

Impact of inter- and intra-molecular movements on thermoset polymerization reactions



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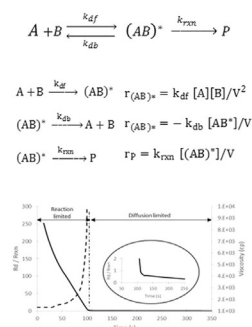
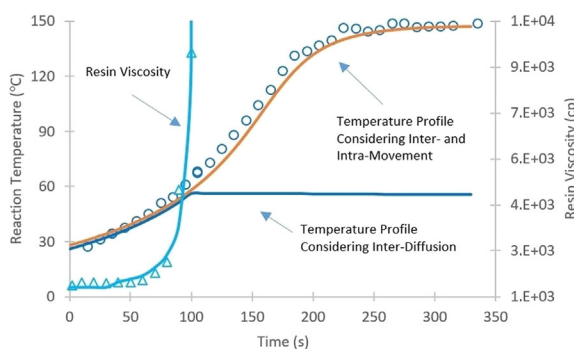
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HIGHLIGHTS

- Two mechanisms were tested and discussed for molecular diffusion of moieties.
- Inter-molecular reaction mechanisms are dominant prior to the gel point.
- Intra-molecular mechanisms are dominant after the gel point.
- Arrhenius frequency factor can account changes in diffusion and molecular movement.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 19 June 2016

Received in revised form 9 November 2016

Accepted 1 December 2016

Available online 2 December 2016

Keywords:

Urethane

Mass transfer

Diffusion

Molecular movement

ABSTRACT

The large increase in viscosity during thermoset reactions leads to reduced frequencies of reacting moiety collisions with respective reduced reaction rates. Molecular diffusion substantially ends after the gel point; however, reactions continue after the gel point through mechanisms involving local movement (and reacting moiety contact) of polymer sections/branches which is referred to as intra-molecular movement. The impact of inter- and intra-molecular movements was simulated for polyurethane reactions to better understand the impact of mass transfer on polymerization reactions.

Inter-molecular reaction mechanisms are dominant prior to the gel point, and intra-molecular mechanisms are dominant after the gel point. Representing the Arrhenius pre-exponential factor as a sum of a viscosity-dependent term and a viscosity-independent term was identified as the most efficient method to model this phenomenon. Good agreement of simulation results for reaction temperature, foam height, and viscosity profile with the experimental data were obtained.

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1. Introduction

Toward the goal of having a reasonably small set of kinetic parameters to describe urethane-forming reactions from dozens

of polyols, Ghoreishi et al. (2014) developed a group contribution approach to characterize the reactivity of polyols in terms of concentration of primary, secondary, and hindered secondary alcohol moieties. Subsequent analysis of this approach questioned the basis of characterizing two different types of secondary alcohol moieties. In addition, unexpected deviations from model predictions occurred in the form of slower reaction rates in higher viscosity polyols than projected by this model.

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Nomenclature

| | | | |
|------------------------|--------------------------------------------|-----------------------|-------------------------------------------------------------------------------------|
| μ | resin viscosity, cp | $k_{d(\text{intra})}$ | rate constant of intra-molecular movement |
| ρ | stearic factor | k_{rxn} | rate constant of reaction |
| A | pre-exponential term in Arrhenius equation | N | Avogadro's number |
| A_1, A_2, A'_1, A'_2 | constants | R | ideal gas constant |
| D_A | diffusivity of component A, cm/s | R^* | critical distance between "A" and "B" necessary to form the encounter complex (AB)* |
| D_B | diffusivity of component B, cm/s | r_A | molecular radius of A |
| E | activation energy | r_B | molecular radius of B |
| K_B | Boltzmann constant | T | reaction temperature, K |
| k_{db} | rate constant of backward diffusion | Z | collision frequency |
| k_{df} | rate constant of forward diffusion | | |
| $k_{d(\text{inter})}$ | rate constant of inter-molecular movement | | |

Thus, a hypothesis was then put forth that in these systems, the reaction rates were viscosity dependent; and an objective was put forth to eliminate the need to classify certain alcohol moieties as "hindered" secondary. A further objective was to have a model that corrected previous deficiencies where the model was not able to predict that higher viscosity polyols would have slower reaction rates. This paper is on research to identify a fundamental basis to incorporate the impact of viscosity on reaction kinetics for polymer forming systems. Ultimately, this fundamental pursuit is one of better understanding the role of mass transfer on reaction kinetics for systems where the viscosity changes by several orders of magnitude during reaction.

Diffusion-controlled (or diffusion-limited) reaction is defined as the reactions that occur quickly and the rate of reaction depends on the rate of diffusion of the reactants through the reaction medium. As the reacting species diffuses to each other, they form a complex that reacts quickly to product. For inter-molecular collision of reacting moieties, diffusion rate is proportional to the time it takes to bring the reactive moieties (or the reactive part in the moieties) into contact to allow reaction. Diffusion-controlled reaction is rare in the gas phase where the rate of diffusion of gas molecules is very high compared to the rate of reaction. However, this phenomenon is more important in liquids, especially when the viscosity is high and the diffusion of the molecules becomes slow.

During reactions which form thermoset polymers, the viscosity of the resin increases due to the formation of product polymer and crosslinking, which causes reduction in the diffusion rate of the reactants. In this stage, the diffusion step becomes the limiting (controlling) step of this reaction. An associated theory was developed first by Smoluchowski (1917), Collins and Kimball (1949), Noyes (1961), and discussed in details by Rice (1985).

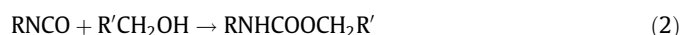
The diffusion and reaction of a simple irreversible reaction of two reactive moieties, A and B, can be represented by the three steps of Eq. (1)

- Diffusion of A and B to a proximity at which attractive chemical forces become dominant to form the pseudo species (AB)*, and either
- Dissociation of the pseudo species (AB)* if the species A and B diffuse apart without reacting or
- Reaction of the pseudo species (AB)* to form product.



(AB)* is described as an active complex if it is at the saddle point of the potential energy surface of A and B or as a collision complex if there is no interaction between A and B. The term "encounter complex" has been used to cover the above two cases (Rice and Bamford, 1985).

Polyurethane forming reactions can be particularly insightful for studying the impact of diffusion on reaction rates because formulations are available that react from flowing liquid to solid in a couple minutes. Polyurethane (PU) is a chain of organic units joined by urethane links. Isocyanate moieties reacting with alcohol moieties to produce urethane (Wirpsza and Kemp, 1993; Kleszczewski, 2001; Ashida, 2006). The general reaction is described in Eq. (2).



The structure and the molecular size of the isocyanate and polyol have a significant impact on the polyurethane produced (Hinrichsen, 1994). Other additives such as catalysts, cross-linkers, and light stabilizers also have an impact of the polymerization reaction of polyurethane (Cavaco and Melo, 2012; Zhao et al., 2013; Zhao and Suppes, 2014).

2. Modeling approaches

Two different approaches are presented in this paper to provide insight into mechanisms and, ultimately, an effective method to more-accurately simulate urethane-forming reactions. The first approach assumes that the reactive moieties diffuse together forming the encounter complex which may either disassociate or react. This approach is described as the inter-molecular movement of the reactive moieties. The second approach considers an intra-molecular movement (bending and rotation without breaking of covalent bonds) in parallel to the inter-molecular movement with the rate of inter- and intra- movement as additive in the collision frequency factor in Arrhenius equation.

2.1. Mass transfer as step in reaction process (inter-molecular diffusion rate)

Alberty and Hammes (1958) demonstrated that diffusion can be modeled in a power-law rate expression where the rate constant is related to diffusivities according to Eq. (3).

$$k_{d(\text{inter})} = 4\pi NR^* (D_A + D_B) \quad (3)$$

Eq. (4) expression of diffusivity suggested by Einstein (1905) and von Smoluchowski (1906) can be used to calculate the diffusivity of A and B moieties in the reaction medium.

Table 1
Expressions of the diffusion and reaction steps.

| Diffusion and reaction and steps | Rate expression |
|--------------------------------------------|-----------------------------------------|
| $A + B \xrightarrow{k_{\text{df}}} (AB)^*$ | $r_{(AB)^*} = k_{\text{df}}[A][B]/V^2$ |
| $(AB)^* \xrightarrow{k_{\text{db}}} A + B$ | $r_{(AB)^*} = -k_{\text{db}}[(AB)^*]/V$ |
| $(AB)^* \xrightarrow{k_{\text{rxn}}} P$ | $r_P = k_{\text{rxn}}[(AB)^*]/V$ |

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