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Structural and thermal degradation properties of novel metallocene-polyurethanes

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ABSTRACT

Thermal degradation of two series of chemically well-defined polyurethane (PU) elastomers have been studied using thermogravimetry coupled with a mass spectrometer (TG-MS), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The samples were synthesised such that they contained two different soft segments (SSs) that are of great interest for aerospace applications. At a given soft fragment, four different hard segments (HSs) based on single diisocyanate molecules (i.e., isophorone diisocyanate (IPDI), toluene-2,4-diisocyanate (TDI), 4,4′-diphenyl methane diisocyanate (MDI) and hexamethylene diisocyanate (HMDI)) were used with no chain extenders. Each segmented PU family was prepared by stoichiometric reactions of macrodiol hydroxyl-terminated polybutadiene (HTPB) and a metallocene-derived one (i.e., (ferrocenylbutyl)dimethylsilane grafted on HTPB, which is also known as Butacene). The structure of the macroglycols and the prepared PUs were studied using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies. Both the catalytic effect of the ferrocenyl group and the influence of the HS nature on the thermal behaviour of these PUs polymers have been elucidated. In addition, the gaseous volatile products released during the thermal decomposition process have been investigated, and these products are of interest in propulsion chemistry. Understanding the structure-property relationships of these advanced organometallic PUs is relevant for application as a solid composite propellant binder.

1. Introduction

Polyurethanes (PUs) are a versatile class of polymers in which the urethane groups are primarily responsible for most of their important physical properties. Due to the presence of hydrogen bonding, PUs are often the best choice in demanding high-performance applications. PUs are typically prepared via polyaddition of low and/or high molecular weight diols and diisocyanates. PU elastomers are an important group of these materials that are widely used as engineering materials and well known for their outstanding mechanical, thermal, and adhesive properties. These elastomers consist of an alternating flexible component or macrodiol, which is known as the soft segment (SS), and a stiff component derived from diisocyanate as well as a chain extender, which is referred to as the hard segment (HS). The interactions between the HSs containing many hydrogen bonds and dipole-dipole interactions provide a pseudo-cross-linked network structure between the linear PU chains [1,2].

One of the most relevant applications for these PUs that contain hydroxyl-terminated polybutadiene (HTPB) as the SSs is as a fuel binder in energetic composite materials in the aerospace field. The telechelic HTPB is the most commonly used polyol because it imparts excellent physical properties to the rubbery phase including a low glass transition temperature, high tensile and tear strength, and good chemical resistance [3,4]. Composite propellants are highly particle-filled elastomers that are used in solid rocket motor technology. Most state of the art composite solid propellants are composed of HTPB, which is a finely divided oxidiser (*i.e.*, typically ammonium perchlorate), and in many cases, incorporate a reducing agent, such as aluminium. Other minor chemical ingredients include diisocyanate, plasticisers, antioxidants, and a burning rate modifier.

Recently, much attention has been focused on the development of functional PUs because applications that are outside of the classical PU market are anticipated. However, the high reactivity and poor selectivity of the diisocyanates have limited the introduction of functional groups onto the PU backbones. One route for

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obtaining functional PUs based on HTPB involves pendant vinyl groups. Side-chain functionalisation is the most applied technique for the introduction of functional groups along the polymer backbone [5–8]. For example, functional metallo-polyols have been obtained from HTPB (*i.e.*, Butacene). This material consists of a (ferrocenylbutyl) dimethylsilane grafted on HTPB and is synthesised from the addition of an organo-silicone ferrocene derivative to the HTPB. This type of material has the potential to be used as a binder and a non-migrating burning rate catalyst in high burning rate solid composite propellants and constitute a family of new metallocene-PUs used in the formulations of these advanced energetic materials [9].

Then, the structure-property relationship in these novel functional PUs are important to study to extend their application fields beyond those sectors related to the improvement of catalytic processes for solid propellants. Therefore, in a previous study, the microphase separation and morphology development in these copolymers have been studied at room temperature. Moreover, dynamic mechanical analysis and differential scanning calorimetry (DSC) have been used to elucidate their relaxation processes and thermal transitions [8]. However, the thermal decomposition of these materials has not been previously investigated. An important characteristic of any material is its thermal stability, especially based on the potential end uses in various fields.

The thermogravimetric analysis (TGA) is a valuable tool for gaining a better understanding of the degradation mechanisms of polymers, such as PUs [10]. In recent years, a TG instrument was coupled to an evolved gas analyser, such as a mass spectrometer (MS), for use as a powerful analytical technique that is highly precise and sensitive. The determination of the volatile products that are released during the thermal degradation and monitoring of their thermal evolution using TG-MS analysis provides insight into the nature and mechanism of the thermal decomposition. In addition, this type of TG-MS analyses of PUs are important because the combustion of solid propellants is known to proceed through a series of physico-chemical processes that are significantly influenced by the polymeric fuel binder, which functions as the continuous phase in the propellants [11].

The aim of this study was to investigate the effect of variation of the SS and HS molecular structures on the thermal decomposition properties of two families of PUs that were synthesised from two distinct SS macrodiols, HTPB and Butacene. In addition, various diisocyanates have explored the development of HSs without chain extenders. The diisocyanates of these rigid blocks are either aliphatic, such as isophorone diisocyanate (IPDI) and hexamethylene diisocyanate (HMDI), or aromatic, such as toluene-2,4-diisocyanate (TDI) and 4,4′-diphenyl methane diisocyanate (MDI). These isocyanates are very common in PU chemistry. In general, these isocyanates are most frequently used in industry, and some of them are employed in energetic materials. To study the structural and thermal degradation properties of these PUs polymers in more detail, we have focused on TGA of the different samples. The measurements obtained using the coupled TG-MS system along with those obtained from differential thermal analysis (DTA) and DSC have been used to evaluate and compare the different thermal features of these PUs polymers, and the structural characteristics of these polymers were examined using Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopies.

2. Experimental

2.1. Materials

Butacene (*i.e.*, (ferrocenylbutyl) dimethylsilane grafted to HTPB) was produced and provided by SNPE (Butacene®800). Butacene synthesis consists of the addition of an organo-silicone ferrocene derivative to a low molecular weight HTPB via the pendant vinyl group. According to the supplier, this metallo-prepolymer has an OH value of 0.33 eq/kg and an iron content of approximately 8 wt.%. The HTPB was manufactured by Santomer (Poly bd® R45M) with an OH value of 0.72 eq/kg. The different isocyanates (*i.e.*, IPDI, HMDI, TDI and MDI) were supplied by Hülls, Aldrich and Fluka and used as received. The chemical formulas corresponding to these reagents are shown in Scheme 1.

2.2. Sample preparation

Both prepolymers (*i.e.*, Butacene and HTPB) were previously dried and degassed for at least one hour under vacuum at 60–70 °C using a rotary flash evaporator, and then, they were maintained under a nitrogen atmosphere prior to use. The polyols were hand-mixed and homogenised using vigorous agitation with each isocyanate for several minutes at room temperature to prepare the PU samples. The stoichiometric ratio between isocyanate and hydroxyl functionalities was one (*i.e.*, $r = [NCO]/[OH] = 1$). After the reactants were thoroughly mixed, the samples were cast and allowed to cure under vacuum at 70 °C for 7 days. The eight studied PU systems are referred to as HTPB-IPDI, HTPB-HMDI, HTPB-TDI, HTPB-MDI, Butacene-IPDI, Butacene-HMDI, Butacene-TDI and Butacene-MDI. The compositions of the synthesised PUs are listed in Table 1.

2.3. PU characterisation and thermal degradation properties

Fourier transform infrared (FTIR) spectroscopy analysis was performed at room temperature with a Perkin Elmer Spectrum 2000 FTIR instrument operating in the 4000-600 cm^{-1} range. A drop of the various reagents was smeared between two sodium chloride windows. In addition, the diisocyanate-prepolymer reactive mixture with an approximate thickness of 0.5 mm were sandwiched between these windows and isothermally cured at 70 °C for one week.

The ^{13}C cross-polarisation magic angle spinning (CP MAS)-NMR spectra were recorded on a Bruker Advance TM 400 EB spectrometer using a standard cross-polarisation pulse sequence at room temperature. The samples were spun at 10 kHz. The spectrometer frequency was set to 100.62 MHz. A contact time of 1 ms and a period between successive accumulations of 5 s were used. The number of scans was 1600. The chemical shift values were referenced to TMS (trimethylsilane). The proton-decoupled ^{13}C NMR spectra of both macroglycols (*i.e.*, HTPB and Butacene) were recorded on a Varian Inova 400 in $CDCl_3$ at room temperature.

Thermal analysis. Thermogravimetry (TG), differential scanning calorimetry (DSC) and differential thermal analysis (DTA) measurements were performed using a simultaneous thermal analyser model SDTQ-600/Thermo Star of TA Instrument. The non-isothermal experiments were carried out under dynamic conditions from room temperature to 1000 °C at a heating rate of 10 °C/min under an argon atmosphere. The average sample weight was ~10 mg, and the argon flow rate was 100 ml/min. A coupled TG-mass spectrometer (TG-MS) system equipped with an electron-impact quadrupole mass-selective detector (model Thermostar QMS200 M3) was employed to analyse the main species evolved during the dynamic thermal decomposition of all of the samples.

3. Results and discussion

3.1. Structural study of PUs

The structural characteristics of both series of the two component PU systems were previously evaluated using NMR and FTIR