Rheological cure characterization of an advanced functional polyurethane

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ABSTRACT

As part of our continuing study of the curing kinetic and chemorheological analysis of a functional polyurethane (PU) segmented block copolymer formation, in the current paper, we focus on the use the rheological measurements to monitor the entire curing process. The curing reaction was between a metallo-polyol derived of hydroxyl-terminated polybutadiene (HTPB), i.e., (ferrocenylbutyl) dimethylsilane grafted HTPB, and isophorone diisocyanate (IPDI). The evolution of viscoelastic properties, such as storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) was recorded in isothermal conditions, at four different temperatures in the range of 50–80 °C. The gel times (t_{gel}s) were determined by the loss tangent ($\tan \delta$) crossover at different frequencies, and the activation energy obtained from them was 69.8 kJ/mol. The rheological properties in the region of the gel point have shown that they follow the percolation theory, demonstrating a power law dependence for the shear modulus with a critical exponent $n = 0.67 \pm 0.01$, for the higher curing temperatures, 70 and 80 °C, and a slightly lower one at lower temperatures, 50 and 60 °C. In addition, three different empirical models, among them the Arrhenius and Kiuna rheokinetic models, were used to predict the change in viscosity of this system with the time in the pre-gel region. These results illustrate the rheological curing behavior of this PU resin, its final application being found in the development of advanced energetic composite materials.

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1. Introduction

Segmented polyurethanes (PUs) consisting of alternating soft (low glass transition) and hard segments are some of the most frequently investigated polymers in the last two decades. This is due to their wide range of properties, which has produced 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. Availability of a very large selection of reactants (diisocyanate, chain extender and diol oligomer) leads to the preparation of a wide variety of segmented PUs, each having specific properties [1–3]. Among the various diol oligomers used (soft segment), possibly one of the best known is hydroxyl-terminated poly-butadiene (HTPB), which finds its major application in solid composite propellant binders [4]. However, in order to achieve new interesting properties for these HTPB-based PUs, chemical modifications of this prepolymer have been investigated, some of

them centered on the transition metal incorporation within its macrostructure [5,6].

Thus, the prepolymer called Butacene, i.e., (ferrocenylbutyl) dimethylsilane grafted HTPB, has been developed. The technical approach was to graft a silico-ferrocene derivative onto HTPB in order 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 can be modelized as shown in Scheme 1. The incorporation of a ferrocenyl group to the polybutadiene main chain results in an increase in the combustion kinetics when this metallo-PU acts as binder in composite propellants. Thus, PU networks based on Butacene draw much attention as advanced propellant binder systems as the drawbacks of the use of ferrocene derivatives as burning rate catalysts have been overcame in this way [7]. Furthermore, it is well-known that transition metals included into macromolecules, such as these PUs, continue to be a subject of interest in the development of new materials with tailored applications due to their exceptional physical and chemical properties [8].

On the other hand, during the past 30 years, dynamic mechanical analysis has been used intensively for the study of

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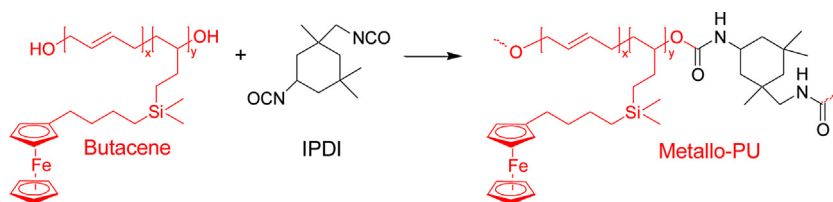
Scheme 1. Reaction of metallo-PU synthesis.

the curing reaction of thermosetting polymers and also for the determination of the viscoelastic properties and transition temperatures of the cured resins. The formation of a polymer network can be evaluated from dynamic measurements by monitoring rheological parameters such as the storage modulus (G'), loss modulus (G''), and complex viscosity (η^*) as a function of time. The most important changes during the entire process of polymer network formation are gelation, *i.e.*, liquid to rubber transition, and vitrification, *i.e.*, rubber to glass transition.

Gelation occurs at a well-defined and often calculable stage in the course of the chemical reaction, and is dependent on the functionality, reactivity, and stoichiometry of the reactants. This sudden and irreversible change from a viscous liquid to an elastic gel, which indicates the first appearance of the infinite network, is called the gel point. The macroscopic consequences of the gelation process are that the viscosity tends to infinity and the elastic properties of the material are acquired, and are not present in the pre-gel state. Though a number of different techniques have been proposed and used to detect this sol-gel transition, gelation is frequently detected and studied using rheological measurements [9–13].

Another relevant event which may occur at any stage during cure and which is distinct from gelation is vitrification of the growing network. Vitrification takes place when the glass transition temperature (T_g) of the reactive mixture reaches the isothermal curing temperature. As described in the literature, when the T_g of the growing network is lower than the cure temperature, the reaction occurs in the liquid state and is controlled by the chemical reactivity of the functional groups. Therefore, for isothermal cures carried out at temperatures below the fully cured material glass transition temperature ($T_{g\infty}$), the reaction may be affected by vitrification phenomena [14]. However, it is important to notice that the usual curing temperatures of HTPB and derivates with isocyanates are higher than the corresponding $T_{g\infty}$s, therefore the vitrification process does not take place in the course of the curing reaction. Consequently, in such reactive systems, gelation becomes the biggest critically important event, and the gel point is the most important kinetic parameter characterizing the curing reaction.

In a previous article, the curing rheokinetics were described, performed by means of viscosity build-up measurements, of Butacene and isophorone diisocyanate (IPDI) in bulk and isothermal conditions [15]. However the application of this method, through measurements made by means of rotational viscometers, as is commonly used in the monitoring of the polymerization rheokinetics of PUs based on HTPB, only allows the determination of viscosities of the cross-linking polymer above the gel point [16–21]. However, in the rheological characterization of such systems the oscillatory shear flow measurements are preferred to those of steady shear because they can be applied to materials not only in the liquid state but also in the rubbery and glassy status (not in this case), practically from the beginning to the end of the cure. Thus, the objective of this study is to carry out the rheological cure characterization of this novel PUs resin in order to reach an understanding of the complete extent of the curing reaction. To the

best of our knowledge, this is the first time that an analysis of the gelation process of a PU based on HTPB has been conducted. Furthermore, it is important to note here that in this research the choice of this derivative of HTPB, which presents a relevant catalytic effect, is fully justified since the reaction rate of the HTPB–IPDI system is extremely slow. In this way, it is anticipated that a better knowledge of the chemorheological behavior of PU network-forming systems may be gained.

2. Experimental

2.1. Materials

Butacene, that is (ferrocenylbutyl) dimethylsilane grafted to HTPB, was produced and was delivered by the SNPE (Butacene® 800). Butacene synthesis consists of the addition of an organo-silicone ferrocene derivative to a low molecular weight HTPB across the pendant vinyl group. According to the supplier, this metallo-prepolymer had an OH value of 0.33 eq/kg, and an 8% in weight of iron content. The isocyanate IPDI was supplied by Hülls, and this product was used as received.

2.2. Sample preparation

Butacene was dried and degassed for a minimum of one hour under continuous vacuum at 60–70 °C using a rotary flash evaporator to remove residual moisture, and then put under a nitrogen atmosphere before being used for the synthesis. For the preparation of PU samples, this polyol was hand mixed by vigorous agitation with IPDI during several minutes at room temperature to obtain an homogeneous slurry mass, with stoichiometric ratio of isocyanate to hydroxyl functionality at unity, $r = [NCO]/[OH] = 1$. Having thoroughly mixed both reactants, samples were prepared for immediate rheological analysis.

2.3. Rheological analysis

The rheological behavior of the PU resins was studied by dynamic oscillation employing a Rheometric Dynamic Analyzer RDA II with parallel plate tools. The polymer samples were heated using a force convection heating oven with temperature stability to ±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 carried out during isothermal cures in the 50–80 °C temperature range in the multifrequency mode (at seven frequencies over the range 0.1–10 Hz). As the cure proceeded, the strain was automatically adjusted to maintain the torque response within the range of the transducer. An initial strain amplitude of 50% in the liquid state at the beginning of the curing was reduced during reaction down to 1% in the solid state to ensure a linear viscoelastic response. The variation of the viscoelastic properties during cure, such as shear storage modulus (G'), loss modulus (G'') and complex viscosity (η^*) were registered as a function of the reaction time.