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Material Behaviour

Compositional elements of thermoplastic polyurethanes for reducing the generation of acetaldehyde during thermo-oxidative degradation

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ABSTRACT

Volatile organic compounds (VOCs) have been become of prime importance in polymer industry due to the increased concerns regarding their effects on the environment and health. Comprehensive understanding of the factor controlling the generation of VOCs and the development of a quantitative analytical tool for tracking the generation of VOCs have thus been an important topic for researchers. In this study, thermoplastic polyurethanes (TPUs) composed of different polyols, diisocyanates, and chain extenders were carefully synthesized to investigate the effect of the compositional factors on the generation of VOCs, especially acetaldehyde (AA). Headspace-gas chromatography equipped with simple flame-ionization detector (HS-GC-FID) was successfully set-up for the quantitative monitoring of the generation of AA at different thermal treatment temperatures and times. The generation of AA was accompanied by the degradation of TPU chains during the thermal treatments, as evidenced by the decreased molecular weight of the TPUs. Interestingly, TPUs with polyester- and polycarbonate-based TPUs exhibited a significant reduction of AA emissions, compared with TPUs with typical polyether-based polyols, poly(propylene glycol). TPUs with aromatic diisocyanates and chain extenders also emitted much less AA during the thermal treatments than TPUs with aliphatic diisocyanates and chain extenders. These results indicated the importance of the compositional factors of the TPUs for the generation of AA. Understanding and optimization of the compositional factors of the TPU by using HS-GC-FID can be a useful tool for reducing the generation of AA.

1. Introduction

Volatile organic compounds (VOCs) are organic chemicals that have relatively high vapor pressure at room temperature. VOCs are one of the most common air pollutants that are often emitted in the gas phase from polymers, leading to environmental hazards [1,2]. The requirements for reducing the amount of VOCs are continuously increasing as air quality becomes an important issue for human health, leading to regulations of the VOC emission levels [3,4]. Acetaldehyde (AA) is one of the most important VOCs generated from polymers. AA has been listed as a Group 1 carcinogen and is considered to be a critical pollutant that can be generated through thermal or thermo-oxidative degradation of polymers [5–11]. Due to the low boiling point of AA (20.2 °C), AA easily diffuses out of polymers, causing environmental and health issues. Therefore, the control and detection of AA emissions have become a mandatory task, especially for the auto industry [12].

Polyurethanes (PUs) are one of the most important classes of

polymers that are widely used in various industries due to their versatility [13–16]. Depending on their chemical compositions and chain structures, thermoplastic to thermoset PUs are readily prepared. Thermoplastic polyurethanes (TPUs) are one of the most important types of PUs and can be used in applications such as automobile parts, sporting goods, and electronic/medical devices, due to their elasticity, transparency and thermal processability [17,18]. TPUs are typically prepared by stepwise polymerization procedures, with the reaction between polyols and diisocyanates to afford prepolymers with urethane linkages in the backbone followed by the reaction of the prepolymers with low molecular weight chain extenders (Scheme 1).

Thermal or thermo-oxidative degradation of polymers has been considered as a main source for the generation of VOCs [19–21]. There have been several reports of investigation of the emission behavior of VOCs from PUs [7,22,23]. Lattuati-Derieux et al. used pyrolysis gas chromatography (GC)-mass spectrometry (MS) and headspace (HS) solid phase microextraction GC-MS to assess the degradation of PU

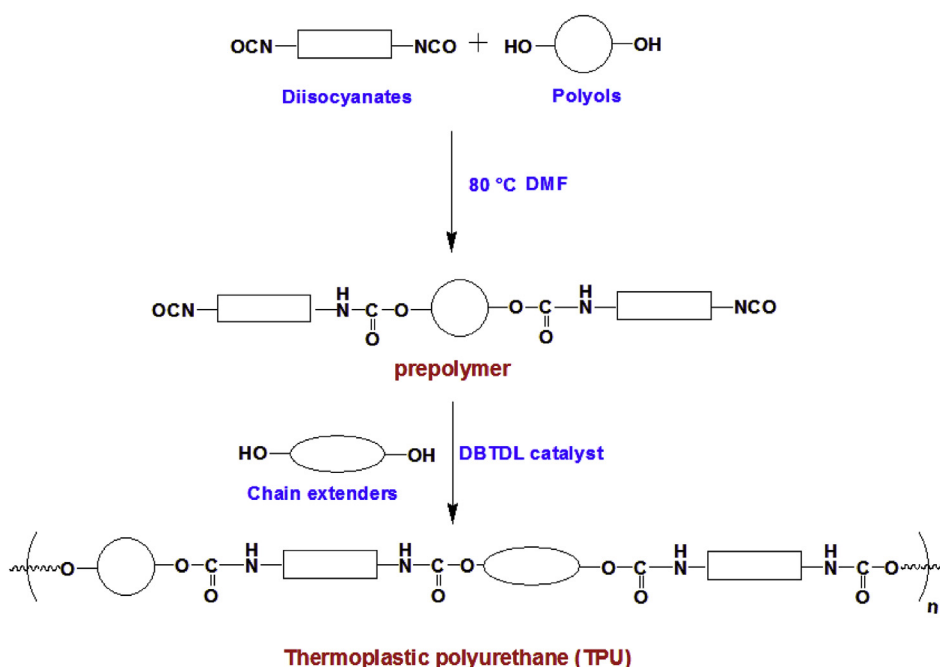
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Scheme 1. Schematic representation of the stepwise preparation of TPUs with different polyols, diisocyanates and chain extenders.

foams [24]. Huang et al. studied VOCs from spray PU foam in residential homes by thermal desorption MS [25]. Allan et al. reported VOCs from the PU foam synthesized from TDI and polyether polyol by thermal volatilization analysis [5]. PU foam with polyester polyol was examined by using an evolved gas analysis coupled to GC with MS detection [26]. However, to the best of our knowledge, there has been no comprehensive report that assessed and compared the effect of the PU compositions on the emission behaviors of AA. Moreover, in the present study, the evolution of AA was readily and quantitatively tracked using simple HS-GC equipped with a typical flame-ionization detector (HS-GC-FID). The HS-GC-FID is not only effective but also economical due to the relatively simple and less expensive equipment required for the experiments.

The aim of this study is to explore the effects of compositional factors of TPUs on the AA generation during thermal treatments in air. Controlled preparations of model TPUs with different chemical compositions were carefully performed. Scheme 2 illustrates the TPUs with different compositions employed in this study for the investigations of their AA generation behaviors [27]. The AA generation was quantitatively tracked by HS-GC-FID. The AA generation behaviors were investigated at different HS thermal treatment temperatures and times to assess the effect of different polyols, diisocyanates and chain extenders.

2. Experimental

2.1. Materials

AA ($\geq 99.5\%$, Aldrich, St. Louis, MO, USA), 2-propanol (99.5%, Aldrich, St. Louis, MO, USA), 4,4'-methylenebis(cyclohexyl isocyanate) (MHI, 90%, Aldrich, St. Louis, MO, USA), 4,4'-methylenebis(phenyl isocyanate) (MDI, 98%, Aldrich, St. Louis, MO, USA), toluene 2,4-diiisocyanate (TDI, 98%, Daejung, Seoul, Korea), 1,4-butanediol (BD, 99%, Aldrich, St. Louis, MO, USA), ethylene glycol (EG, 99.8%, Aldrich, St. Louis, MO, USA), 1,4-benzenedimethanol (BM, 99.0%, TCI, Tokyo, Japan), dibutyltin dilaurate (DBTDL, 95%, Aldrich, St. Louis, MO, USA), *N,N*-dimethylformamide (DMF, 99%, Samchun Chemicals, Seoul, Korea), and methanol (99.5%, Samchun Chemicals, Seoul, Korea) were used as received. Polyols, such as poly(tetrahydrofuran) diol (PTMEG, Aldrich, St. Louis, MO, USA), poly(propylene glycol) (PPG, Aldrich, St.

Louis, MO, USA), polycaprolactone diol (PCL, Aldrich, St. Louis, MO, USA) and CO₂-based polyol (Converge 212–20, Novomer, Boston, MA, USA), were also used without purification. The number average molecular weights (M_n) of the polyols were all approximately 2000 g/mol.

2.2. Preparation of TPUs with different compositions

TPUs were synthesized in a three-necked flask equipped with a mechanical stirrer, condenser, nitrogen inlet, and thermometer. The reactions were carried out in two steps. In the first step, NCO-terminated prepolymer was prepared by reacting polyol and diisocyanate ($[\text{NCO}]/[\text{OH}] = 1.2$) in DMF at 80 °C for 2 h. In the second step, chain extender and DBTDL (0.01 wt%) as catalyst were added to the reaction mixture at room temperature. The reaction mixture was further heated to 80 °C for 1–16 h depending on the type of polyols and diisocyanates used. Through close monitoring of the increase of the viscosity, the reaction was quenched by adding methanol at M_n values similar to those of the TPUs (Table 1). The resulting TPUs were recovered by the precipitation of the polymer from the reaction mixture under a 10-fold excess of methanol or methanol/water (70/30 vol/vol). The TPUs were then dried under vacuum at 40 °C for 24 h.

2.3. GC procedures

A Shimadzu GC-2010 instrument equipped with a flame-ionization detector (FID) was employed for the GC experiments. The GC-FID instrument was equipped with a DB-624 (60 m \times 0.25 mm \times 1.4 μm) capillary column purchased from Agilent. The injector and detector temperature were set at 250 °C. Split mode injection was used with the split ratio of 10:1. The flow rate of the nitrogen gas was 30 mL/min. The temperature of the oven was programmed to stay at 40 °C for 10 min, followed by the ramping of the temperature at the rate of 10 °C/minute from 40 °C to 120 °C. After holding the temperature at 120 °C for 3 min, the oven temperature was further increased to 210 °C at the rate of 30 °C/minute, followed by holding at the temperature for 7 min. Manual HS was purchased from Netel India Ltd. and used for the collection of gas-phase samples after various thermal treatments at 60 °C–130 °C for 5–40 min (Fig. 1). Chemical identifications of the peaks of HS-GC-FID chromatograms were conducted by independent

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