

Experimental and molecular dynamics studies of the thermal decomposition of a polyisobutylene binder

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Abstract

Polymer debinding is involved in many powder metallurgy processes, where clean removal of the binder is essential to ensure a sound product. This investigation focuses on polyisobutylene (PIB) as a fugitive binder, with titanium powder as a model system. The kinetics and products of debinding were evaluated using thermogravimetry, Fourier transform infrared evolved gas analyses and gas chromatography/mass spectrometry. The monomer isobutylene was identified as the most abundant decomposition product; however, other species including 2,2,4-trimethylpentane and oligomers of isobutylene were also observed. Computer simulations were carried out using a reactive molecular dynamics code, to clarify further the decomposition mechanisms, reaction paths and the possible effect of titanium on decomposition. Both computer and experimental results indicate that the presence of the titanium does not affect the kinetics of the decomposition of PIB, but does influence secondary reactions, e.g., further dissociation of the monomer.

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1. Introduction

Powder metallurgy is a widely used manufacturing process in industry. Fugitive binders are employed in many powder pre-processing stages to produce near-net shapes or pre-forms, and have to be cleanly removed at an intermediate temperature before sintering of the final product. Particular examples are titanium (Ti)-based alloys, intermetallics and composites, which are attracting great attention from the aerospace, automobile, healthcare and sports industries, due to their high weight specific mechanical properties and corrosion resistance. Traditionally, components of Ti-based alloys are manufactured via casting and/or forming processes. However, powder metallurgy is increasingly favoured for improved microstructural control and mechanical properties. The addition of a fugitive binder

into the powder offers further flexibility and capability in powder-based manufacturing, such as slurry powder processing of Ti/SiC composites [1,2] and near-net shaping via injection moulding [3,4]. Here, it is critical that the binder undergoes complete decomposition into small and volatile (non-toxic) compounds, without leaving any residues in the pre-form. Hence, it is important to understand clearly the decomposition mechanisms of the binder and whether it interacts with metallic powder particles.

Polyisobutylene (PIB) is a potential fugitive binder because of its favourable rheological properties. Furthermore, the thermal decomposition profile of PIB is much simpler than other known binders [5], and it is capable of undergoing complete decomposition at relatively low temperatures. Thermal decomposition of PIB has been the subject of several investigations in the past [6–9], and its potential application as a binder has also been reported [5,10–14]. Previous experimental studies suggest that the thermal decomposition of PIB is initiated by random

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scissions of the polymer chain, which produce primary and tertiary macroradicals [10–14]. Once formed, these macroradicals are believed to undergo β -scission and hydrogen transfer reactions, producing a broad distribution of molecular fragments, such as monomers, dimers and a variety of saturated and unsaturated hydrocarbons. However, there is a lack of detailed and quantified understanding of PIB thermal decomposition, due to the limitations of the experimental techniques used previously. Although the decomposition products and possible reactions were deduced via experimental observations, there is no information on the actual reaction paths and the influences of the reaction paths on the final products at different debinding conditions. Moreover, it is unclear whether the powder particles influence the thermal decomposition reactions and their kinetics. On the theoretical front, kinetic modelling of diffusional monomer removal in a powder compact or powder/fibre compact has been reported in several publications [15–19]. However, there has been little study of the fundamental mechanisms, reaction products and kinetics of binder decomposition. All of the above are essential in order to understand the decomposition behaviour and to optimise the processing parameters in powder processing. In the study reported here, both experimental and modelling approaches were employed to tackle these issues.

Thermogravimetric (TG) and spectroscopic measurements were carried out to provide further insight into the thermal decomposition of PIB and the possible effect of Ti powder on the decomposition. Computational simulations were carried out using reactive molecular dynamics (RMD) to further investigate the reaction paths, transient reactions and the influence of local molecular environment on the reactions. The results were compared with experimental observations for the binder system.

RMD is a molecular dynamics (MD) simulation method with reactive force fields, and can be used to simulate chemical reactions in large atomic and molecular systems. RMD has been employed to simulate thermal decomposition reactions in previous investigations using a computer program, MD_REACT [20–27]. This programme is based on a dynamic force field representation of the potential energy surfaces for a wide range of elementary chemical reactions. While classical MD has been used extensively in the past for the investigation of phase transitions, molecular transport and other properties that depend on conformational structure, MD_REACT represents the first systematic effort to extend this approach to model thermally induced chemical transformations in large molecules in condensed phases.

The main feature that distinguishes MD_REACT from other implementations of MD is that covalent bonds are allowed to break and form during the simulations. This provides the ability to simulate chemical reactions, which are modelled by the following algorithm. After each time step of simulation, a fractional bond order is computed for all the covalent bonds in the system. These bond orders are compared to a pre-defined criterion for bond dissocia-

tion (BDC) [21]. If the bond order is less than or equal to BDC, the bond is eliminated and the information about the covalent connection is erased from the database. The atoms that were connected by the former bond are considered to be chemically active and are labelled accordingly. At the next stage, a new set of potential bonds is generated, consisting of all possible covalent interactions between the chemically active atoms. The most energetically favourable bonds are retained. The maximum number of bonds for each atom is determined by the rules of atomic valence. Once the bond analysis is complete and the structural information is updated, the next time step of MD is executed. Further details of the MD_REACT algorithm and force field can be obtained from our previous publications [20–29].

2. Experimental

The materials used in the experimental part of the investigation were PIB as the binder (number average molecular mass: 4.0×10^5 g mol⁻¹; polydispersity: ~ 1.8) [29], and angular-shaped pure Ti powder with a maximum particle size of 150 μ m in diameter. The binder was first dissolved in cyclohexane. Ti powder was added to this organic component to produce homogeneous slurry. This slurry was then cast into a tape containing 90% Ti and 10% PIB by weight. Details of green tape preparation via tape casting have been reported elsewhere [10]. Samples for investigation were obtained from the dried powder tape.

The kinetics of the sample mass-loss was investigated using TG with a Perkin–Elmer TG7 analyser. Samples of about 5 mg of pure PIB and 10 mg of Ti/PIB were heated from 353 to 973 K at 5, 15 and 45 K min⁻¹. The experiments were conducted in a nitrogen atmosphere (the furnace was continuously purged with 80 cm³ min⁻¹ of ultrahigh-purity nitrogen). Every sample was kept in the nitrogen flow at 353 K for 2 h before the beginning of the test.

The rate constants were directly calculated from the dynamic TG data over the temperature range 620–730 K using the formula

$$k_d = -\frac{\Delta m}{\Delta t(m - m_{\text{res}})} \quad (1)$$

where m is the instantaneous mass, Δm is the change in the mass during the time Δt and m_{res} is the residual mass at the end of the experiment. In the case of Ti/PIB samples, the mass of the sample at 773 K was used as m_{res} . The rate constant data obtained from each TG experiment were fitted to the Arrhenius expression [30]:

$$\ln k_d = \ln A - \frac{E_a}{RT} \quad (2)$$

where R is the gas constant and T is the absolute temperature in kelvin. The activation energies, E_a , and pre-exponential factors, A , were obtained from the average values of the slopes and intercepts from the linear fits to each of the TG experiments.

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