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## Progress in Organic Coatings

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# Waterborne polyurethane modified with poly(ethylene glycol) macromer for waterproof breathable coating

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### ARTICLE INFO

#### Article history:

Received 15 June 2016

Received in revised form 2 October 2016

Accepted 3 October 2016

Available online xxx

#### Keywords:

Waterborne

Polyurethane

Coating

Breathable

Poly(ethylene glycol)

Macromer

### ABSTRACT

Waterborne polyurethane (WPU) was modified with poly(ethylene glycol) (PEG) macromer, containing a terminal acrylic group to be polymerized by a radical mechanism, to endow breathability. The water vapor permeability (WVP) of WPU was effectively improved by the modification to introduce in the WPU network other polymer chains with PEG brushes. Other problems resulting from the introduction of the PEG segment were minimized by this new approach. The modified WPU exhibited a good balance of WVP and water resistance. In addition, the deterioration of tensile properties and tackiness generation by the introduced PEG segment were moderate. The modified WPU exhibited a temperature-responsive WVP due to the crystallinity of the PEG segment.

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## 1. Introduction

Polyurethanes (PUs) are widely used in industries as soft coatings for textiles or leathers and as hard coatings for wood because their perceived quality as well as physical properties, such as flexibility, adhesion, and abrasion resistance, are superior compared with other polymeric materials. In addition, a tailor-made chemical structure, and thus the desired property, can be designed appropriately, because various monomeric materials for fine tuning are commercially available. In recent decades, waterborne polyurethanes (WPUs) have been replacing solvent-borne polyurethanes in various applications, due to growing environmental and legislative pressures, because little solvent is required for WPU to suit the changing demands [1–3].

In order to prepare waterproof breathable clothes through which water vapor can pass easily but water droplet cannot pass, porous polyurethanes or hydrophilic nonporous polyurethanes are coated on a fabric [4,5]. These polyurethanes also are being replaced by WPUs. In the preparation of hydrophilic PU, the poly(ethylene glycol) (PEG) segment, which is hydrophilic and thus water vapor can easily penetrate, is normally utilized as a hydrophilic soft seg-

ment to endow high water vapor permeability (WVP). However, the PEG segment can worsen waterproof ability or water resistance to protect the penetration of water in its liquid state. Therefore, for the good balance of WVP and water resistance, a balanced amount and a well-thought-out arrangement of hydrophilic and hydrophobic segments in the PU as well as additional crosslinking are important [4,6]. Furthermore, the PU with a PEG segment located at the main chain is gelled easily in water at relatively low polymer content because the PU swells significantly in water. Many studies have reported that a PEG segment located at the side chain, instead of the main chain, can alleviate this problem [7–11].

Polymers with side chains of a specific structure can be prepared readily using a macromer with a specific structure, because the macromer, a high molecular weight monomer with a functional group to be polymerized at one terminal, becomes side chain attached to a main chain after polymerization. Therefore, macromers are utilized effectively in the design of polymers for coatings, adhesives, encapsulation, and even lubricating oil to endow specific surface or bulk properties resulting from the side chains [12,13].

We anticipated that if polymeric chains with PEG brushes were grafted onto and interpenetrated in the WPU network, as shown in Fig. 1, the WVP can be improved effectively with minimal increase of water swell and minimal reduction of water resistance. For this purpose, in this study, a PEG macromer with a terminal acrylic

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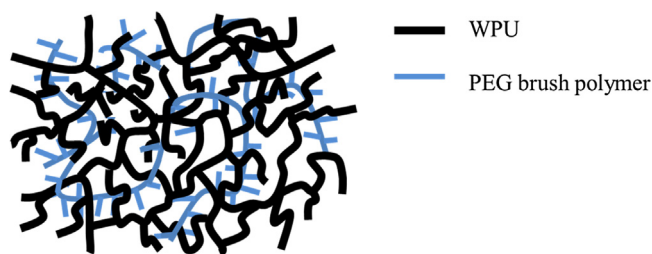


Fig. 1. Schematic presentation of the WPU modified with PEG macromer.

group to be polymerized by a radical mechanism, was utilized to design a high performance breathable WPU-based coating material as a new approach. The WVP and water resistance as well as the physical and thermal properties were examined to evaluate the performance of this newly designed breathable coating material.

## 2. Materials and methods

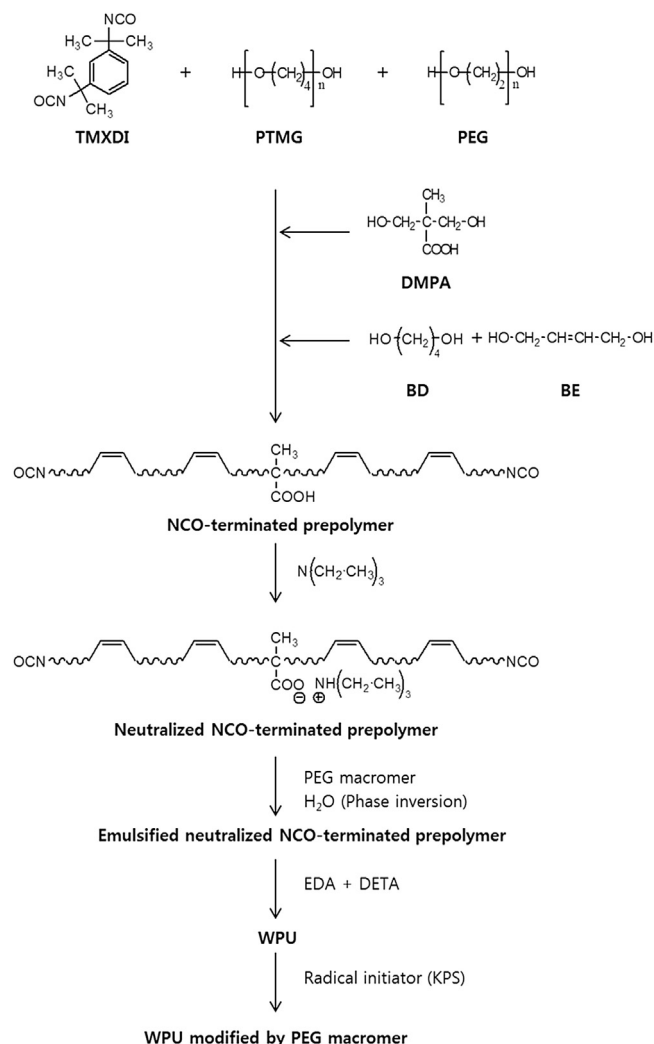
### 2.1. Materials

Poly(tetramethylene glycol) (PTMG) (1000 g/mol; Korea PTG Co., Korea) and poly(ethylene glycol) (PEG) (KONION SK-45T, 2000 g/mol; KPX Green Chemical, Korea) were dried and degassed at 95 °C under a vacuum for 48 h. Dimethylol propionic acid (DMPA, Sigma-Aldrich) was dried at 60 °C for 48 h in a vacuum oven. 1,4-Butanediol (BD, Sigma-Aldrich), 2-butene-1,4-diol (BE, Sigma-Aldrich), *m*-tetramethylxylene diisocyanate (TMXDI, Allnex), dibutyltin dilaurate (DBT, Sigma-Aldrich), potassium persulfate (KPS, Sigma-Aldrich), acetone (Sigma-Aldrich), poly(ethylene glycol) methyl ether methacrylate macromer (PEG macromer, average molecular weight; 950 g mol<sup>-1</sup>, Sigma-Aldrich), a methoxymethyl methylol melamine type crosslinker (Cymel P707, 80% aqueous solution; Cytec), and a thickener (Acrysol RM-825, 25% aqueous solution; Rohm and Haas) were used as received. Ethylenediamine (EDA, Sigma-Aldrich), diethylenetriamine (DETA, Sigma-Aldrich), and triethylamine (TEA, Sigma-Aldrich) were dried with a 4 Å molecular sieve before use. Poly(ethylene terephthalate) (PET) textile, woven with 50 denier draw textured yarn to have 188 × 116 threads per in.<sup>2</sup>, was coated with WPU to examine WVP and water resistance.

### 2.2. Preparation of WPU modified with PEG macromer

A 2 L round-bottomed, four-necked separable flask with a mechanical stirrer, a thermometer, and a condenser attaching a drying tube at the outlet was used as the polymerization reactor. The reaction was carried out in a heating mantle with a temperature controller under nitrogen atmosphere. The NCO-terminated prepolymer was prepared by reacting TMXDI and PTMG and PEG at 80 °C for 6 h in the presence of DBT (0.03 part per 100 part of solid WPU) (Scheme 1). Then, DMPA was fed into the reactor to perform an additional reaction at 95 °C for 20 h. BD and BE were fed into the reactor in sequence to react for 3 h each at 80 °C. Some amount of acetone was added to the reactor when the viscosity became too high, and the solution was then cooled to room temperature. Afterward, TEA was fed into the reactor and was agitated for 1 h to neutralize the DMPA unit in the NCO-terminated prepolymer. The neutralized NCO-terminated prepolymer was emulsified by feeding water at room temperature slowly for 30 min into the reactor under agitation. EDA and DETA were dissolved in water (10 wt%) and were fed into the emulsion at 20 °C. Chain extension by these amines was carried out for 2 h to get WPU.

In order to modify the WPU, the PEG macromer was fed and thoroughly mixed with the NCO-terminated prepolymer at 60 °C for 1 h.



Scheme 1. The process for the preparation of the WPU modified by PEG macromer.

The PEG macromers can not only polymerize by themselves but can also graft onto WPU by a radical mechanism with a radical initiator. We used BE together with BD as chain extenders because the double bond of the BE unit can improve the grafting efficiency of PEG macromer on WPU. After the chain extension of NCO-terminated prepolymer with EDA and DETA, the radical initiator, KPS (0.5 part per 100 parts of macromer) dissolved in water (10 wt%) was fed drop-wise into the emulsion for 1 h to graft or to polymerize the PEG macromer through a radical mechanism at 60 °C for 2 h. The recipe used to prepare the WPU modified with the PEG macromer is shown in Table 1. The sample designation codes provide information on the amount of soft segment (PTMG and PEG segments) and hard segment in WPU, as well as the amount of PEG macromer used to modify the WPU. For example, the weight ratio of the hard segment, soft segment, and PEG macromer for H70S30M50 is 70/30/50. That is, the WPU, whose hard and soft segment contents are 70 wt% and 30 wt%, respectively, was modified with 50 parts of PEG macromer per 100 parts of solid WPU (50 parts per hundred resin, 50 phr). The WPUs H60S40M0 and H50S50M0, which were not modified with PEG macromer, were also prepared for comparison. We tried to prepare H70S30M0, which has a higher hard segment content, however, the synthetic process was difficult to carry out. The WPU modified with PEG macromer was a stable emulsion with a solid content of about 25 wt% and a viscosity of 6000–8000 cP.

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