A breathable waterborne poly-(urethane/urea) coating containing PO-EPO triblock copolymer

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Abstract

A breathable waterborne poly-(urethane/urea) (WPU) coating for textiles was synthesized by a pre-polymer method with 4,4′-Disocyanate dicyclohexylmethane (H2MDI), Poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) triblock diols (PO-EPO diols), and Polytera-methylene glycol (PTMG). The PO-EPO diols were incorporated into the WPU to improve the swelling issue of frequently observed in the polyethylene glycol (PEG) segments. The stability, mechanical property, thermal properties, and breathability of PO-EPO, including WPU were investigated by varying PTMG/PO-EPO diol ratios. The PO-EPO incorporated WPs showed excellent mechanical properties: 250% of tensile elongation and breaking stress of 15–27 MPa. The breathability reached 620–15 000 mm of water pressure resistance H2O and 2717–63 822 g H2O 24 h m−2 of vapor permeability. The highly breathable, WPU coating contained with different PO/E0 fraction of PO-EPO diols will play an essential role in the garment-textile industry to convert to a greener process.

1. Introduction

Polyurethane is a widely used industrial polymer with diversified chemical and physical characteristics. Solvent-based polyurethane has been commonly used in the adhesive [1], and waterproof coating [2] in the textile industry [3]. Depends on the compositions of isocyanate and polyol, polyurethane has excellent properties in good adhesion [1] on numerous substrates, toughness [5], and flexibility [6].

Nowadays, reducing or avoiding the emission of volatile organic compounds (VOCs) becomes an essential issue for coating procedures and replacing the solvent-based polyurethane [7]. The waterborne PUs usually contain internal [8] and external [9] emulsifiers. The internal emulsifiers, the anionic [10], cationic [11], and non-ionic type [12], play the role of maintaining the stability of waterborne PU in the specific range of pH values. Internal emulsifiers form the micelles in water by the ionic content. The ionic content of waterborne PUs affect the physical and mechanical properties is also reported [13].

Waterproofness and vapor transferability are the significant components of breathability. These properties are obtained by the microporous and/or the non-porous films laminated or coated on the textiles. The resistance to certain static water pressure usually measures waterproofness. The ability of a substrate such as textiles to transfer vapor is regulated by the amount of vapor to be transferred under certain static pressure for a fixed period. Microporous breathable films are those fabricated with a pore size that is less than 100 μm. This is generally accepted to be small enough to prevent the water molecules from passing through, while the vapor or moisture can migrate through. Non-porous breathable films, on the other hand, consists of polymers with
hydrophilic behaviors such as poly(ethylene oxide) (PEO) [14]. PEO absorbs and transfers the moisture to the low humidity side of the film. The breathability, in particular the vapor transfer capability, could be obtained from coating with instead of film lamination. However, the water pressure resistance of reported studies is still not sufficient for the critical applications that require substantial waterproofness.

However, PEO modified PU coatings are reported to their weak water pressure resistance and high water swelling behavior. Swelling also adversely affects the PU’s mechanical properties to loose tensile and tear strength [15]. The swelling phenomenon could be further reduced by improving the interaction between the hard and soft segments of PU by mixed the PEO with less hydrophilic polyols, such as poly(tetramethylene ether) glycol (PTMG), poly(propylene oxide) (PPO), and Polyester diols. Yen and coworkers [16] reported a breathable WPU that was made of PCL(Polycaprolactone)-PEG(Polyethylene oxide)-PCL(Polycaprolactone) triblock diol to achieve the water permeability up to 2500 g H₂O 24 h m⁻² at 32 °C. Moreover, Han et al. developed a methyl acrylate-modified PEO [17] to prevent the swelling issue by grafting PEO segment onto the Polyurethane backbone. They reported that the water-vapor permeability (WVP) and the water pressure resistance (WPR) have been in 15 500 g H₂O 24 h m⁻² at 32 °C, and on the order of 6000 mm H₂O, respectively. The good W.P.R. could due to the good micro separation, which makes hydrophilic segments be surrounded by hydrophobic segments. Poly(ethylene oxide)-b-(propylene oxide) (EO-PO) has been implemented in the breathable WPU coating by Meng’s group [18]. To promote the phase arrangement They proposed that the hard segments formed a mesh structure surrounding the hydrophilic segments and reduced swelling. The WPU coating had a water vapor permeability of 910–990 g H₂O 24 h m⁻², and the W.P.R. reach 2000–10 000 mm H₂O.

The different sequencing distribution of PO-EO-PO [19] could promote the forming of corona structures of hydrophilic segments on the surface of micelles by a self-assembling behavior underwater condition [20] and stabilize the emulsion. No breathability related research contained PO-EO-PO found.

In this work, the poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) triblock diols (PO-EO-PO diols) are in cooperated into the WPUs synthesis. The interaction of hydrogen bonds between the hard and soft segments amongst the ether groups in the PO-EO-PO diols is less than that of the ester diols. Because of the arrangement of EO/PO, it is also likely that the swelling behavior is further reduced by promoting the microphase separation in the PO-EO-PO diols [21]. The possible dispersion mechanism of PO-EO-PO diols within WPUs has also been confirmed via the zeta potential and the stability measurements. The tuning of breathability was achieved by adjusting the composition between PO-EO-PO/PTMG and the length of EO/PO.

2. Experiment materials and methods

2.1. Materials and waterborne poly-(urethane/urea) (WPU) polymerization

Waterborne poly-(urethane/urea) (WPU) were prepared by using 4,4’-Diisocyanate dicyclohexylmethane (H₂₂MDI, Tokyo Chemical Industry, Japan), Polyether diol glycol (PTMG, Mw = 2000 g mole⁻¹, Lidye Chemical, Taiwan).

Poly(propylene oxide)-b-poly(ethylene oxide)-b-poly(propylene oxide) triblock diols (PO-EO-PO diol.), diol-50 (EO/PO = 50/50 wt%, Mw = 2800 g mole⁻¹), 3520 (EO/PO = 35/65 wt%, Mw = 2000 g mole⁻¹), diol-25 (EO/PO wt% = 25/75, Mw = 2200 g mole⁻¹), diol-70 (EO/PO = 70/30 wt%, Mw = 1500 g mole⁻¹), sourced from Enhou polymer chemical, Taiwan

2,2-Bis(hydroxymethyl)butyric acid (DMBA, Sigma-Aldrich, China), Triethylamine (TEA, Sigma-Aldrich, United States), Ethylenediamine (EDA, Sigma-Aldrich, United States), 3,3,5,5-Tetramethyloxysulfophthalein (Bromphenol blue, Sigma-Aldrich, United States), and sodium hydroxide (NaOH, Sigma-Aldrich, United States). Dibutyltin dilaurate (DBTDL, Tokyo Chemical Industry, Japan) was used as a catalyst.

Acetone dehydrated by the molecular sieve was used as a solvent. De-ionized water (DI water) was used in the experiments. All the chemicals, reagents, and solvents used were the analytical grade for the WPU synthesis.

For the WPU coating, the additives, CL-30W (polyisocyanate bridging agent, Farsmart Co., Ltd, Taiwan), CH-025 (deforming agent, Farsmart Co., Ltd, Taiwan), CH-03(leveling agent, Farsmart Co., Ltd, Taiwan), DA (thicker, Farsmart Co., Ltd, Taiwan) were acquired commercially.

The WPU was synthesized by the prepolymer method (scheme 1), and the composition is listed in table 1. Before manufacturing, the diols were dried under vacuum at 120 °C for 120 min. The information of diols that were used in this study is in table 2. The diols, DMBA, and H₁₂MDI were added into a condenser-connected 4-neck round flask and stirred. Then, the mixture was heated to 95 °C and stirred for 90 min under a nitrogen atmosphere. After the measurement of isocyanate content (–NCO content) by the back-titration method, the oligomer was cooled to 50 °C when –NCO concentration reached theoretical value. Acetone was added to control viscosity; then, TEA was used to neutralize the oligomer for 30 min. EDA/water solution was inserted into the oligomer through rigid stirring for emulsification and chain-extending process under room
temperature (R.T.). The excess TEA and acetone were removed by a rotary evaporator. The final WPU product was fabricated after the removal of the excess acetone and TEA by rotary evaporator.

2.2. Determination of isocyanate content

During the synthesis, a back-titration method was used to track the isocyanate concentration to monitor the progress of polymerization. 0.5 N hydrochloric acid solution was prepared as the titrant and n-dibutyl amine (DBA) in tetrahydrofuran (35 ml l⁻¹) and used as a solvent for oligomer. The analyte contained 1 g of the prepolymer, 50 ml reaction solution, and the indicator (bromophenol blue). When the solution reached the endpoint of the titration, the color will change from blue to yellow-green.

Scheme 1. Synthesis route of waterborne poly-(urethane/urea) with PO-EO-PO diols.
2.3. Preparation of films

The WPUs were cast in a polytetrafluoroethylene mold with a thickness of approximately 1 mm. Films were left at room temperature until dried; then, the films were placed in an oven at 145 °C for 5 min to activate the bridging agent. The films were prepared for the dynamic mechanical analysis (DMA), the differential scanning calorimetry (DSC), tensile test, and further swelling test.

2.4. Measurements

Perkin Elmer Spectrum One FT-IR Spectrometer was employed to obtain the spectra of films produced in 2.3. All the samples were measured by only the attenuated total reflection (ATR) mode of 1.0 cm⁻¹ resolution from 650–4000 cm⁻¹ for 16 scans was collected in this study.

The particle size, Zeta potential, viscosity, and accelerated life and aging tests were conducted to check the stability of WPUs. A Brookhaven 90 plus Nanoparticle Size Analyzer in the dynamic light scattering (DLS) mode was used for particle size distribution, and the Zeta potential measurements of WPUs emulsions diluted to 5% in di-water. The viscosity of WPUs was measured by a Brookfield RVDV-E viscometer. WPUs were centrifuged with 3000 rpm for 15 min under R.T. to simulate the stability of WPU for 6 months hold under room temperature. The aging characteristic of WPU samples was affected by leaving samples in a 60 °C oven for 7 days. Samples are visually examined upon the completion of the aging cycle for discoloration and particulate forming.

To obtain the solid content of WPU, WPU was weighted in a pre-weighed glass sample bottle and left in an oven at 95 °C for 10 h. The solid content of WPUs was calculated by the average of five measurements from the difference in weight of WPUs before and after drying.

The gel permeation chromatography was taken by Malvern GPC with 270 and 3580 RI detectors, and Shodex™ GPC KF-805L column. Samples were dissolved in 5 ml DMF (0.02 M LiBr) solution.

The DSC analysis was performed using a DSC7000 (Hitachi, Japan). The DSC measurement was carried out from −70 to 210 °C with a heating rate of 5 °C min⁻¹ under a nitrogen atmosphere. The samples were pre-dried below 100 °C overnight to ensure the dehydration was completed.

The DMA was taken from −90 to 70 °C at a frequency of 1 Hz, the amplitude of 10 μm, and the heating rate of 5 °C min⁻¹ by SEIKO SII EXSTAR 6100 DMS.

The mechanical properties were measured by using a Comtech QC-508 M1F testing machine with a 500 N load cell at room temperature. The tensile testing speed is 500 mm min⁻¹, and data analysis was based on the ASTM D638-V.

### Table 1. The composition of WPUs.

| Item   | H₂-MDI (g) | PTMG2000 (g) | Diol-70 (g) | Diol-50 (g) | Diol-35 (g) | Diol-25 (g) | DMBA (g) | TEA (g) | EDA (g) | R² |
|--------|------------|--------------|-------------|-------------|-------------|-------------|----------|---------|---------|----|
| WPU-0-0 | 13.01      | 34.99        | —           | —           | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-40-25⁵ | 12.77     | 20.32        | —           | —           | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-40-30⁵ | 12.77     | 21.00        | —           | —           | —           | 14.00       | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-20-50⁵ | 12.55     | 26.26        | —           | 9.19        | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-30-50⁵ | 12.35     | 22.28        | —           | 13.37       | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-40-50⁵ | 12.15     | 18.54        | —           | 17.31       | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-20-70⁵ | 13.32     | 29.20        | 5.48        | —           | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-30-70⁵ | 13.49     | 26.11        | 8.39        | —           | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|
| WPU-40-70⁵ | 13.67     | 22.89        | 11.44       | —           | —           | —           | 2.00     | 1.50    | 1.00    | 1.6|

a The sample’s name was given with PO-EO-EO diols content in soft segments, and the name of PO-EO-EO diol. Ex. WPU-40(40% of PO-EO-EO diol in soft segments)-50 (diol-50).
b $R = \frac{[NCO]}{[OH]}$.

### Table 2. The compositions of the diol.

| Item   | EO content (wt%) | PO content (wt%) | $M_n$ (g mole⁻¹) |
|--------|------------------|------------------|------------------|
| Diol-70| 70               | 30               | 1500             |
| Diol-50| 50               | 50               | 2500             |
| Diol-35| 35               | 65               | 2000             |
| Diol-25| 25               | 75               | 2200             |
2.5. Fabrication of WPUs coated fabric
The WPUs were mixed with CH-025 (0.2%), CH-03 (0.2%) and CL-30W (2.5%). The viscosity of mixtures was controlled in the range of 18 000–20 000 cps by adding thickener (DA) while stirring. The WPU was coated onto the polyester knitted fabric by a knife coating method with a targeted coating thickness of 500 μm. The WPU coated fabric was dried at 100 °C for 2 min and cured at 145 °C for 3 min.

2.6. Characterization of breathability of WPUs coated fabric
Water pressure resistance (WPR) of WPU coated knit fabric was tested following JIS L 1092. The testing speed is 100 KPa min⁻¹. The specimen was cut into 20 × 20 cm. Three or more water pressure samples are tested, and results are averaged. The WPU coated fabrics’ water vapor permeability (WVP, in g H₂O*24 h* m⁻²) of WPU coated fabric was tested per JIS-1099. For determining the surface morphology of WPU coated samples, a scanning electron microscope (SEM) was taken by JEOL SM-7610F, and all the WPU coated samples were done with gold sputtering before measurement.

2.7. Swelling test of casted WPU films
The casted films were cut into 1 cm² and soaked in DI-water for 1 h. The samples were weighed before and after soaking into water. The water uptake was calculated by dividing increased weight by original weight and show as the percent. The water uptake was taken by the average of five measurements from the difference.

3. Results and discussion
3.1. Characterization of the waterborne poly-(urethane/urea)
The FT-IR spectra of WPU samples are shown in figure 1. FT-IR results corroborated the expected WPU structures that are found in the samples studied in this work.

The N–H groups of urethane-urea are associated with N–H stretching vibration and are usually presented as absorptions centered between 3400–3640 cm⁻¹. The additional stretching of the C=O group in the urethane was also observed near 1706–1713 cm⁻¹. The peaks at 2980 cm⁻¹ were correlated to –C.H. stretching related to the polymer backbone. The intense absorption peak in 1706–1713 cm⁻¹ is related to the stretching of C–O–C groups in the soft segment. The C–C stretching peaks at 1410–1413 cm⁻¹ were detected in all samples as well.

The absence of –NCO absorption peak at 2260 cm⁻¹ in all the WPUs synthesized indicated the complete polymerization in samples characterized.

3.2. Morphology, particle size, viscosity, solid content, and stability of waterborne poly-(urethane/urea)
The stability of dispersions could be affected by the chemical structures and the size of micelles. In waterborne emulsions, the hydrophobic segments are usually located in the core of micelles, and the hydrophilic segment tends to form the corona structure on the surface of micelles under the aqua condition [22]. The particle size and zeta potential of the WPUs were measured through DLS measurement. For the morphology study of the coated fabrics, SEM images were taken among all the samples, including uncoated substrate (figures 2(a)–(j)). All the
Figure 2. The SEM images of the uncoated and WPU coated samples (uncoated fabric (a), WPU-0-0 (b), WPU-40-25 (c), WPU-40-35 (d), WPU-20-50 (e), WPU-30-50 (f), WPU-40-50 (g), WPU-20-70 (h), WPU-30-70 (i), WPU-0-0 (j)), which shown the morphology of the WPU films and indicated the non-porous films were fabricated by knife coating.
coated samples exhibited a smooth and film without pore by the knife coating process, indicating the non-porous waterborne coating was fabricated and covered the substrate fabric continuously. In table 3, the swelling behavior was observed at higher content of EO segments according to the particle size of the WPUs was increased with the increase of EO segments within PO-EO-PO diols. High zeta potential of WPU-0-0 and WPU-20-50 suggesting the cationic abundance groups on the surface of micelles. Lower zeta potential (∼30–50 mV) of the other samples indicated less ionic group density on the surface of micelles. Even though the samples with low zeta potential, all the samples exhibited excellent stability by centrifuging tests. It suggested that the stabilization of WPUs was not only attributed to DMBA but also the corona structure of PO-EO-PO diols.

The viscosity of WPU should be controlled via different processing procedures, i.e., knife coating, roll coating, and dip coating, etc [24]. The viscosity can be adjusted by adding thickener or diluting by water. However, the viscosity of the WPUs could be reduced by dilution, but the higher cost of the processing could occur due to lower solid content. To prevent the limitation of commercial applications, reducing the viscosity of the WPUs and remain the solid content of WPU is necessary.

Figure 3. DSC trace of (a) WPUs with neat PTMG, different PO-EO-PO diols, and same PTMG/PEP Ratio. (b) WPUs with varied PTMG/diol-50 ratio (c) WPUs with varied PTMG/diol-70 ratio.

Table 3. The stability of WPUs.

| Item      | Solid content (%) | Particle size (nm) | Zeta potential (mV) | Viscosity (cps) | $M_n$ (g mole$^{-1}$) | Stability |
|-----------|-------------------|--------------------|---------------------|-----------------|----------------------|-----------|
| WPU-0-0   | 19                | 569.5 (±113.2)     | −117.20 (±0.75)     | 1830            | $7.21 \times 10^4$   | >6 month  |
| WPU-40-25 | 26                | 21.0 (±9.3)        | −44.95 (±12.32)     | 50              | $6.91 \times 10^4$   | >6 month  |
| WPU-40-35 | 26                | 30.0 (±17.2)       | −36.05 (±7.23)      | 80              | $6.83 \times 10^4$   | >6 month  |
| WPU-20-50 | 22                | 140.5 (73.7)       | −116.77 (±4.27)     | 200             | $6.51 \times 10^4$   | >6 month  |
| WPU-30-50 | 21                | 134.6 (±68.2)      | −48.73 (±3.91)      | 300             | $7.77 \times 10^4$   | >6 month  |
| WPU-40-50 | 22                | 253.8 (±121.3)     | −30.11 (±0.75)      | 500             | $7.22 \times 10^4$   | >6 month  |
| WPU-20-70 | 22                | 180.7 (±83.2)      | −37.40 (±2.44)      | 720             | $6.94 \times 10^4$   | >6 month  |
| WPU-30-70 | 23                | 163.4 (±89.5)      | −30.80 (±3.33)      | 800             | $6.33 \times 10^4$   | >6 month  |
| WPU-40-70 | 24                | 326.5 (±190.5)     | −40.10 (±1.55)      | 2770            | $7.40 \times 10^4$   | >6 month  |
The viscosity of the WPUs was observed to be declined by the methyl side group of PO segments of PO-EO-PO diols (<3000 cps, table 3) [26–28]. PEO segment also showed the effect of viscosity due to its high hydrophilicity, which is displayed in the swelling test. With higher EO content, the intermolecular interactions were promoted to raise the viscosity of EO involved samples [27]. However, WPU-0-0 showed higher viscosity as its lacking of PO in the soft segment [22]. Hence, larger particle size with higher viscosity was attained in synthesized WPUs. The molecular weight was analyzed via GPC measurement. All WPU samples exhibited sufficient molecular weight to form films after oven drying for further testing.

3.3. Differential scanning calorimetry (D.S.C.)

The crystallinity of WPU is mainly owing to the crystallization of the soft segments. The crystallinity of WPU is possible to enhance the mechanical properties, which like tensile strength, etc. The thermograms (figure 3) show the melting temperature of the soft segment ($T_m$) of the WPU WPU-0-0 showed a melting peak at 21.4 °C with 26.5 J g$^{-1}$ (table S1 is available online at stacks.iop.org/MRX/7/105303/mmedia), which suggests the crystallization of PTMG segments. With higher PO content, the lower endothermal peaks appear (figure 3(a)) because of the molecular chain arrangements that were interrupted by the side chain on PO. The side chain effect could also be observed in the Diol-50 series (figure 3(b)). $T_m$ and $\Delta H_m$ were decreased with increasing the diol-50 content (figure 3(c)), confirmed that the methyl side groups of the PO could reduce the crystallinity of the PTMG.

EO segment may act as a nucleating site to drive the crystallization of PTMG, for the reason that the conformation of PEO was similar to the PTMG [29]. The Diol-70 involved WPUs show significant endothermal peak (figure 3(c)), caused by abundance EO content in triblock diols.

The mixing behavior between PO-EO-PO diols and PTMG could be improved by increasing the EO content. It is owing to the lower PEO length, which induced larger size but smaller numbers of the formed spherulites of soft segments. This is in good agreement comparing to the diol-50 series with the study on the
Figure 5. Mechanical property data of (a) WPUs with different PO-EO-PO diols, and same PTMG/PEP ratio. (b) WPUs with varied PTMG/diol-50 ratio (c) WPUs with varied PTMG/diol-70 ratio.

| Item       | Young’s Modulus at 100% (MPa) | Young’s Modulus at 300% (MPa) | Stress at break (MPa) | Elongation at break (%) |
|------------|-------------------------------|-------------------------------|------------------------|-------------------------|
| WPU-0-0    | 3.39                          | 5.66                          | 35.03                  | 1524.8                  |
| WPU-40-25  | 1.90                          | 2.93                          | 22.87                  | 3437.0                  |
| WPU-40-35  | 1.43                          | 2.08                          | 17.54                  | 3127.1                  |
| WPU-20-50  | 4.01                          | 5.65                          | 31.37                  | 1795.0                  |
| WPU-30-50  | 1.89                          | 2.90                          | 18.41                  | 2708.3                  |
| WPU-40-50  | 0.99                          | 1.39                          | 16.82                  | 3453.6                  |
| WPU-20-70  | 1.43                          | 2.08                          | 26.44                  | 3199.4                  |
| WPU-30-70  | 1.54                          | 2.22                          | 24.05                  | 3093.8                  |
| WPU-40-70  | 1.27                          | 1.80                          | 24.37                  | 3046.4                  |

Table 4. Mechanical property Data of WPUs with different PTMG/PO-EO-PO diols ratio, and PO/EO ratio in PO-EO-PO diols.

| Item       | WVP (g H₂O 24 h m⁻²) | WPR (mm H₂O) |
|------------|-----------------------|--------------|
| WPU-0-0    | 230                   | >15 000      |
| WPU-40-25  | 2717                  | >15 000      |
| WPU-40-35  | 2743                  | >15 000      |
| WPU-20-50  | 3627                  | 832          |
| WPU-30-50  | 20 513                | 736          |
| WPU-40-50  | 63 822                | 620          |
| WPU-20-70  | 2700                  | 12 140       |
| WPU-30-70  | 10 880                | 9650         |
| WPU-40-70  | 16 617                | 3755         |

Table 5. Breathability of WPUs with different PTMG/PO-EO-PO diols ratio, and PO/EO ratio in PO-EO-PO diols.
PCL-PEG-PCL triblock copolymer [19]. From the DSC results, Diol-70 can introduce more PEO segments without highly reduced the crystallinity of soft segments.

3.4. Dynamic mechanical analysis (DMA)
The microcosmic inter-molecular interaction of the WPU films with different PO-EO-PO diols was studied by DMA. The diagram includes the variation of tan δ as a function of temperature is given in (figure 4). T_g of soft segments increased with increasing PPO content in PO-EO-PO diols; exhibiting the methyl side group within PO could be restricted the rotation of the molecular chain (figures 4(a) and (b)) Besides, PEO segments could be enhanced the interaction to hard segments by forming hydrogen bonds and cause the shifting of T_g [30]. The broad peaks obtained in the diol-70 series (figure 4(c)) resulted in the polarity of soft segments, which could be improved the locally packing of soft segments domain by temperature deviation [31]. The lowest T_g appeared at WPU-0-0 (figure 4(c)), which is owing to the flexibility of a linear ether chain without side groups [32].

Table 6. Comparison of breathability between this study and other EO-containing WPU.

| WPU composition                  | WVP (g H_2O 24 h m^{-2}) | WPR (mm H_2O) | Reference         |
|----------------------------------|---------------------------|---------------|-------------------|
| Human Sweating rate underactive walking | 11 500                    | —             | Williams, JT [38] |
| HMDI/PTMG/PO-EO-PO              | 2717–63 822               | 620–15 000    | This study        |
| TMXDI/PTMG/Acrylate modified PEG | 5400–15 500               | 2200–6000     | Han et al [17]    |
| HMDI/PCL-PEO-PCL                | 900–2500                  | —             | Yen et al [16]    |
| IPDI/PO-EO                      | 910–990                   | 2000–10 000   | Meng et al [18]   |

3.5. Effect of variation of PTMG/PO-EO-PO diol composition on the mechanical performance of the waterborne poly-(urethane/urea)
For good water pressure resistance of the coated fabric, the mechanical properties of coating material are concerned. During the pressure arising process, the film will expand to resist the water pressure. For higher water pressure resistance, higher modulus and tensile strength is more important than elongations. WPU-0-0 exhibited the highest stress at break and the modulus (figure 5(c) and table 4), caused by the flexibility and the crystalline properties of PTMG. The modulus and the stress at break of synthesized WPU were reduced by decreasing the PO ratio of PO-EO-PO diols (figure 5(a)), demonstrated the higher modulus, and the stress at the break was observed in PPO-rich content, and the modulus tended to reduce at EO-rich content in WPU [23, 28, 33]. These results displayed a positive influence on water pressure resistance with PTMG and PO involvement in the soft segment.

The increase of diol-50 content could be lowered the modulus resulted in the side group effect that caused by PO in PO-EO-PO diols, which limited the forming of hydrogen bonds between hard segments. However, the stress hardening effect was displayed in higher EO content within all the synthesized samples containing diol-70, which provided a good condition for crystallization happens. These results indicated that the existence of EO in Diol-70 provided better conditions for the crystallization of EO, which could increase the tensile strength with stress hardening effect during elongating.
3.6. Effect of variation of PTMG/PO-EO-PO diol composition on the breathability & water swelling behavior of waterborne poly-(urethane/urea)

A water pressure resistance (WPR) and water vapor permeability (WVP) test measured the breathability property in this study. The WVP value was enhanced with higher PO-EO-PO diols content by arising EO content in the samples with the diol-50, and diol-70. (table 5). Moreover, the sample with higher PO content in PO-EO-PO diols could be highly improved the WPR to obtain better mechanical property. Lomax et al.[34] proposed the moisture-transferring mechanisms of PEO, which could be self-assembled as helix structure, and the water molecules could interact with intra- and inter-molecular PEO chains to deliver the water through the ‘stepping stone’ mechanism. However, the PTMG and PPG were more hydrophobic compared to PEO, and the O-O bond could be arranged to lowering the WVP value [33].

Comparing the breathability data with DSC results, Diol-70 with higher EO content but showed lower WVP value than Diol-50. It indicated that the higher crystallinity of soft segments could limit the moisture transfer efficiency. Higher WVP of Diol-50 means higher water absorbency, which is the main reason for water swelling. It can explain that the Diol-50 series showed much lower WPR value than WPU-20-50 but with a similar tensile strength to WPU-0-0. Comparing to the tensile strength among the different PO-EO-PO diols (figure 4(a)) to the WPR results, we found that the tensile strength could not directly correspond to WPR value without taking consideration to the swelling behavior. In figure 6, The swelling behavior between different PO-EO-PO content and EO/PO ratio in WPU samples was tested, Diol-50 series exhibited significantly higher water uptake, and even Diol-50 is not the one with the highest EO content. It indicated that not only EO content but also the phase mixing behavior could affect water uptake by taking consideration of the results that we found in DSC. Diol-25 and Diol-35 series showed high WPR value because of their low EO content, which highly limited the swelling effect, so the WVP value is lowest among the samples contained PO-EO-PO diol. Because of the high hydrophilicity and the chemical nature, the WPU in this study is a potential biodegradable polymer. From previous studies, polyester type WPU is with higher biodegradability than polycarbonate type [35]; the weight loss is 46 ± 18 wt% (6 months in vivo/PTMG). Another strategy is to use the ester-based diol with EO contained diol [36]. The high hydrophilicity of EO will absorb moisture/water into the polymer. With high humidity, the hydration of the ester bond will be triggered and exhibit biodegradability [37].

The WPU's consisting of the diol-70 exhibited an excellent value of WPR and reasonable WVP value; this is due to the excellent crystallinity from abundance EO content in diol-70, which could take a higher value of stress at the break by avoiding losing tensile strength from water-absorbing, and showed WPR in 9650 mm H2O. Moreover, stress hardening was also observed in the Diol-70 series. However, even WVP value was restricted by the crystallinity of soft segments, WPU-30-70 still exhibited WVP in 10 880 g H2O 24 h m -2. It’s close to the human sweating rate (11 500 H2O 24 h m -2/active walking) [38]. These results conclude that a balanced breathability property for waterborne breathable coating for textiles is achieved by choosing Diol-70 as hydrophilic soft segments. Comparing to the literature survey, as shown in table 6, our system has adopted a simple strategy to manufacture a breathable coating with amphiphilic tri-block copolymer by a classic approach. Unlike the system using PCL-PEO-PCL [16], the ether-based copolymer could provide better hydration resistance than ester-based polyl. Moreover, the moisture transfer efficiency of our system is higher than the human sweating rate, revealing the potential of our study to be utilized in the breathable textile coating by showing higher WVP and WPR.

4. Conclusions

In summary, we have developed a waterborne poly-(urethane/urea) with PO-EO-PO diols by the prepolymer method. Furthermore, good crystallinity of synthesized WPU's was carried out in the series of diol-70, which contained 70 wt% of PEO. From the breathability testing, the excellent crystallinity of soft segments could bring a high value of WPR in the diol-70 series with reducing WVP value. The increment of WPR in the diol-70 series was also ascribed to the stress hardening process. WPU-30-70 was suggested to be the more balanced properties of WPR and WVP. Due to appropriate PO content, WPU-30-70 maintains the mechanical properties without the reduction of moisture transferability. A green waterborne breathable coating WPU's for textile with PO-EO-PO diols have been investigated the interaction between PPO and PEO in waterborne-poly-(urethane/urea), and the balance between modulus and EO content of WPU is located in a critical relationship.

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References

[1] Remley K H 1977 Polyurethane Textile Adhesive US4048001A (https://patents.google.com/patent/US4048001A/en)
[2] Wang H, Zhou Y, He M and Dai Z 2015 Effects of soft segments on the waterproof of anionic waterborne polyurethane Colloid Polym. Sci. 293 875–81
[3] Zafar F, Ghosal A, Sharma R, Chaturvedi R and Nishant N 2019 A review on cleaner production of polymeric and nanocomposite coatings based on waterborne polyurethane dispersions from seed oils Prog. Org. Coat. 131 259–75
[4] Honarkar H 2018 Waterborne polyurethanes: a review J. Dispers. Sci. Technol. 39 507–16
[5] Wang Z, Li W, Yang X, Cao J, Tu Y, Wu R and Wang W 2018 Highly stretchable and compressible shape memory hydrogels based on waterborne polyurethane network and supramolecular interaction Mater. Today Commun. 17 246–51
[6] Szycher M 1999 Szycher’s Handbook of Polyurethanes (Boca Raton, FL: CRC Press) pp 13–35
[7] Zhou X, Li Y, Fang C, Li S, Cheng Y, Lei W and Meng X 2015 Recent advances in synthesis of waterborne polyurethane and their application in water-based ink: a review J. Mater. Sci. Technol. 31 708–22
[8] Noble K-J 1997 Waterborne polyurethanes Prog. Org. Coat. 32 131–6
[9] Chen G-N, Ling H-J and Chen K-N 1999 Aqueous-based polyurethane hybrids Adv. Eng. Mater. 1 114–8
[10] Coutinho F M B, Delpech M C and Alves I S 2001 Anionic waterborne polyurethane dispersions based on hydroxyl-terminated polybutadiene and poly(propylene glycol): synthesis and characterization J. Appl. Polym. Sci. 80 566–72
[11] Liu Y and Larock R C 2010 Soybean oil-based, aqueous cationic polyurethane dispersions: synthesis and properties Prog. Org. Coat. 69 31–7
[12] Liie H, Yongtao D, Zhihui Z, Zhenghong S and Zhihua L 2015 Synergistic effect of anionic and nonionic monomers on the synthesis of high solid content waterborne polyurethane Colloids Surf. Physicochem. Eng. Asp. 467 46–56
[13] Pérez-Liminiana M A, Arán-Ais F, Torró-Palau A M, César Orgilés-Barceló A and Miguel Martín-Martínez J 2005 Characterization of Waterborne Polyurethane Adhesives Containing Different Amounts of Ionic Groups 25507–17
[14] Mueller C, Topolkaeva V, Soerens D, Hiltner A and Baer E 2000 Breathable polymer films produced by the microlayer coextrusion process J. Appl. Polym. Sci. 78 816–28
[15] Schledewski R, Schultze D and Imbach K-P 1997 Breathable protective clothing with hydrophilic thermoplastic elastomer membrane J. Coat. Flux. 27 105–14
[16] Yen M-S and Kuo S-C 1997 PCL–PEG–PCL triblock copolydiol-based waterborne polyurethane. I. Effects of the soft-segment composition on the structure and physical properties J. Appl. Polym. Sci. 65 885–92
[17] Jeong H, Han Y C, Yang J H, Kwak D S and Jeong H M 2017 Waterborne polyurethane modified with poly(ethylene glycol) macromer for waterproof breathable coating Prog. Org. Coat. 103 68–75
[18] Meng QB, Lee S-I, Nah C and Lee Y-S 2009 Preparation of waterborne polyurethanes using an amphilic diol for breathable waterproof textile coatings Prog. Org. Coat. 66 382–6
[19] Wu J, Xu Y, Dabros T and Hamza H 2005 Effect of EO and PO positions in nonionic surfactants on surfactant properties and demulsification performance Colloids Surf. Physicochem. Eng. Asp. 252 79–85
[20] Liu S, Bao H and Li L 2013 Role of PPO–PEO–PPO triblock copolymer in phase transitions of a PEO–PPO–PEO triblock copolymer in aqueous solution Eur. Polym. J. 71 425–39
[21] Kwiatkowski K and Nachman M 2017 The abrasive wear resistance of the segmented linear polyurethane elastomers based on a variety of polyols as soft segments Polymers 9 705
[22] Owen S C, Chan D P Y and Moschet S M 2012 Polymeric micelle stability Nano Today 7 53–65
[23] Diez-Garcia I, Santamaria-Achour E, Acevedo A and Tercjak A 2018 Triblock copolymers containing hydrophilic PEO blocks as effective polyls for organic solvent-free waterborne polyurethane–urea resins React. Funct. Polym. 131 1–11
[24] Sen A K 2007 Coated Textiles: Principles and Applications (Boca Raton: CRC Press)
[25] Kästner U 2001 The impact of rheological modifiers on water-borne coatings Colloids Surf. Physicochem. Eng. Asp. 183–185 805–21
[26] Liu X, Xu K, Liu H, Cai H, Su J, Fu Z, Guo Y and Chen M 2011 Preparation and properties of waterborne polyurethanes with natural dimer fatty acids based polyether polyl as soft segment Prog. Org. Coat. 72 612–20
[27] Silver J H, Karayianni E and Cooper S L 1996 Effect of polysulfide croslinker on the structure and anticoagulant activity of water-soluble sulfonated polyurethane J. Colloid Interface Sci. 178 219–32
[28] Zhang S, Chen J, Han D, Feng Y, Shen C, Chang C, Song Z and Zhao I 2015 Effect of polyether soft segments on structure and properties of waterborne UV-curable polyurethane nanocomposites J. Coat. Technol. Res. 12 563–9
[29] Beamson G, Pickup B T, Li W and Mai S-M 2000 XPS studies of chain conformation in PEG, PTO MO, and PTMG linear polymers J. Phys. Chem. B 104 2656–72
[30] Luo N, Wang D-N and Ying S-K 1997 Hydrogen-bonding properties of segmented polyether poly(urethane urea) copolymer Macromolecules 30 1405–9
[31] Mofokeng I P, Luyt A S, Tabi T and Kovcs J 2012 Comparison of injection moulded, natural fibre-reinforced composites with PP and PLA as matrices J. Thermoplast. Compos. Mater. 25 927–48
[32] Yen M S and Cheng K L 1994 The effects of soft segments and water vapor permeability of H12MDI-PU cast films J. Appl. Polym. Sci. 52 1707–17
[33] Holker J R and Lomax R 1985 Breathable, non-porousomeric polyurethane films GB2157703A
[34] Lomax G R 2007 Breathable polyurethane membranes for textile and related industries J. Mater. Chem. 17 2775–84
[35] Christenson E M, Anderson J M and Hiltner A 2007 Biodegradation mechanisms of polyurethane elastomers Corros. Eng. Sci. Technol. 42 112–23
[36] Yang Z and Wu G 2020 Effects of soft segment characteristics on the properties of biodegradable amphiphilic waterborne polyurethane prepared by a green process J. Mater. Sci. 55 3139–56
[37] Yang Z and Wu G 2020 Synthetic scheme to improve the solid content of biodegradable waterborne polyurethane by changing the association relationships of hydrophobic fragments RSC Adv. 10 28680–94
[38] Williams J T 2017 Waterproof and Water Repellent Textiles and Clothing (UK: Woodhead Publishing)