

A study on recyclable waterborne polyurethane process with a photo and thermal hybrid treatment system

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ABSTRACT

Development of a novel recycling process of waterborne polyurethane (WBPU) with a poly(oxytetramethylene) glycol (PTMG) soft segment was performed using characteristics of nitroxyl radical (TEMPO) dormant bond. A TiO_2 /hindered amine light stabilizer (HALS) combination produced the dormant bond in a 24 h UV irradiated WBPU. The WBPU extraction rate was 66% with a water-ethanol solvent, and its bond was found to contain a PTMG sequence by Py-GC/MS measurement. The binary blend of extracted WBPU and PTMG was immiscible and converted to miscible one by thermal treatment at 120 °C for 0.5 h in nitrogen. The WBPU was partially *graft*-polymerized onto the PTMG by the treatment and worked as a compatibilizer. The change to miscibility showed that the blend was recyclable as PTMG material.

1. Introduction

Polyurethane (PU) is a coating material [1–5]. To fulfill consumer demand, PU has been continuously improved and the commercial market has developed for a long time. Recently the intense use has created an environmental problem and has given rise to an intensive interest in waterborne polyurethane (WBPU) [6–14]. Since the aqueous dispersion is eco-friendly, it has been used in coatings, foams and non-porous materials such as adhesives, elastomers or thermoplastics [6–18]. Moreover, the recycling technology of PU has been vigorously developed, and commercial product has been partially recycled [16,]. For example, glycolysis has reached such a level that WBPU can be acceptably recycled as feedstock [19]. Hydrolysis of PU has been studied for many years as well [20], and decomposition product can be used as fuels [16]. The feedstock and thermal recycling methods are certainly useful; however, the value of obtained product is economically low. To obtain product with additional value, a novel PU decomposition technology is required.

A polymer reaction of poly(vinyl chloride) (PVC) has been frequently studied as a target for upgraded recycling since the product, e.g. polyene and poly(vinyl alcohol), has been attractive [21–25]. It seems that a polymer reaction is applied to WBPU as upgraded recycling as well. On the other hand, the PVC polymer reaction has a problem to be accompanied by crosslinking reaction [21]. The crosslink seriously impairs processability including melt moldability and has prevented practical applications. A WBPU polymer reaction would certainly cause it without a countermeasure as well. In our previous

work [26], photodegradation of WBPU was studied in detail, showing that the soft segment (PTMG) was selectively degraded. The PTMG degradation was composed of a chain scission and crosslink. If it is possible to perform the degradation without crosslinking reaction, development of the recycled product with additional value can be achieved. In particular, controlling the chain scission can supply a more useful high molecular weight product having a long PTMG segment. PTMG offers great flexibility and is commonly used as elastic fiber material [27]. Therefore, a recycled WBPU containing the long segment is expected for various applications, including fiber material. We have succeeded in developing a paint-type TiO_2 /PEO/HALS photodegradation catalyst system for selective decomposition of a flame retardant in polystyrene [28]. The PEO was photo-catalytically degraded by the TiO_2 , then H_2O , OH radical species (initiator), acid and aldehyde (accelerator) compounds were produced to facilitate photodegradation. The HALS produced TEMPO to prevent excess radical production [28]. The TEMPO is formed during the oxidative photodegradation, traps alkyl radical species ($\text{R}\cdot$) and then produces a dormant bond [29]. The $\text{R}\cdot$ is released from the dormant bond by thermal treatment, and its amount is controlled by adjusting the elevated temperature and retention time. It seems that the TEMPO nature would be applied to retardation of crosslinking reaction because of controlling excessive occurrence of the radical species. It should be noted here that the polymer chain contains the dormant bond; the polymer is regarded as a macromer. For example, it can react with a new polymer chain by thermal treatment and produces a *graft*-polymer and/or chain extended polymer. This macromer synthesis method is available for developing

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recycled WBPU, which has a high added value.

In this study, a novel recycling of WBPU was performed with a TiO_2 /HALS hybrid photo and a thermal degradation catalyst system. The decomposition and recycling behavior was studied with gel permeation chromatography (GPC), FT-IR, NMR and pyrolysis gas chromatography/Mass (Py-GC/MS) measurements. In addition, the macromer application was evaluated by radical reaction with PTMG polymer.

2. Experimental

2.1. Materials

A poly(oxytetramethylene)glycol (PTMG; number average molecular weight: $M_n = 1826$) sample was supplied from Asahi Kasei Fibers Co. and Nippon Polyurethane Industry Co., Ltd. The PTMG was dried in nitrogen gas bubbling under a reduced pressure and then was used as monomer in the WBPU polymerizations. Isophorone diisocyanate (IPDI) and dimethylol propionic acid (DMPA) were purchased from Tokyo Chemical Industry Co., Ltd. 1,4-butanediol (BD), triethylamine (TEA), acetonitrile (AcN) and dibutyltin(IV) dilaurate (DBTL) were purchased from Wako Pure Chemical Industries, Ltd. The IPDI was purified by distillation without desiccant agent. The DMPA was dried in a vacuum desiccator for 24 h and then was used. The BD, TEA and AcN were purified by distillation with CaH_2 . The DBTL was used without more purification. TiO_2 (anatase-type, particle size < 25 nm) was purchased from Sigma-Aldrich Co. LLC. and was used without more purification. HALS [LA-77: Bis(2,2,6,6-tetramethyl-4-piperidyl) sebacate] was supplied by ADEKA Co.

2.2. Polymerization of waterborne polyurethane (WBPU) and preparation of TiO_2 composite

The synthesis method and chemical structure of waterborne polyurethane were shown in Fig. 1. The soft (SS) and hard (HS) segments approximately corresponded to the PTMG and IPDI ones, respectively. The synthesis of WBPU composite was performed as follows: 82.3 ml AcN, 13.0 mmol PTMG, 13.2 mmol DMPA, 39.0 mmol IPDI, 1.26×10^{-3} mmol of DBTL and/or 5 per hundred resin (phr) TiO_2 were put into a 300 ml three-necked separable flask equipped with a

mechanical stirrer, nitrogen inlet, thermometer, and reflux condenser. After these were stirred to synthesize prepolymer at 75 °C for 6 h, 13.0 mmol BD was added and then were stirred for another 30 min. After the cooling to room temperature, 13.1 mmol TEA neutralizer was added, and they were stirred for 30 min. The composite obtained was dispersed into water. In order to remove the AcN fraction, the 20 wt% composite aqueous solution was purified with a rotary evaporator.

2.3. Film preparation

In order to characterize the degradation behavior with various measuring apparatuses, the composite films were prepared by solvent-casting method. The HALS (0.1, 1 phr) was put into the aqueous solution containing 20% WBPU composite dispersion, and they were slowly dried at 60 °C for 3 days with an oven. The film specimen was $20 \times 20 \times 0.4$ mm. The film thickness was measured with a micrometer (OM-125, Mitutoyo Co., Ltd.).

2.4. Photo and thermal treatment condition

Photo and thermal treatment was performed in air. The photo treatment sample was laid on a petri dish. A mercury vapor lamp of 400 W (Toshiba H-400P, luminance value = 200 cd/cm^2) was used as a UV light source. The distance between specimens and the lamp was ca. 40 cm. The photo treatment was carried out under air at 30 °C. The treatment time was 24 h, 48 h and 72 h, respectively. The thermal treatment was performed in an oven in air.

2.5. Water-ethanol extraction condition

The sample (ca. 100 mg) is stirred in a flask with 50 ml of solvent (water: ethanol = 66:34 v/v%) at r.t. for one day. The insoluble part was separated, dried up and then was analyzed by NMR. The extraction solvent was evaporated to dryness, and then the obtained solid fraction was analyzed by GPC, NMR and DSC, respectively. The thermal treatment was performed in a DSC device (see Section 2.10) in nitrogen.

2.6. Polymer blend preparation

The PTMG (ca. 25 mg) and extracted sample (ca. 25 mg) were put

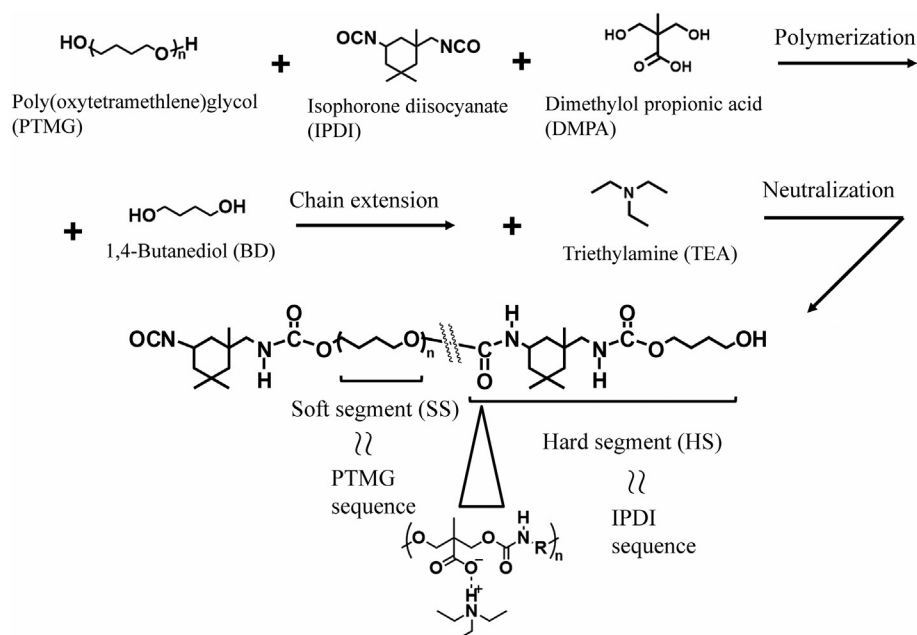


Fig. 1. Synthesis method and chemical structure of waterborne polyurethane.

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