented with a semi-empirical diffusional model describing the branching rate. The model allows an accurate prediction of the final epoxy value, which characterize the quality of the final solid resin. Although the model has been developed on the base of a pure resin (Dgeba), one have to keep in mind that impurities present in the overall industrially resins can lead to modifications of the kinetic parameters.

Acknowledgments

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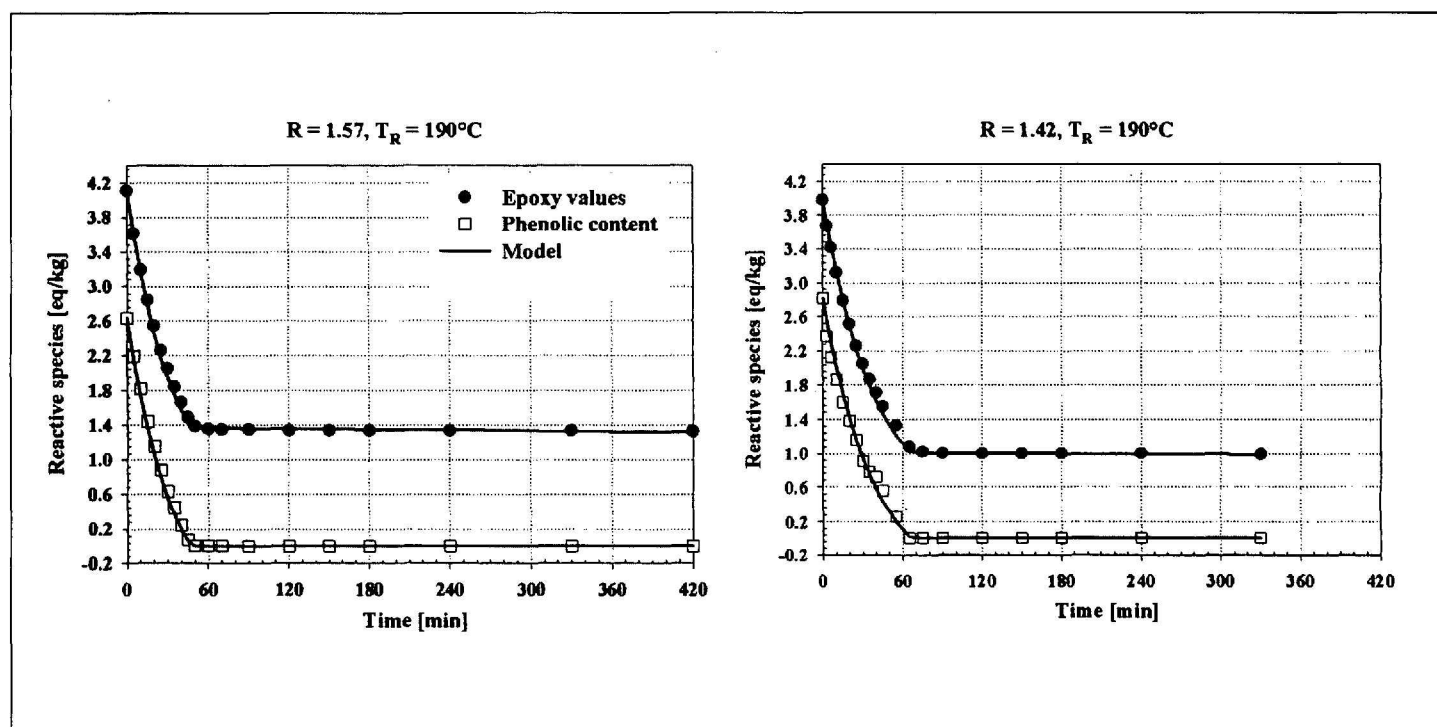[8] Matlab, Using Matlab, **1996**.

Fig. Comparison between experimental measurements and kinetic modeling.