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Rheokinetic analysis on the formation of metallo-polyurethanes based on hydroxyl-terminated polybutadiene

Beatriz Lucio, José Luis de la Fuente *

Instituto Nacional de Técnica Aeroespacial "Esteban Terradas", INTA, Ctra. de Ajalvir, Km 4, 28850 Torrejón de Ardoz, Madrid, Spain

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ABSTRACT

Rheokinetics for the formation of an advanced functional polyurethane (PU) from Butacene, which is (ferrocenylbutyl)dimethylsilane grafted hydroxyl-terminated polybutadiene (HTPB), and from isophorone diisocyanate (IPDI), has been studied through viscosity build-up during cure reaction in bulk and in isothermal conditions at different temperatures (50–80 °C). The viscosity increases with curing time in an exponential way, and hence the kinetic model of Arrhenius was applied before gelation. The rheokinetic graphs obtained by plotting ln (viscosity) *versus* time, showed the presence of two well-defined stages. This fact is due to the nature of this functional metallo-polyol and to the use of a diisocyanate with two non-equivalent reactive groups. The rate constants in both stages, $k_{\eta 1}$ and $k_{\eta 2}$, were determined from these plots and the contributions of the different chemical reactions to each stage is discussed. In addition, activation energies were determined for the curing reaction under study. The catalytic effect of the ferrocenyl group covalently linked to the polybutadiene chain has been evaluated. This catalytic activity for the macrodiol Butacene was compared with those obtained when a conventional organometallic compound, such as dibutyltin dilaurate (DBTL) or ferrocene, is used as catalyst instead of this novel prepolymer.

1. Introduction

Polyurethanes (PUs) are widespread in the chemical and building industries due to the fact that a large variety of starting materials with specific properties can be used for their formation. They are used, for example, as coatings, adhesives, foams, thermal protection, packaging and cushioning as well as in energetic composite materials [1,2]. In this latter application the modern high performance composite propellants continue to use PUs with hydroxyl-terminated polybutadiene (HTPB) as the prepolymer because of its unique physico-chemical properties such as excellent flow characteristic and storage capacity compared to other known binders [3].

Composite propellants are highly particle-filled elastomers used in solid rocket motor technology. These composite materials are made by embedding a finely divided solid oxidizing agent, generally ammonium perchlorate, in a plastic, resinous, or elastomeric matrix. The matrix material usually provides the fuel for the combustion reaction, although solid reducing agents such as aluminum are frequently included in the compositions. The urethane network obtained by curing HTPB with a suitable diisocyanate (curative) provides a matrix for inorganic oxidizer and metallic fuel which are dispersed in the propellant grain. Other ingredients (additives) are plasticizers, bonding agents, stabilizers and catalysts [4–8].

Simple ferrocene compounds are commonly used as burning rate catalysts in practical applications of composite solid propellants, mainly because of (1) their general binder solubility and uniform microscopic distribution; (2) their fluidity, which eases catalytic combustion both in the condensed and gas phases; and (3) the better

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* Corresponding author. Fax: +34 91 5201611.
E-mail address: fuentegj@inta.es (J.L. de la Fuente).

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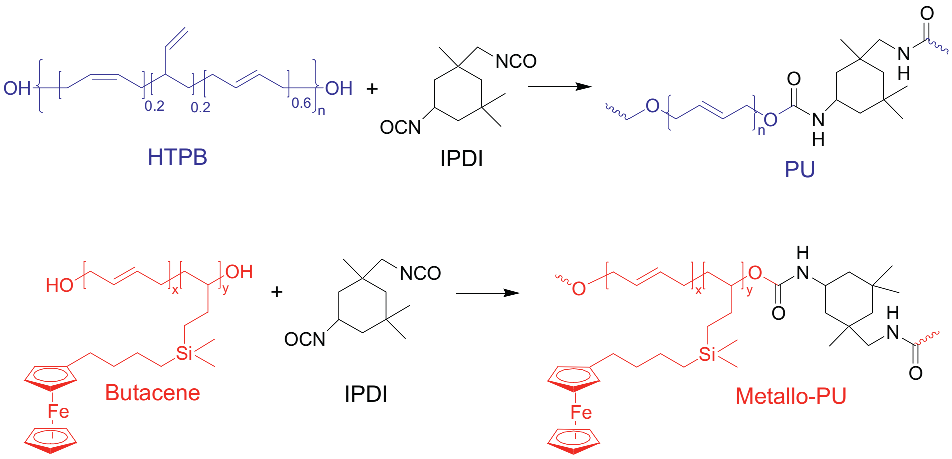
ignitability of the propellant compared to ones containing conventional inert solid catalysts, generally transition metals oxides and their mixtures. However, their use as burning rate catalysts in composite propellants has inherent drawbacks arising from their tendency to migrate in the bulk of the material, and their sensitivity toward oxidation by air. These undesirable features may lead to malfunctioning of the propellant which can cause a catastrophic failure [9]. To obviate these problems and also to improve the efficiency of ferrocene-based burning rate catalysts, attempts have been made, using appropriated ferrocene derivatives, to link covalently the ferrocene moiety to the polymeric matrix [10]. For this purpose, Butacene (achieved at SNPE, France) is one of these advanced functional prepolymers where a ferrocene derivative is grafted on pendant vinyl groups of HTPB, whose simplified structure is shown in Scheme 1. Furthermore, nowadays it is well-recognized that metallo-polymers represent a key emerging field. Thus, a great deal of interest has arisen in the synthesis and characterization of novel metal-containing polymers as a result of their intriguing properties such as conductivity, ferromagnetism, electroluminescence, nonlinear optical properties, chemical sensing, and catalyst as in the present case [11–13].

The mechanism and kinetics of curing determine PU's network morphology, which in turn dictates the physical and mechanical properties of the cured product. Thus, understanding the cure kinetics of PUs is essential for process development and quality control. The kinetics of urethane formation has been extensively studied in the solvent media and bulk [14,15]. However, the studies of kinetics in the bulk polymerization mode will be more relevant to propellant processing, and hence of more interest. Nevertheless, extremely high viscosity of the curing polymer in the bulk could be an impediment to satisfactory estimation of functional groups, and consequently those methods which measure the concentration of reactants or product species, as for example spectroscopic methods, are not suitable. Besides, as the conventional chemical and spectroscopic analytical methods can only reveal the extent of functional group consumption during the cure reaction, they have limited applicability in estimating the branching status of the cross-linking system, which essentially determines the pot life. In consequence, indirect methods, which measure a physical property that can be related to the extent of reaction (for example viscometry and calorimetry) can be useful for monitoring the curing process, by overcoming the limitations mentioned previously for direct methods. In addition, perhaps the most important properties of polymer materials regarding their processing behavior are the rheological properties [16,17].

Viscosity control during processing of PUs is particularly critical, because the viscosity varies not only with the temperature and flow conditions, but also with the time due to the polymerization reactions. Therefore, it is important to understand the relationship between the curing kinetics and rheological behavior in order to control curing effectively, and to optimize the processing schedules and the properties of the final product [16,17]. For these reasons, a great number of works focused on the study of curing reaction of PUs based on HTPB–diisocyanate have been developed by rotational viscometry [18–23]. This experimental technique has proven its ease and versatility in reaction monitoring, allowing rheokinetic parameters and information related to mechanistic aspects to be obtained. Therefore an understanding of the factors which influence the processability characteristics of HTPB polymers and their derivatives, such as Butacene, is crucial in controlling the pot life of propellant slurry.

The aim of the present work is to evaluate the kinetic parameters associated with the urethane network formation based on Butacene and isophorone diisocyanate (IPDI), the most frequently isocyanate used with HTPB in this application, with the reference to viscosity build-up during the cure reaction. Influence of reaction temperature and the effect of the ferrocene group in the reactivity of HTPB were also analyzed. To the best of our knowledge, this is the first time that a systematic kinetic study of this metallo-PU based ferrocene-grafted HTPB has been conducted.



Scheme 1. Reactions of PU synthesis.