Assessment of Biobased Polyurethane Reaction Kinetics through DSC and FTIR Analysis

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Abstract. The polyurethane (PU) formation reaction of liquid monomers involves a combination of physical and chemical phenomena, promoting the rapid transformation of a liquid mixture of low molecular weight components into an often solid and spongy structure. The kinetics of polymerization of polyurethanes through the reaction of the HDT isocyanate with ricinoleic acid (major fatty acid in castor oil) was analyzed. The NCO/OH ratio used in this study was 1.5 for HDT. The analyses were performed by Differential Scanning Calorimetry (DSC) with both dynamic and isothermal methods. With the dynamics methods (heat flow as a function of temperature), it was possible to determine reaction mechanism (nᵗʰ order) and conversion (~100%), as well as the needed activation energy (range from 60 to 65 kJ.mol⁻¹) to form an activated complex (product). Through the isothermal methods (heat flow as a function of time) it was determined that the formation reaction of PU is a reaction of nᵗʰ order or an autocatalytic reaction. The synthesized PU was also evaluated by Infrared Spectroscopy (FTIR) in order to investigate the possible combinations between functional groups.

Keywords: Polyurethanes, Cure Kinetics, Polymer Characterization, Ricinoleic Acid, Activation Energy.

1. INTRODUCTION

Discovered and patented by Otto Bayer and co-workers in the end of the 1930s, polyurethanes (PUs) have been occupying positions of increasing importance among the most used polymers due to their great versatility in terms of technological applications, ranging from paints, adhesives, thermal and acoustic insulators, kitchenware, toys, coatings and packaging to implants in human beings (biomaterials) (Rodrigues et al., 2005; Xue and Greisler, 2003; Mahkam and Sharifi-Sanjani, 2003; Ren and Robinson, 2002). For such applications, a wide variety of monomers can be used, allowing synthesizing the polymer according to the final product, including materials derived from renewable resources. PUs have as a chemical characteristic the presence of urethanic bonds in PUs chains is a chemical characteristic, which is a result of the reaction between an isocyanate (di or polyfunctional – NCO) and a polyl, containing two or more reactive groups (OH). Besides, different compounds, such as cure and expansion agents, catalysts, additives and fillers, are commonly employed in the manufacture (Wegener et al., 2001; Trovati et al., 2010; Cordeiro et al., 1997).

The cure reaction of thermosetting polymers involves the formation of a rigid three-dimensional network and it is a complex process. Understand the mechanisms and kinetics of the cure reactions are essential for designing materials with required properties and applications. The kinetic method based on calorimetry concepts appears as a good alternative to investigate the structure-property relationships and how operating conditions affect the obtained material. Models for curing kinetics are generally developed by analyzing extensive experimental results obtained by DSC both in the isothermal and dynamic methods. Differential scanning calorimetry (DSC) which measures the heat flow of the resulting system is a very convenient tool to study the overall cure of polyurethanes and others thermosetting polymers (Barbosa et al., 2009; Vinnik and Roznyatovsky, 2003; Ghaemy et al., 2007; Ramírez et al., 2007; Vyazovkin and Shirazuki, 1996).

The synthesis of vegetable oil-based PU has received much attention in the last decades, especially due to the renewable nature of this feedstock and its ecological appeal, which makes that research with this type of material follow the global trend. In this study, the employed polyl was ricinoleic acid (12-hydroxy-octadec-9-enoic acid), derived from castor oil (85 -
95% of the oil composition) (Elwell et al., 1996), (Hablot et al., 2008), (Suarez, 2007). The polyol reaction was developed with one type of isocyanate derived from HDI (hexamethylene diisocyanate): HDT (trimer of hexamethylene diisocyanate).

The purpose of this study is to determine the cure conditions of polyurethanes, the activation energy and the analysis of the functional groups present in the formed polymers. The chosen techniques for data obtention were Differential Scanning Calorimetry (DSC) with both dynamic and isothermal methods and Fourier Transform Infrared Spectroscopy (FTIR).

![Fig. 1: Polymerization reaction between HDT and ricinoleic acid](image1)

![Fig. 2: Product (PUT 1.5) of the reaction between HDT and ricinoleic acid](image2)

2. MATERIALS AND METHODS

2.1. Materials

Ricinoleic acid was provided by A. Azevedo Ind. e Com. de Óleos LTDA (Brazil). Properties: acidity index of 186.6 mgKOH/g; saponification index of 198.6 mgKOH/g and hydroxyl index of 167.6 mgKOH/g. The ricinoleic acid is stored in plastic bottles and kept away from light, heat and humidity. The informed purity was of 99%; thus, the polyol was used without further purification. The employed isocyanate, derived from HDI, was the HDT (trimer of hexamethylene diisocyanate), a medium-viscosity aliphatic polyisocyanate. These HDI-derived isocyanates were chosen due to their easy handling.
and, especially, for presenting lesser toxicity than other available isocyanates. According to Perstorp, HDT (viscosity of 2400 mPa.s; 100% of solids and under 0.2% of free monomers) present 22% of NCO.

2.2. Methods

DSC is a technique that measures the temperature and heat flow associated to material transitions (reactions) as a function of time and temperature in a controlled atmosphere. Thus, acid ricinoleic + HDT system was monitored and analyzed through DSC in a Mettler Toledo DSC 823e calorimeter. The measurements were carried out on samples weighing between 7 and 8 mg and an empty cell as a reference. The samples were prepared adopting NCO/OH ratio equal to 1.5 (PUT 1.5). Then, the samples were placed in aluminum pans, which were hermetically sealed and put in the DSC equipment for analysis. Dynamic analyses were performed at 5, 10 and 20 K/min heating rates and in the temperature range from 300 to 525 K. A nitrogen source was used as purge gas, with a flow rate of 50 ml/min.

The isothermal method (heat flow as a function of time) and the non-isothermal or dynamic method (heat flow as a function of temperature) present advantages in comparison to traditional ones due to their quickness and simplicity in the determining kinetic parameters with DSC analysis (Machado and Matos, 2004), (Canevarolo, 2004). Depending on the chemical elements involved, the reaction may be represented by a $n^{th}$-order or an autocatalytic reaction.

Isothermal analyses were carried out at the temperatures of 318, 333, 348, 363 and 378 K for 30 min each. All results were obtained using the Vyazovkin method (Vyazovkin and Sbirrazzuoli, 1996).

FTIR technique is especially useful in the measurement of the degree of polymerization in the manufacture of polymers, thus being interesting in this study. The infrared spectra were obtained with a Nicolet 6700 equipment from Thermo Scientific and the measurements were made in the transmittance mode with the TRANSMITANCE accessory in the 4000-400 cm$^{-1}$ wave number range, with 32 scans and resolution of 4 cm$^{-1}$. These methods are advantageous in being more precise and sensitive, requiring less sample quantities and obtaining results in short time (Souza et al., 1998).

![Fig. 3: DSC curves (dynamic method) for PUT 1.5 synthesis](image)

3. RESULTS AND DISCUSSIONS

The reaction between the HDT isocyanate and ricinoleic acid, shown in Fig. 1, generates PUT 1.5 polyurethane (Fig. 2) as the main product and also releases CO$_2$.

The first OH to react must be the one from the acid function, because its hydrogen is more acid than that of the alcohol function and better stabilizes the negative charge. Besides, the carbinolic hydroxyl (from the alcohol) is secondary and more sterically hindered, i.e., the bonded alkyl groups partially and
spatially difficult the reaction with it. The reaction control must be due to kinetics and the bonds are mainly intermolecular: it is more favourable for a NCO group to approach the second hydroxyl and react than to reach a certain spatial conformation able to react with the second NCO group from the same molecule.

The PUT 1.5 presented exothermic reaction behavior. The curves for the different heating rates, the heat amount and the temperature range necessary to polymer cure are shown in Fig. 3. It was observed that the reactions occurs between 352 and 400 K. With higher heating rates, it is possible to perceive a great heat flow variation between the initial and maximum temperatures (reaction’s peak temperature). Through the plots, it can be determined in which temperature range the polymerization takes place, i.e. the polymer cure. At the beginning of the reaction the process is very rapid and disordered, so that is difficult to establish any kinetic parameter at this stage as well as at the end of the reaction. In this latter case
the reason is that few groups are still available to respond, and again the description of this curing phase is not representative of the kinetics as a whole. The exothermic event is recorded in lower temperatures at lower the heating rate, because low heating rates allow to observe the conversion of a majority of chemical groups present in the reaction of thermosetting polymers (Costa et al., 2005), (Costa et al., 2006). The lowest observed peaks in the beginning of the dynamic section are due to a start-up effect (effect of the oven’s initial thermal inertia).

Fig. 6: Isothermal profiles for the PUT 1.5 system

Fig. 7: FTIR spectra of reactants and PUT 1.5 polymer

Fig. 4 shows the experimentally-obtained conversion and Fig. 5 present the activation energy ($E_A$) calculated by the Vyazovkin method for the studied PUT 1.5 system. It can be observed that, for lower heating rates, the polymerization reaction starts at lower temperatures. This behavior is justified
through the fact that the sample remains under heating action for longer periods, thus favoring energy distribution and polymer cure, according to mentioned above.

The chemical kinetics is often limited by diffusion and/or mobility control. In principle, the reaction can proceed to a point $T_p > T_{ure}$, where all movement ceases and the chain reaction is not more extended due to the complete absence of polymer chains mobility. This conduces to a lower conversion end to the unit of diffusion under controlled conditions, which can causes differences in the activation energy (EA) (Fig. 5). The final conversion can also be lower due to the fact that other reactive groups can not react even in the absence of any diffusion impediment. It is important to take into account the cure rate as a function of conversion fraction, temperature and time, since the temperature at which a chemical reaction occurs affects significantly the reaction rate (Ghaemy et al., 2007). The $E_A$ values experimentally determined are reasonable and consistent with the literature for activation energies. This energy is the necessary amount to form an activated complex (product) from the reactants.

Considering the dynamic analyses, isothermal analyses were performed to identify the nature of the reaction mechanism. Analyzing the plot in Fig. 6, it can be seen that, the greater the temperature to which the material is exposed, the greater is the thermal energy amount supplied to the system and, in consequence, lower the time for reaction completion. It is possible to assume that the PUT 1.5 polymerization reaction is of $n^\text{th}$ order. Curves in Fig 6 remain unchanged after 15 min of analysis time.

Isocyanate consumption is directly linked to polymerization kinetics, i.e., to the formation of urethanic bonds (conversion of the NCO group into a urethanic group). Through FTIR analysis (Fig. 7), it is possible to know if conversion was total or if traces of excess isocyanate are still present after polyurethane synthesis. The isocyanate groups present axial deformation of double bonds accumulated in the 2280 cm$^{-1}$ region (Silverstein et al., 2006). These peaks almost disappear in the polymer spectra since these bonds are broken in order to form urethane bonds.

Characteristic peaks of PU were observed in the range of 3360 cm$^{-1}$, which represent the NH group belonging to the urethane bond; of 2928-2856 cm$^{-1}$, characteristic of asymmetrical and symmetrical vibrations of the CH$_2$ group respectively; of around 1690 cm$^{-1}$, assigned to C=O bonds of urethane and ester groups; of 1456 cm$^{-1}$, characteristic of the asymmetrical vibration of the CH$_2$ bonds; of 1239 cm$^{-1}$, assigned to the CO-O ester group, being in agreement to the results found in the literature (Trovati et al., 2010), (Elvell and Ryan, 1996).

4. CONCLUSIONS

Reaction monitoring using DSC analysis, with the dynamic and isothermal methods, was adequate to determine the behavior, the temperatures and the heat involved in PUT 1.5 synthesis. It was possible to calculate the kinetic parameters of the synthesis reaction (activation energy) and those of the cure process of the PUT 1.5. FTIR spectroscopy showed the characteristic absorption region of each material, being an useful technique in polymer characterization. These results allow the study of the applicability of this polymer in rapid prototyping techniques. The characterization and evolution kinetics of the formed PUs were investigated in order to provide a comprehensive study on the subject, complementing the data on equivalent systems currently available in the literature.

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