



# Kinetic and thermodynamic analysis of the polymerization of polyurethanes by a rheological method



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## ARTICLE INFO

### Article history:

Received 17 November 2015

Received in revised form

21 December 2015

Accepted 22 December 2015

Available online 25 December 2015

### Keywords:

Kinetic

Polyurethane

Metallo-prepolyol

Kamal

Autocatalysis

## ABSTRACT

As part of an investigation into the mechanism and chemorheology of linear segmented polyurethane (PU) systems, this paper presents the kinetic and thermodynamic characterization of the reaction between an advanced functional metallo-polyol derivative of hydroxyl-terminated polybutadiene (HTPB), (ferrocenylbutyl)dimethylsilane grafted HTPB, and isophorone diisocyanate (IPDI). The evolution of viscoelastic properties, such as the storage modulus ( $G'$ ), was recorded in bulk under isothermal conditions at four different temperatures between 50 and 80 °C, and a resin curing degree profile was obtained for this elastic modulus. The use of the Kamal-Sourour autocatalytic kinetic model was proposed, describing the overall curing process perfectly. All the kinetic and thermodynamic parameters, including reaction orders, kinetic constants and activation energy, were determined for the polyaddition reaction under study. A relevant autocatalysis effect, promoted by the urethane group, has been found. The isoconversion method was also used to analyze the variation of the global activation energy with conversion. The global activation energy increases slightly as the curing reaction proceeds with a maximum value reached at approximately 30% conversion. In addition, the Eyring parameters were calculated from the obtained kinetic data.

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## 1. Introduction

Polyurethanes (PUs) are perhaps the most versatile family of polymers for the creation of promising new materials. This is principally due to the way in which they are synthesized and the wide range of components that can be used to form numerous PUs. This means that PUs can present with a large variety of properties, resulting in a large increase in the number of final applications in both traditional and newly expanding areas such as protective coatings, adhesives, biomaterials and high performance elastomers, among others [1–3].

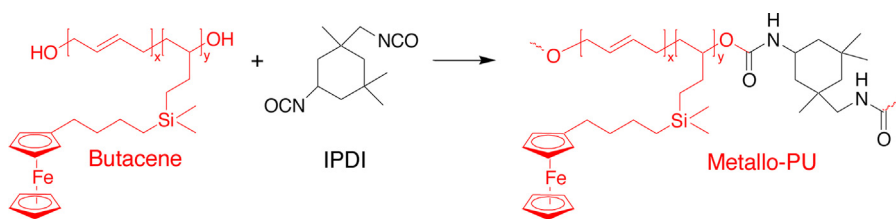
PUs based on hydroxyl-terminated polybutadiene (HTPB) are widely used as a fuel binder in solid composite propellants all over the world [4]. Nevertheless, for more specific applications, many of these PUs are limited in scope because of the functionalities available on the backbone for further modification and tailoring. For example, to achieve new and interesting properties for these HTPB-based PUs, chemical modifications of this telechelic prepolymer have been investigated, some of which are based on the incorporation of a transition metal within its oligomeric structure

[5,6]. A clear example in line with this is the prepolymer called Butacene, which is a (ferrocenylbutyl)dimethylsilane grafted HTPB. A silico-ferrocene derivative was grafted onto HTPB to produce a new prepolymer with novel properties. Butacene synthesis consists of the addition of an organo-silicone ferrocene derivative to a low molecular weight HTPB across the pendant vinyl group. The chemical formula corresponding to this prepolymer is modelled in Scheme 1. The incorporation of ferrocenyl units into the polybutadiene main chain results in an increase in the combustion kinetics when this metallo-PU acts as a binder in composite propellants. Therefore, PU networks based on Butacene attract significant attention as advanced propellant binder systems, overcoming the drawbacks of conventional ferrocene derivatives used as burning rate catalysts [7].

In contrast, the cure mechanism and kinetics determine the network morphology, which in turn dictates the physical and mechanical properties of the cured product. Therefore, knowledge of the kinetic parameters of a reactive resin is essential for the design and processing of polymer and composite technologies. A large number of characterization methods have been used to monitor the kinetics of polymerization reactions. These methods fall into two groups: indirect methods, which measure a physical property that can be functionally related to the extent of the reaction, and direct methods, which measure the concentration of a reactant or

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**Scheme 1.** Components of the reactive blend under studied.

product. Rheometry and thermal methods fall into the first group, while titration and spectroscopy belong to the second.

Similarly, there are two main forms of kinetic models that have been proposed in the literature to describe curing reactions: empirical and mechanistic models. Empirical models assume an overall reaction order and fit this model to the kinetic data. This type of model generally employs indirect monitoring methods and provides no information on the kinetic mechanism of the reaction. Mechanistic models are derived from an analysis of the individual reactions involved during curing, which requires detailed measurements of the concentration of reactants, intermediates, and products. The determination of most appropriate kinetic models for an application will depend on the type of system, and the accuracy of the results [8].

Among the indirect thermal methods used to monitor the polymerization kinetics, differential scanning calorimetry (DSC) is the most popular technique for monitoring the curing process. However, this method is not entirely suitable to monitor the reaction of HTPB with some isocyanates [9,10]. On the other hand, rheological properties are also useful for monitoring the curing process, overcoming the disadvantages of the commonly used DSC technique. One relevant parameter for the study of the curing process is the storage modulus ( $G'$ ), which is proportional to the crosslinking density of the network being formed by chemical bonds [11–14].

The curing rheological characterization and gelation analysis of the Butacene and isophorone diisocyanate (IPDI) system in bulk under isothermal conditions has been described previously [15,16]. However, the kinetic and thermodynamic aspects of this polyaddition reaction were not performed in detail. Therefore, in this work, the rheological parameters are used to acquire the conversion *versus* time data, and the Kamal-Sourour autocatalytic kinetic model and an isoconversion method are applied to study the reaction of the chosen PU system. To the best of our knowledge, this is the first time that a kinetic analysis of a PU has been conducted using rheological data, and our aim is to obtain a more comprehensive understanding of this complex reaction.

## 2. Experimental

### 2.1. Materials

Butacene, a (ferrocenylbutyl)dimethylsilane grafted HTPB, was produced and delivered by the SNPE (Butacene<sup>®</sup>800). The Butacene synthesis consists of the addition of an organo-silicone ferrocene derivative across the pendant vinyl group of a low molecular weight HTPB. According to the supplier's specifications, this metallo-prepolymer has an OH value of 0.33 eq/kg, and an iron content of 8%. Logically the average functionality (OH groups) of Butacene [17] are similar to that of the parent HTPB [18–20]. The isocyanate IPDI was supplied by Hüls, and this product was used as received.

### 2.2. Sample preparation

Butacene was dried and degassed for a minimum of 1 h under a continuous vacuum at 60–70 °C using a rotary flash evaporator to

remove residual moisture, and then placed under a nitrogen atmosphere before use. To prepare the PU samples, the macroglycol was hand-mixed by vigorous agitation with IPDI for several minutes at room temperature until a homogeneous slurry was achieved with a stoichiometric ratio of the isocyanate to hydroxyl functionality,  $r = [\text{NCO}]/[\text{OH}]$ , equal to 1. Having thoroughly mixed both reactants, the samples were prepared for immediate rheological analysis.

### 2.3. Rheological measurements

The procedure followed to characterize the rheological behaviour of the curing reaction for this PU resin was carried out by dynamic oscillation employing a Rheometric Dynamic Analyser RDA II with parallel plate tools. The polymer samples were heated using a force convection heating oven with temperature stability to  $\pm 0.2$  °C. All experiments were performed under a continuous purge of dry nitrogen to prevent oxidative and hydrolytic degradation. The plate diameter and its gap were 25.0 and 0.50 mm, respectively. Measurements were performed during isothermal cures in the 50–80 °C temperature range with a frequency of 1 Hz. As the cure proceeded, the strain was automatically adjusted to maintain the torque response within the range of the transducer. The variation of the viscoelastic properties during cure, such as shear storage modulus ( $G'$ ), were registered as a function of the reaction time.

### 2.4. Methodology

#### 2.4.1. Kinetic modelling

Rheokinetic models allow the entire network formation process to be monitored from the evolution of  $G'$ , which is generally proportional to the density of the network formed by chemical bonds and physical entanglements. The rheological degree of conversion,  $\beta$ , is defined as follows [11–14]:

$$\beta = \frac{G'_t - G'_0}{G'_\infty - G'_0} \quad (1)$$

where  $G'_\infty$  is the value of  $G'$  at the end of the curing reaction. This value is proportional to the maximum cross-linking density the network reached under given curing conditions.  $G'_0$  is the storage modulus at the beginning of the reaction (time zero when the reacting system is placed on the pre-heated parallel plates), and  $G'_t$  is the storage modulus at time  $t$ .

A number of phenomenological models for cure kinetics have been developed to characterize the curing process for different resin systems. The simplest one is the  $n$ th-order rate equation:

$$\frac{d\beta}{dt} = k(1 - \beta)^n \quad (2)$$

$$k = Ae^{-E_a/RT}$$

where  $\beta$  is the rheological degree of conversion,  $n$  is the reaction order,  $t$  is the reaction time, and  $k$  is the reaction rate constant, which is an Arrhenius function of temperature,  $A$  is the frequency factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is the absolute temperature. This simple model was applied by

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