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Thermal volatilisation analysis of TDI-based flexible polyurethane foam

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ABSTRACT

The thermal degradation behaviour of a polyurethane foam, synthesised from TDI and a polyether polyol, is reported. The thermal degradation behaviour of this material was evaluated by a combination of thermogravimetric analysis (TGA) and thermal volatilisation analysis (TVA). The results demonstrated that the thermal degradation is a complex process which consists of competing mechanisms which yield an array of degradation products. The TVA results revealed that the degradation occurs in two steps, with the initial step corresponding to degradation of the urethane linkages by two competing mechanisms. The first mechanism, proposed to be the predominant mechanism, involves simple depolymerisation of the urethane bond to yield TDI and polyol. A second, competing mechanism is proposed to occur which involves dissociation of the urethane linkages to yield DAT, CO_2 and alkene-terminated polyol chains. The second degradation step has been shown to involve degradation of the polyol which was regenerated in the first degradation step. This is proposed to occur by random radical chain scission of the polyol to yield propene, formaldehyde, acetaldehyde, C_3H_6O isomers and high molar mass polyol chain fragments of various structures. Isothermal TVA studies have revealed that this occurs as low as 250 °C under vacuum but does not become significant until temperatures greater than 300 °C.

1. Introduction

Polyurethanes are one of the most versatile classes of polymers which find vast use in today's society. However, a major drawback of these materials is their ease of flammability and the toxic nature of the gases which are evolved. Polyurethane foams, in particular, are widely used in upholstery and home furnishings and, as a result, are often major contributors to fires. At present there are effective fire retardant formulations available, although many of these are now regarded as environmentally unacceptable. There is, therefore, the need to develop new formulations for use in polyurethane foams. The behaviour of a polymer in a fire is closely associated with its degradation behaviour and, as a result, much research has been conducted to study the thermal stability and degradation of polyurethane materials. The chemistry occurring during the degradation, and the effect of fire retardants on this process, must be fully understood if fire retardant systems are to be effectively employed. Polyurethane foams are complex materials which contain a variety of functional groups (*e.g.* urethane, urea, biuret, allophonate) that lend the foams different physical properties and which can even vary across the cross-section of a foam as a result of temperature gradients during processing [1–3]. The thermal degradation of polyurethane is, therefore, unsurprisingly complex; it depends on the structure of the material, making it strongly dependent on the type of polyol or polyisocyanate from which it is synthesised. The presence of additives, such as fire retardants, can also significantly affect the degradation processes which occur.

It is generally accepted throughout the literature that the purely thermal degradation of the urethane linkages within polyurethane (the primary degradation step) occurs between 200 °C and 250 °C by one or more of the three mechanisms shown in Fig. 1 [4–7]. Reaction I involves the breaking of one N—H bond (386 kJ mol^{-1}) and one C—O bond (358 kJ mol^{-1}). Reaction II on the other hand requires a greater input of energy in order to break the C—N (305 kJ mol^{-1}), C—O (358 kJ mol^{-1}) and C—H (411 kJ mol^{-1}) bonds. Reaction III is the least energetic involving the rupture of a C—N (305 kJ mol^{-1}) and a C—O (358 kJ mol^{-1}) bond. It has been reported by many authors that the depolymerisation reaction (I) is the predominant degradation reaction for the urethane linkage [4,5,7–9]. If depolymerisation occurs the diisocyanate will be the major volatile species which can be evolved, although it can also undergo secondary decomposition reactions. Depolymerisation of

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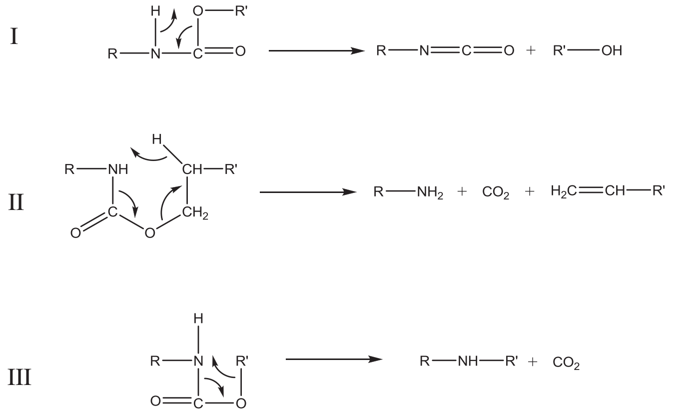

Fig. 1. Mechanisms of degradation of the urethane linkages. Mechanism I involves depolymerisation of the urethane group to yield the original isocyanates and polyol monomers. Mechanism II involves dissociation of the urethane group *via* a six-membered ring transition state to form a primary amine, an olefin and carbon dioxide. Mechanism III involves dissociation of the urethane group *via* a four-membered ring transition state to form a secondary amine and carbon dioxide.

the urethane linkages would leave a residue containing almost exclusively regenerated polyol. If, on the other hand, the diisocyanate cannot volatilise it will become trapped within the pyrolysis zone and the reverse of reaction I can occur, i.e. the polyol and isocyanate can recombine to reform the urethane bond, and equilibrium would therefore become established. It has been reported in this situation that mechanism II, which is slower but irreversible, would become the more favoured reaction [4,5] and the major degradation products evolved would be an amine and carbon dioxide. In this case the residue would resemble the polyol but with an unsaturated end group. It has also been reported that degradation *via* mechanism II can become predominant if the alcohol or polyol employed has a β-hydrogen [10,11]. There have, however, been few reports of mechanism III occurring to any great extent.

Following the primary degradation step, the polyol or polyol-based material generated will then undergo degradation reactions to produce secondary degradation products. The majority of polyether polyols employed in the production of flexible polyurethane foams are derived from poly(propylene oxide) (PPO) and poly(ethylene oxide) (PEO), or co-polymers thereof [12,13]. These materials are believed to undergo thermal degradation *via* random homolytic chain scission along the polymer backbone to yield a variety of degradation products containing hydroxyl, carboxyl, carbonyl and ether groups [14–17].

A number of studies have been published on the thermal degradation chemistry of polyurethane materials; however, the literature concerning the degradation of foams is limited. The majority of studies have been concerned with elastomers and model compounds usually containing only one functional group, such as a urethane bond. In particular, there is more limited knowledge on the processes which occur during the degradation of toluene diisocyanate (TDI) based foams as most studies have been conducted on methylene diphenyl diisocyanate (MDI) based materials. This is despite the fact that TDI is the isocyanate of choice for the majority of flexible foam formulations in the UK and North America. In this communication we report on the thermal degradation behaviour of a TDI-based polyurethane foam with the aim of expanding on the limited knowledge available on these systems. The thermal stability and degradation mechanisms of this material have been studied in detail, with particular use of the technique of thermal volatilisation analysis (TVA), an invaluable tool for studying polymer degradation.

2. Experimental

2.1. Materials

Flexible polyurethane foam was prepared in the University of Strathclyde following a patented flexible foam formulation [18]. The isocyanate employed was TDI (with an isocyanate index of 108) and the polyol was Alcupol F-5611 (a trifunctional polyether polyol of molar mass 3000 g mol^{-1} and hydroxyl index 56 mg KOH g^{-1}). Typically, the isocyanate was incorporated at a level of 46 parts per hundred polyol (pph). Water (3 pph) was employed as the blowing agent and the catalysts employed were dimethylethanolamine (DMEA, 0.3 pph), triethylenediamine (Dabco 33LV, 0.3 pph) and stannous octoate (Kosmos 29, 0.8 pph). A silicone-based surfactant (L620LV, 1 pph) was also employed. It should be noted that the levels of surfactant and catalyst present are sufficiently low to assume that these do not participate in or affect the degradation reactions which occur.

2.2. Thermogravimetric analysis (TGA)

All TGA experiments were carried out using a Perkin Elmer TGA7 thermogravimetric analyser with 3–5 mg cylindrical foam samples being analysed. The system was initially heated to 50 °C and held isothermally for 5 min. Following this, the sample was heated at a rate of 10 °C min^{-1} from 50 °C to 800 °C under a flow of 30 ml min^{-1} of helium. The mass loss as a function of temperature was monitored and from this the first derivative of the mass loss curve was calculated as a function of temperature. The temperature at which the onset of degradation occurs has been determined from the TGA curves and will be reported herein as the temperature at which the material has lost 5% of its original weight.

2.3. Thermal volatilisation analysis (TVA)

All TVA analyses were carried out using a TVA line which was built in-house, based upon the apparatus and techniques described by McNeill et al. [19] The apparatus consisted of a sample chamber (heated by a programmable tube furnace) connected in series to a primary liquid nitrogen cooled sub-ambient trap. The whole system was continuously pumped to a vacuum of 1×10^{-4} Torr by means of a two stage rotary pump and oil diffusion pumping system. Volatile condensable products could be initially trapped at two stages: the water jacket cooled 'cold-ring' immediately above the heated area of sample tube which condenses high boiling point materials which are not volatile under vacuum at ambient temperature, and the primary liquid nitrogen cooled sub-ambient trap which collected all the lower boiling point species which are volatile under vacuum at ambient temperature but which condense under vacuum at liquid nitrogen temperatures. A linear response Pirani gauge positioned at the entrance of the primary sub-ambient trap monitored the evolution of the total volatiles (condensable and non-condensable species) from the sample as a function of pressure *vs*. temperature/time. A second Pirani gauge at the exit of the primary sub-ambient trap monitored the evolution of the non-condensable volatiles (carbon monoxide, methane, hydrogen) as a function of pressure vs. temperature/time. Trapped, low-boiling species could be distilled into separate secondary cold traps by slowly heating the primary sub-ambient trap to ambient temperatures. These fractions could be subsequently removed into gas-phase cells for FTIR and GC–MS analysis. A series of non-linear Pirani gauges were placed at the entrance and exits of all secondary traps to monitor the pressure changes as volatile species were distilled into separate traps and gas-phase IR cells.