

## Preparation and characterization of waterborne polyurethane containing PET waste/PPG as soft segment

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**ABSTRACT:** Soft drinks poly(ethylene terephthalate) (PET) bottles were depolymerized by glycolysis using a 1 : 3 molar ratio of PET repeating unit to glycols like neopentyl glycol (NPG) and dipropylene glycol (DPG). Further, a series of waterborne polyurethanes (WPU) was synthesized using pure polypropylene glycol (PPG), and glycolized oligoesters/PPG blends in different molar ratios as soft segment. Thermal property of WPU was tested by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Moreover, viscosity and particle size of WPU were also investigated. The results show that introduction of a certain amount of glycolized oligoester to soft segment makes the degree of hard-soft domain microphase separation smaller, and can also improve thermal stability of WPU. Furthermore, WPU synthesized from glycolized oligoesters and PPG blends possess larger particle size, better particle size distribution, relative lower and more stable viscosity. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42757.

**KEYWORDS:** degradation; polyurethanes; properties and characterization; thermal properties; thermoplastics

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### INTRODUCTION

In the past few years, more attention has been paid to reducing the emission of toxic and polluting materials into the atmosphere during production processes.<sup>1</sup> Solvent-borne coatings not only pollute the environment but also threaten human health because of the relatively high volatile organic components (VOCs) present in them. Waterborne polyurethanes (WPU) are taking an important role in polyurethane industry<sup>2,3</sup> because of the fact that they are eco-friendly and can be formulated into coatings containing little or no co-solvent.<sup>4,5</sup> WPU makes an effective substitute for solvent-based analogues. While a wide variety of properties known from polyurethane chemistry and technology is also achievable from an aqueous medium, WPU has properties that are very close to solvent-borne polyurethanes. Furthermore, WPU possesses superior properties such as abrasion resistance, high flexibility at low temperature, excellent adhesion to glass surfaces and film-forming ability at ambient temperature,<sup>6–9</sup> which leads to continuously increasing applications in many fields including coating, printing, ink, adhesive and fibre processing.<sup>10,11</sup>

WPU is a binary colloidal system, which is classified into anionic, cationic and nonionic systems, with particles dispersed in an aqueous phase.<sup>12</sup> The main methods of preparing WPU are the acetone, prepolymer, hot melt and ketamine/ketazine processes, of which the acetone and prepolymer processes are the two most commonly used methods in industry. In research, ace-

tone and prepolymer processes are usually mixed to synthesize WPU, where acetone is added to prepolymer and the hydrophilically modified prepolymer is directly mixed with water, and acetone is removed through evaporation in the end.

Poly(ethylene terephthalate) (PET) is a very popular packaging material because of transparency, light-weight with high strength, high chemical inertness, selectively permeability to gases, filter proof and user-friendliness.<sup>13</sup> Nevertheless, extensive applications of PET cause a large number of solid wastes annually.<sup>14,15</sup> Although there are several proposed methods for recycling waste PET,<sup>16–18</sup> it is suggested that chemical glycolysis is the most attractive method as PET waste can easily be decomposed into corresponding monomers or raw chemicals<sup>19–21</sup> Glycolysis of PET using different alcoholysis agents, such as ethylene glycol (EG), diethylene glycol (DEG), propylene glycol (PG), polyethylene glycol (PEG), tetraethylene glycol (TEG) and neopentyl glycol (NPG), has been widely studied.<sup>21–23</sup> Pardal and Tersac<sup>24</sup> have compared the reactivity of different glycols in PET glycolysis, including DEG, dipropylene glycol (DPG), glycerol (Gly) and mixtures of these glycols. They found that PET was not digested more quickly in mixtures of these glycols than in pure glycols except for mixture of DPG and Gly. Colomines *et al.*<sup>25</sup> depolymerized PET with oligoesters, which were synthesized via the trans-esterification of dimethyl isophthalate with NPG or TEG. The study showed a dependence of glass transition temperature ( $T_g$ ) and thermal stability of glycolysates on

the nature of oligoesters. Cakić *et al.*<sup>26</sup> also depolymerized PET bottles by glycolysis with different molar ratios of PET to propylene glycol (PG), TEG and PEG. Later, these glycolyzed oligoesters were used to synthesize WPU. The study indicated that WPU with a lower molar ratio of PET/glycol in glycolysis process showed lower thermal stability but higher film hardness.

These glycolyzed oligoesters of PET waste obtained using different alcoholysis agents can be used to produce fresh industrial products such as unsaturated polyesters, polymer-composites, polymer concrete and others.<sup>27–29</sup> Among them, WPU synthesized from the production of PET waste has attracted much attention recently. Saravari *et al.*<sup>30</sup> prepared urethane oils from glycolyzed products of PET waste using PPG and found that properties of these urethane oils were comparable to those of commercial urethane oil. Aiensa-art *et al.*<sup>31</sup> synthesized polyurethane foams from glycolyzed products of PET waste with different glycolysis catalysts. It was found that the thermal behaviour of the prepared foams was similar while their morphology was affected by the catalyst used. Cakić *et al.*<sup>32</sup> prepared WPU with the soft segment PPG and found that it had good thermal property. Patel *et al.*<sup>1</sup> depolymerized PET by glycolysis with 1,4-butanediol (BDO) and then synthesized WPU only with these glycolyzed oligoesters in the soft segment. They found that WPU had a high glass transition temperature ( $T_g$ ), good flexibility and poor chemical and solvent resistance. However, as we can see from these studies, WPU was synthesized either with polyols or glycolyzed oligoesters as the soft segment, and no attempt has been made to prepare WPU with polyols and glycolyzed oligoester blends as the soft segment. Besides, other aspects of WPU, such as particle size, particle size distribution and viscosity, are also seldom studied.

Hence, in this study we used NPG and DPG as alcoholysis agents to obtain glycolyzed PET oligoesters, mixed oligoesters with PPG in different molar ratios as the soft segment to prepare WPU and investigated their properties including thermal stability, particle size and particle size distribution and viscosity. This research is significant for not only offering an effective way (namely glycolysis method) to recycle PET waste, but also synthesizing WPU with high overall performance. Furthermore, this work can make a contribution to protecting the environment and potentially alleviating the energy crisis.

## EXPERIMENTAL

### Materials

Postconsumer waste PET bottles with an average molecular weight from 2.5 to  $3.0 \times 10^4$  g/mol were collected. NPG and DPG were received from Sinopharm Chemical reagent Co., Shanghai, China. N-Butyl titanate, supplied by Kelong Chemical, Chengdu, China, was used as the trans-esterification catalyst for the depolymerization of PET. Isophorone diisocyanate (IPDI), PPG (molecular weight  $M_w = 2000$ ) and dimethylolpropionic acid (DMPA) were obtained from Jingchun Chemical, Shanghai, China. BDO, triethylamine (TEA, 99 wt % purity) and 1-methyl-2-pyrrolidone (NMP, 99 wt % purity) were purchased from Fuchen Chemical, Tianjin, China. Dibutyltin dilaurate (DBTDL) was supplied by Qingxi Chemical, Shanghai, China. Acetone of about 15–20 mL was used throughout the

process to reduce the viscosity and deionized water was used as dispersing phase at last.

### Preparation of Starting Materials

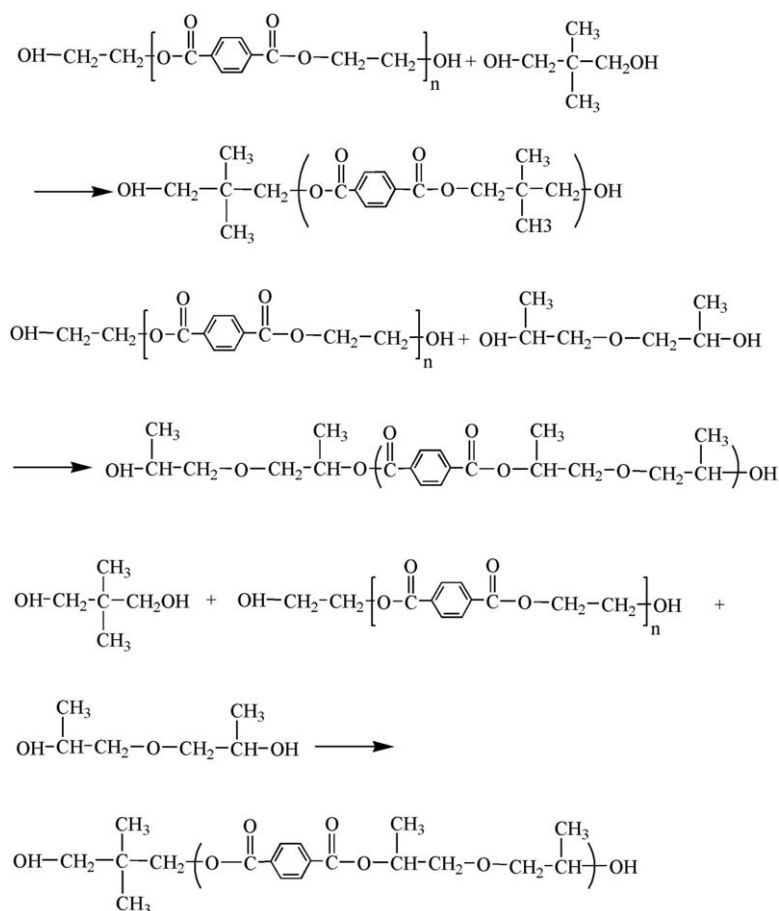
Waste soft drink PET bottles, after removing caps and labels, were cut into chips (average size 5 mm×5 mm). Then these chips were washed with deionized water to remove adhesive materials and dried in a vacuum drying oven at 50°C and 0.05 MPa for 4 h prior to use. PPG and oligoesters which were prepared by glycolysis of PET were dried and degassed in a vacuum at 120°C for 2 h prior to use. All other chemicals were used as received without further treatment.

### Glycolysis of PET Waste

Small chips of PET waste were glycolyzed by NPG and DPG with the molar ratio 1 : 3 of PET repeating unit to glycol. These mixtures and 0.5 wt % n-Butyl titanate catalyst were charged in a four necked glass reactor equipped with a mechanical stirrer, thermometer and spiral condenser in an electric-heated thermostatic oil bath. The glycolysis reaction was carried out at 190°C for 1 h, subsequently the temperature was raised up to 210°C under reflux in nitrogen atmosphere for about 5 h until all the solids disappeared. The obtained glycolyzed oligoesters were dried in a vacuum drying oven at 45°C and 0.05 MPa for 8 h. Then these oligoester polyols were used to synthesize WPU. The glycolysis of PET waste with NPG and DPG proceeds according to Scheme 1.

### Synthesis of WPU from Glycolyzed Oligoesters/PPG Blends with Different Molar Ratios and Pure PPG as Soft Segment

A series of WPU samples was synthesized via a simple and environmental process that combined the prepolymer isocyanate process with the acetone process. Glycolyzed oligoesters and PPG were utilized as oligomer polyols, which were mixed with each other using different molar ratios of glycolyzed oligoesters: PPG = 1 : 5, 2 : 4, 3 : 3, 3.5 : 2.5, and 4 : 2. These mixed oligomer polyols and IPDI (molar ratio of isocyanate groups to hydroxyl groups, NCO/OH = 4) were charged in a four necked glass reactor equipped with a mechanical stirrer, thermometer and spiral condenser in an electric-heated thermostatic water bath. The reaction was carried out at 80°C for 2.5 h, then DBTDL was added to the mixture as a catalyst and reacted for 30 minutes, afterwards, a certain amount of DMPA dispersed in NMP at 60°C was added. The reaction was allowed to proceed at 80°C for 2 h. Subsequently, the obtained prepolymer was cooled to approximately 35°C, and then BDO with a small quantity of acetone and TEA dispersed in 120 g deionized water were added to the glass reactor. Meanwhile the resulting prepolymer was stirred under high speed for 30 min to obtain a homogenous polyurethane dispersion. Eventually the removal of acetone was completed in a vacuum drying oven at 50°C and 0.05 MPa for 1 h. A moderate amount of acetone was introduced into the system to reduce the viscosity throughout the course of the experiment. PU2, PU3, PU4, PU5 and PU6 are short for WPU in synthesis of glycolyzed oligoesters and PPG blends with molar ratio of 1 : 5, 2 : 4, 3 : 3, 3.5 : 2.5, and 4 : 2. As a comparison, WPU was prepared by using pure PPG as the oligomer polyol separately with the same process, which is



**Scheme 1.** The glycolysis reaction of PET waste with NPG and DPG.

named PU1. The reaction scheme for synthesis of polyurethane dispersion is illustrated in Scheme 2.

### Preparation of WPU Films

Films were prepared by casting the aqueous dispersions on the teflon surface, and allowing them to dry at room temperature for 3 days and then at 40°C in a vacuum drying oven for 12 h to allow the complete removal of solvent. Afterwards the films with teflon were kept in a desiccator to avoid moisture absorption.

### Characterization of WPU

**Fourier Transforms Infrared Spectrometer (FT-IR).** FT-IR was performed on the dried polyurethane films to confirm the formation of WPU, and the FT-IR spectra are recorded as a film on KBr formed tablets under vacuum press in spectrophotometer (SHIMADZU FTIR-8400S (CE)), in the wave band ranging from 400 to 4000  $\text{cm}^{-1}$ . An average of 20 scans were run to reach a resolution of 16.0  $\text{cm}^{-1}$ .

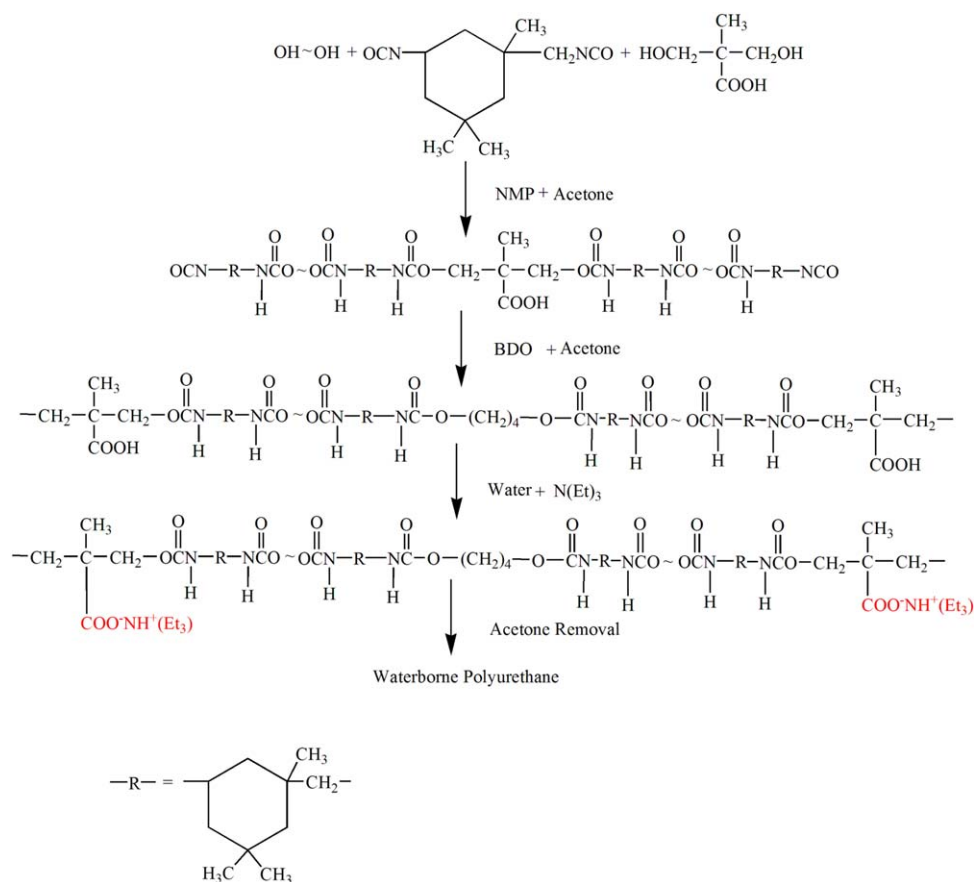
**H-Nuclear Magnetic Resonance ( $^1\text{H}$  NMR).** Proton nuclear magnetic resonance spectroscopy ( $^1\text{H}$  NMR) spectra were obtained on a Bruker-400MHz spectrometer, using sodium 2, 2-dimethyl-2-silapentane-5-sulfonate (DSS) as an internal standard, with  $\text{CDCl}_3$  as solvent.

**Gel Permeation Chromatography (GPC).** GPC (USA Waters, ALLIANCE) was performed on WPU to determine molecular

mass distribution, which was analysed with a DAWN EOS ( $\lambda=690.0$  nm) and RI detector (Shodex RI-71). All samples were dissolved in tetrahydrofuran (THF) of HPLC grade at the constant concentration 0.1 wt %. The flow rate of carrier solvent was 1.00 mL/min. Sample injection volume was 10  $\mu\text{l}$ . The average molecular masses,  $M_n$ ,  $M_w$  and polydispersity index  $Q$  were determined by the software Agilent ChemStation. Poly(methyl methacrylate) standards were used to make a calibration curve.

**X-ray Diffraction (XRD).** XRD was performed on the polyurethane films to analyze the crystallinity with an X-ray diffractometer (XRD-7000, SHIMADZU LIMITED, Japan). A scanning of  $2\theta$  angles between 10°C and 60°C below the scan speed of 8.0000 deg/min was carried out.

**Particle Size and Particle Size Distribution.** The mean particle size and the particle size distribution of WPU were measured in Coulter LS230 system (Beckman Coulter, Miami, FL), provided with laser diffraction and polarized light detectors. A small amount of sample was added into the deionized water tank. The statistical model used to obtain the particle size distribution assumed that the particles were polystyrene and took into account the refraction index of the polystyrene (1.6) and the water. The mean particle size was calculated as the average of two experimental determinations.



**Scheme 2.** Synthesis route of WPU dispersions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Viscosity.** The viscosity of WPU was measured by using Brookfield viscometer DV-II+ (Brookfield Engineering Laboratories, Stoughton, MA). About 250 mL of sample was placed in a beaker at a room temperature of 25°C and using the spindle no.61 with a stirring speed of 100 rpm. The Brookfield viscosity of every sample was calculated as the average of three experimental determinations.

**Thermogravimetric Analysis (TGA).** TGA was performed under nitrogen atmosphere with METTLER TOLEDO TGA/DSC 1 analyzer and Gos Controller GC10 STAR<sup>c</sup> System. Film samples ranging from 4 to 10 mg were placed in an alumina ceramic crucible and heated from 30 to 700°C with an air flow of 100 mL/min and heating rates of 15°C/min. During the heating period, the weight loss and temperature difference were recorded as a function of temperature.

**Differential Scanning Calorimetry (DSC).** DSC analysis was performed under nitrogen atmosphere with METTLER TOLEDO DSC 823<sup>c</sup> equipment to acquire thermograms of WPU. The heating rate employed was 10°C/min and the sample weight was 5–15 mg. DSC was performed twice to ensure a consistent thermal history with a temperature range from –50 to 200°C on the second run.

**Transmission Electron Microscope (TEM).** Transmission electron microscope (TEM) was performed using a JEM-3010

microscope working at accelerating voltage of 200 kV. The samples were prepared through diluting one drop dispersion with 30 mL deionized water.

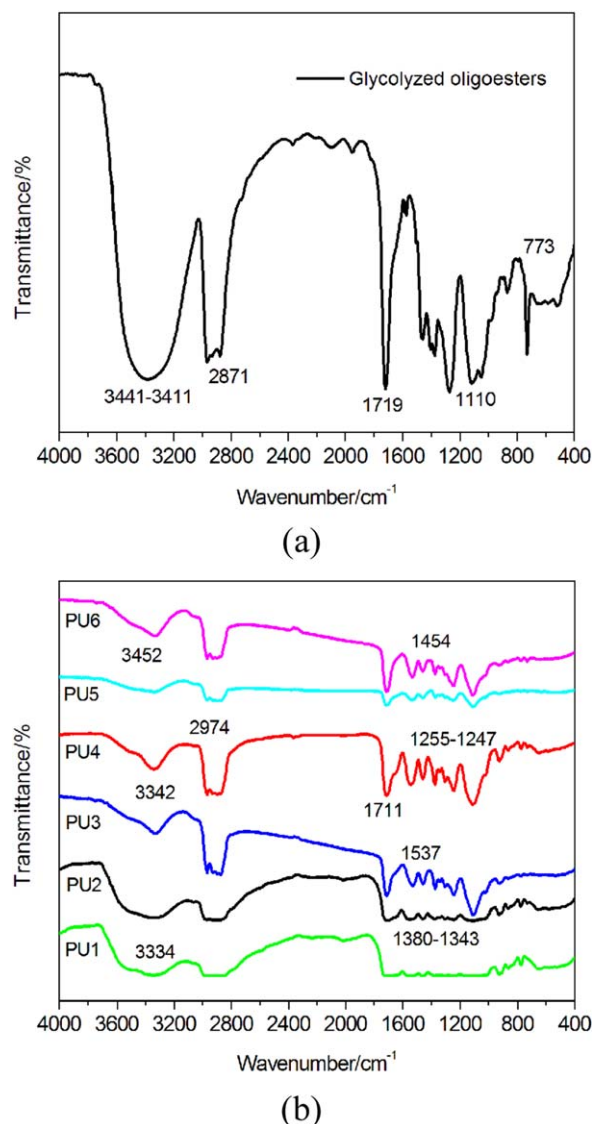
**Liquid Chromatography-Mass Spectrometer (LC-MS).** Liquid chromatography-mass spectroscopy of PET glycolized oligoesters was performed using LC-MS-IT-TOF (Shimadzu, Tokyo, Japan). The sample was prepared through dissolving in THF at a constant concentration 100 µg/mL. MS scan in positive ESI mode. Nitrogen was used as carrier gas with the flow rate of 1.5 l/min. The *m/z* scanning range was from 100 to 3000.

**Dynamic Mechanical Analysis (DMA).** Dynamic mechanical analysis (DMA) was conducted on METTLER TOLEDO DMA 1 STAR<sup>c</sup> System in the shear mode at a frequency of 1 Hz with a heating rate 3°C/min by scanning the films from –80 to 40°C. The shear modulus ( $G'$ ,  $G''$ ) as a function of temperature was also obtained.

## RESULTS AND DISCUSSION

### Analysis of Bulk Structure of WPU

Figure 1(a) shows the Fourier transform-infrared (FT-IR) spectra of PET glycolized oligoesters obtained from glycolysis. A strong and broad characteristic transmission band of the free hydroxyl group from 3411 to 3441  $\text{cm}^{-1}$  is observed. Bands around 1719 and 1110  $\text{cm}^{-1}$  are attributed to the ester bonded C=O and C–O–C stretching vibration, respectively, which is



**Figure 1.** FT-IR spectra of the samples (a) PET glycolized oligoesters; (b) The obtained WPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

an evidence of the presence of the ester group. 2871 and 2926  $\text{cm}^{-1}$  are characteristic bands of the C—H stretching vibrations in saturated hydrocarbons containing methyl groups. Besides, the characteristic transmission bands around 773  $\text{cm}^{-1}$  originate from the out-of-plane vibration of the aromatic ring. The analysis of the FT-IR spectra suggests that PET glycolized oligoesters contain the ester group, the aromatic ring and the alkyl group.

The chemical structure of WPU has been estimated by FT-IR methods. Figure 1(b) shows the FT-IR spectra of WPU in synthesis of pure PPG as PU1, and glycolized oligoesters-PPG blends with molar ratio of 1 : 5, 2 : 4, 3 : 3, 3.5 : 2.5 and 4 : 2 as PU2, PU3, PU4, PU5 and PU6, respectively. According to Rueda-Larraz *et al.*,<sup>33</sup> the free stretching vibration of the N—H group and the C=O group is confirmed by the presence of

transmission bands from 3445 to 3450  $\text{cm}^{-1}$  and 1730 to 1740  $\text{cm}^{-1}$ . Once the N—H or C=O group is hydrogen bonded, the transmission bands will move to low wave number. Meanwhile, Garcia-pacios *et al.*<sup>34</sup> pointed out that the transmission bands from 1690 to 1700  $\text{cm}^{-1}$  are assigned to the free urea C=O stretching vibration, while the characteristic peak of the hydrogen bonded C=O group moves to 1640  $\text{cm}^{-1}$ . Because of hydrogen bonding, FT-IR spectroscopy bands become wide and strong, besides, the frequency of the functional group shifts in an obvious range.

The assignment of the most characteristic IR bands is listed in Table I.<sup>35,36</sup> As seen in Figure 1, the FT-IR spectra of six samples are quite similar. Strong and broad transmission bands at 3334 (PU1, PU2), 3342 (PU3, PU4) and 3452  $\text{cm}^{-1}$  (PU5, PU6) are ascribed to the stretching of the hydrogen bonded N—H group. A medium transmission band around 2974  $\text{cm}^{-1}$  implies the presence of the C—H group. Peaks at 1711, 1537 and 1454  $\text{cm}^{-1}$  correspond to the appearance of the ester and urethane hydrogen bonded C=O stretching, urea C—N stretching, bending N—H vibration, and symmetric  $\text{COO}^-$  stretching. Besides, weak peak at 1647  $\text{cm}^{-1}$  (PU3, PU4), relatively sharp peaks from 1247 to 1255  $\text{cm}^{-1}$  and at 1113  $\text{cm}^{-1}$  (PU2, PU3, PU4, PU5, PU6) indicate the urea disordered hydrogen bonded C=O stretching, non-symmetric NCOO and C—O—C stretching and C—O—C stretching. According to these characteristic peaks, the formation of the urethane group (—NHCOO—), urea group (—NHCONH—) and biuret group (—NHCONCONH—) are confirmed. The presence of —NHCOO— and —NHCONH— units are linked to the side reaction during synthesis of polyurethane. Moreover, the characteristic peak of NCO at 2270  $\text{cm}^{-1}$  disappears, indicating the complete conversion of isocyanate to polyurethane.

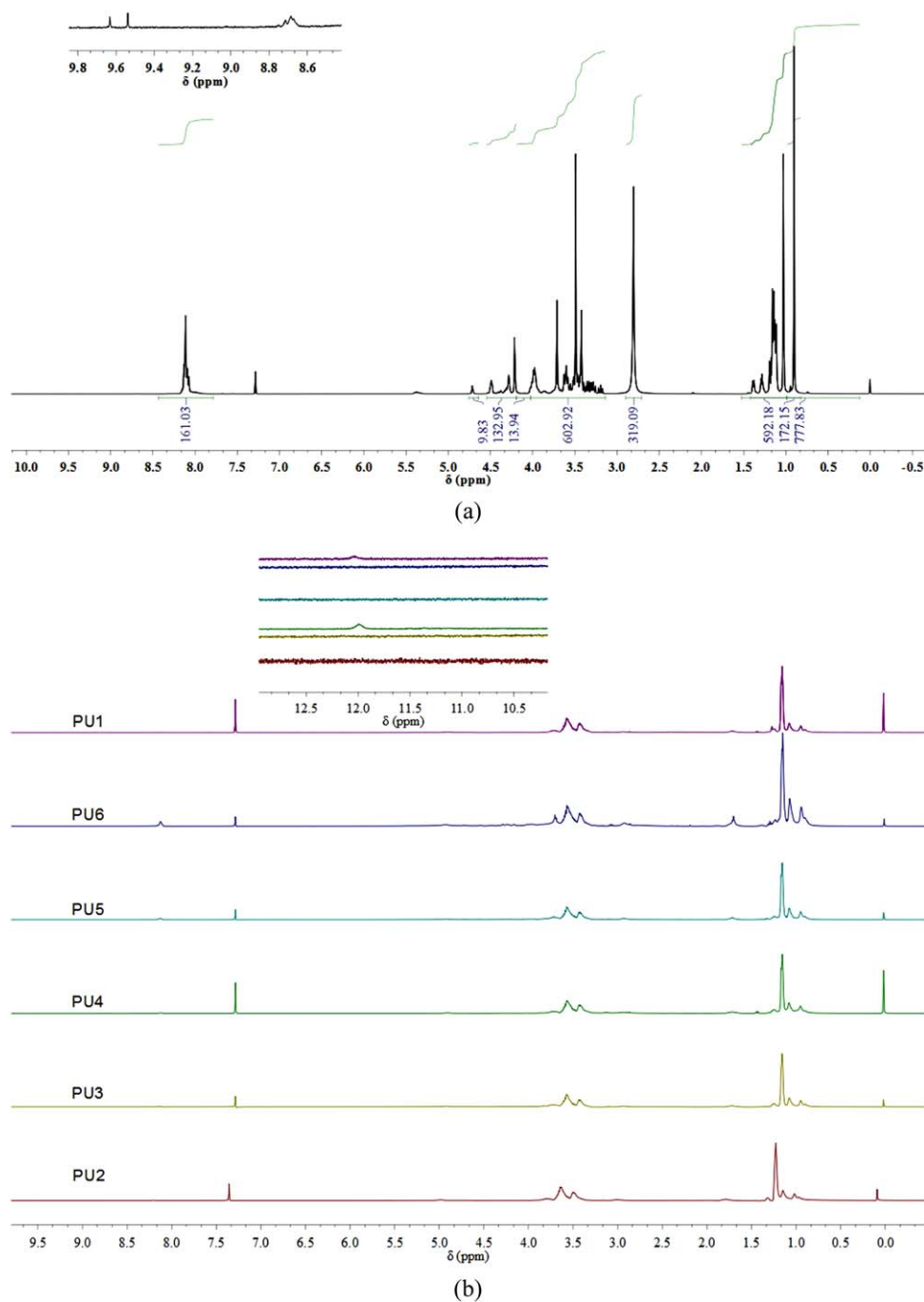
**Table I.** Characteristic IR Bands of the WPU

Wavenumber ( $\text{cm}^{-1}$ )	Assignment
3446	st N—H (free)
3330	st N—H (bonded)
3000-2840	st C—H
2270	st N=C=O
1712-1707	st C=O (bonded ester and urethane)
1662-1618	st C=O (bonded disordered urea)
1610-1550	st C—N + $\delta$ N—H
1475-1450	$\delta$ $\text{CH}_2$
1470-1430	$\delta$ asym $\text{CH}_3$
1450-1400	st sy ( $\text{COO}^-$ )
1395-1365	$\delta$ sy $\text{CH}_3$
1255-1247	st asym N—CO—O + (C—O—C)
1124-1101	st (C—O—C)
770	out-of-plane $\delta$ aromatic ring

st, stretching;  $\delta$ , bending; sy, symmetric; asym, non-symmetric; bonded disordered urea: C=O of urea bonded to only one NH group nearby an urea or urethane.

In comparison with PU1, other samples have transmission bands from 1380 to 1343  $\text{cm}^{-1}$ , which arises from the presence of symmetric  $\text{CH}_3$  in branched hydrocarbons, e.g., in the neopentyl group. Meanwhile, peaks around 773  $\text{cm}^{-1}$  due to aromatic ring, with a lower intensity compared to that of the glycolized products, can be found in all samples except for PU1, according to Figure 1(a), which demonstrates that glycolized oligoesters have participated in the reaction and have been successfully incorporated into the main chain of the polyurethane.

$^1\text{H}$  NMR can detect and quantify the chemical-shift effects of hydrogen atoms in different constitutional situations. Figure 2(a) shows the  $^1\text{H}$  NMR spectrum of glycolized oligoesters. The peak at 8.13 ppm is attributed to the presence of an aromatic entity in the structure. Peaks at 4.21 and 4.30 ppm arise from the  $\text{C}-\text{CH}_2-\text{O}-\text{CO}$  linked to  $\text{CH}_2$  present at the  $\alpha$ -position, which implies the presence of the substituted neopentyl group.<sup>13</sup> Furthermore, the peak at 4.01 ppm is attributed to the presence of ethylene units in the structure. The peak at 1.02 ppm is assigned to  $\text{C}-\text{CH}_2$  attached as a  $\beta$ -substitution to the  $\text{CH}_3$



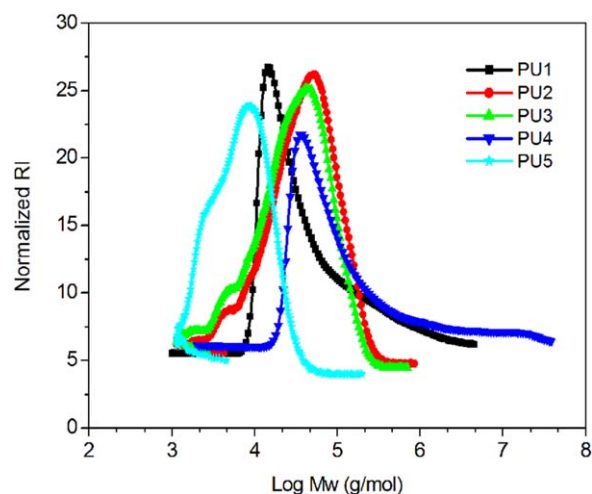
**Figure 2.**  $^1\text{H}$  NMR spectroscopy of the samples (a) PET glycolized oligoesters; (b) The obtained WPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

group. The peak observed at 3.49 ppm is attributed to the  $\text{CH}_2\text{—OH}$  group attached as  $\alpha$ -substitution. From what has been discussed above, the glycolysis reaction can be confirmed.

As seen in Figure 2(b), the  $^1\text{H}$  NMR spectroscopies of all WPU are quite similar, indicating that types and frequencies of most of the functional groups in WPU are nearly the same. It can be seen that the peak at 7.29 ppm is attributed to  $\text{CDCl}_3$ , which is used as a solvent during measurement. Peaks from 0.88 to 1.00 ppm are attributed to the H protons of IPDI. Meanwhile, peaks at 1.08, 3.08 and 3.34 ppm in PU1, PU3, PU4, PU5 and PU6 are assigned to the methyl, methyne, and methylene protons in the PPG blocks, respectively, while peaks at 1.02 and 3.01 ppm in PU2 are also assigned to the methyl and methyne protons in the PPG blocks, respectively. The absent peaks for methylene protons in PU2 in the  $^1\text{H}$  NMR spectrum may arise from the strong interference of the solvent. In addition, the peak at 3.48 and 2.08 ppm is ascribed to the methylene protons of  $\text{—CH}_2\text{CH}_2\text{—O—}$  in the BOD block and the  $\text{—CH}_3$  adjacent to the  $\text{—CH}_2\text{—NH—}$  on the alicyclic chain, respectively. Two sharp peaks at 1.71 and 1.16 ppm (PU1, PU3, PU4, PU5 and PU6), and at 1.78 and 1.15 ppm (PU2) are attributed to the methylene protons of macroglycol and the methyl protons of DMPA, respectively. Furthermore, two extremely weak peaks at 7.02 and 7.54 ppm (PU1, PU3, PU4, PU5, PU6) may be assigned to the imino group of  $\text{—CH}_2\text{NHCOO—}$ ,  $\text{—NHCOOCH}_2\text{—}$  linked with the alicyclic chain, and the peak at 7.35 ppm in PU2 may also be attributed to  $\text{—NHCOOCH}_2\text{—}$  linked to the alicyclic chain, which is evidence that WPU is successfully synthesized from polyol and isocyanate. Moreover, the peak at 8.13 ppm ascribed to the presence of an aromatic entity can be discovered in all WPU except for PU1 demonstrating that glycolyzed oligoesters are involved in synthesis of polyurethanes, which is in accordance with the FT-IR results. In all samples, characteristic peaks at 1.71 and 1.16 ppm in PU4 are the strongest, indicating that the amount of  $\text{—NHCOO—}$  is the largest. The reason may be that only when PET-glycolyzed oligoesters and PPG are in a molar ratio of 3 : 3 (PU4) can they completely react with isocyanate to synthesize WPU, namely more  $\text{—NHCOO—}$  groups. However, for PU1, PU2 and PU3, compared with PU4, more PPG is added to WPU, preventing the extra PPG from being embedded in the main chain of WPU, namely less  $\text{—NHCOO—}$  group. Inversely, for PU5 and PU6, the PET glycolyzed oligoester content is much more than PPG, leading to redundant PET glycolyzed oligoesters, which remain unreacted. These results correspond to TGA data, which shows that in the second thermal decomposition, two decomposition peaks are observed in PU5 and PU6 because of the existence of both glycolyzed oligoesters and PPG.

### GPC Analysis

GPC evaluates the molecular weight distribution of the prepared WPU. Figure 3 shows the GPC chromatograms of WPU synthesised from pure PPG, and glycolyzed oligoesters–PPG blends with different molar ratios. The number average molecular mass ( $M_n$ ) of PET waste used in soft drink bottles is generally in the range of  $2.5\text{—}3.0 \times 10^4$  g/mol.<sup>26</sup> It was found that on glycolysis of PET waste, the weight average molecular mass ( $M_w$ ) and number average molecular mass ( $M_n$ ) of the obtained



**Figure 3.** GPC chromatograms of the obtained WPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

oligoesters decrease, which is shown in Table II. The  $M_n$  and  $M_w$  of oligoesters are observed to be 1499 and 1800 g/mol, respectively. The reduction in molecular mass is approximately 6% of the mass of raw PET used for reaction. GPC chromatograms of pure WPU (PU1) and WPU synthesised from depolymerized PET (PU2, PU3, PU4, and PU5) are obtained. However, PU6 synthesised from glycolyzed oligoesters and PPG in the molar ratio of 4 : 2, has not been tested because of the insolubility in THF. Table II, which includes the number average molecular mass ( $M_n$ ), the weight average molecular mass ( $M_w$ ) and the polydispersity index, shows that by using PET waste, the molecular weight of the polyurethane dispersion is decreased. The  $M_n$  of PU1 ( $M_n = 20,010$  g/mol) is higher than that of PU2 ( $M_n = 13,584$  g/mol), PU3 ( $M_n = 11,758$  g/mol), PU4 ( $M_n = 15,290$  g/mol) and PU5 ( $M_n = 4904$  g/mol). Compared with PU1, the polydispersity index of other samples increases (except for PU4), which presents quite a broad molecular weight distribution. These results imply that the introduction of different molar ratios of glycolyzed oligoesters increases the possibility of forming chains of polyurethane dispersions with varying lengths. It may be because that two types of glycolyzed oligoesters were formed during glycolysis reaction. When using these various molar ratios of mixed glycolyzed oligoesters as the soft segment, they exhibit different reactivity kinetics and thus a reduction in molecular weight is expected.<sup>35</sup>

**Table II.** Average Molecular Masses and Polydispersity Index of Glycolyzed PET Oligoesters and WPU

Samples	$M_n$ (g/mol)	$M_w$ (g/mol)	$M_w/M_n$
Glycolyzed oligoesters	1499	1800	1.20
PU1	20,010	28,290	1.41
PU2	13,584	42,951	3.16
PU3	11,758	35,113	2.99
PU4	15,290	20,990	1.37
PU5	4904	9436	1.92

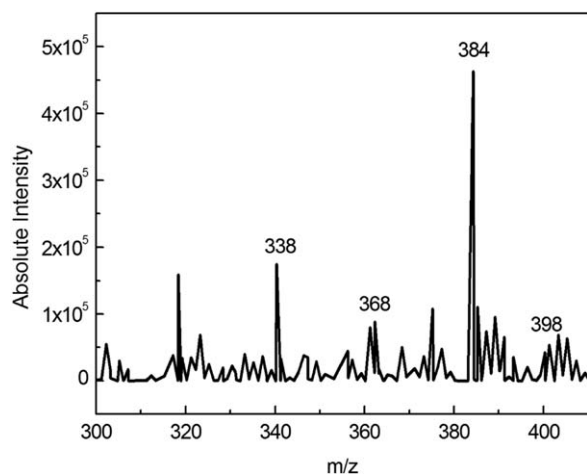


Figure 4. LC-MS analysis of PET glycolized oligoesters.

### LC-MS Analysis

GPC analysis shows that the molecular mass of the oligomeric product is reduced to nearly 6% of the mass of PET. This decreasing trend of the molecular weight confirms the breakdown of polymer structure, namely, the glycolysis reaction of PET. Further, the possible structure of monomers in glycolized oligoesters can be inferred by LC-MS analysis. As seen in Figure 4 the molecular weight of the product is 338, 368 and 398 g/mol, which indicates that there would be two possible structures of monomeric units. One possibility is that the monomeric unit contains neopentyl group or hydroxypropyl group at both sides of the aromatic ring attached by ester group whereas the other possible structure contains one unit of neopentyl and hydroxypropyl group each. The possible structure of monomer as predicted based on FT-IR,  $^1\text{H}$  NMR and LC-MS analyses is as shown in Figure 5.

### XRD Analysis

Polyurethane resin is a kind of block polymer where the hard segment is present as the dispersed phase in the continuous soft segment. The structure of the soft and hard segment in the molecular chain and the degree of microphase separation will affect the crystallization capacity of hard and soft segments, and ultimately determine properties of WPU film.<sup>37</sup> Hence, this study investigates the crystallization capacity of WPU in synthe-

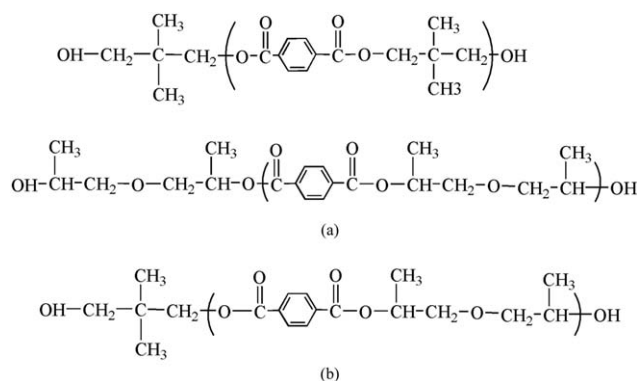
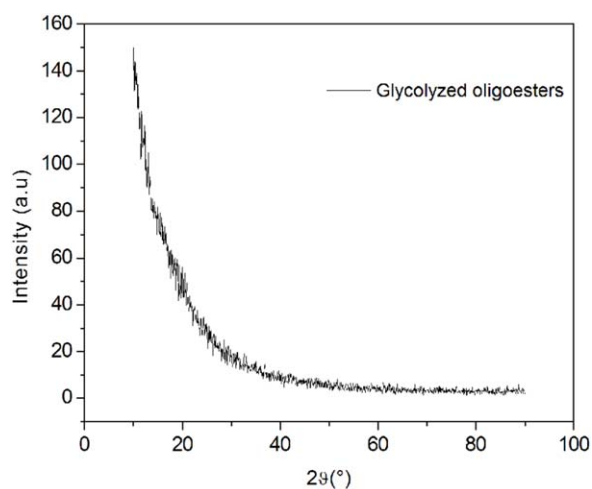


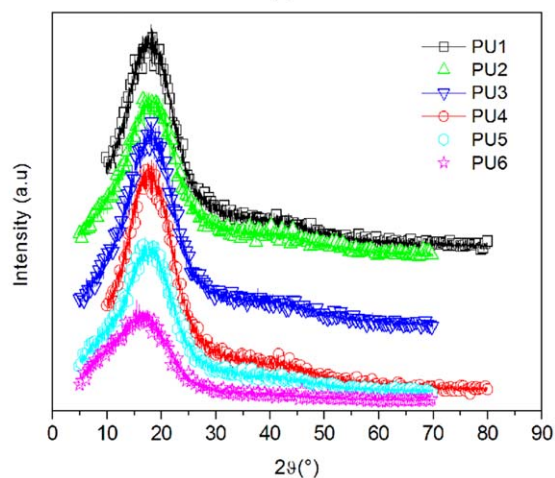
Figure 5. Structure of monomeric product (a) with both NPG or DPG units; (b) with NPG and DPG units.

sis of pure PPG, and glycolized oligoesters-PPG blends with different molar ratios. For polyurethane, crystallization is always ascribed to the function of hydrogen bond, which causes order in the segment.<sup>38</sup>

XRD patterns for glycolized oligoesters and WPU are shown in Figure 6. The study of glycolized oligoesters depicted in Figure 6(a) shows the absence of crystalline peaks, which proves that these compounds are totally amorphous. The reagents (NPG and DPG) used in synthesis of glycolized oligoesters seem to decrease or prevent crystallization of polyesters because of their different chemical structures compared to the repeating PET units. In Figure 6(b), two main diffraction peaks can be clearly observed at  $2\theta$  from  $15^\circ$  to  $20^\circ$  (main diffraction peak) and  $43^\circ$  for each sample, indicating a certain degree of crystallization, which are the characteristic peaks of the soft segment in segmented polyurethanes.<sup>34</sup> As shown in Figure 6(b), from PU1 to PU3, peaks ( $2\theta \approx 15^\circ$ - $20^\circ$ ) shift to the right and the intensity of diffraction peaks ( $2\theta \approx 15^\circ$ - $20^\circ$ ) decreases. However, the



(a)



(b)

Figure 6. XRD of the samples (a) PET glycolized oligoesters; (b) The obtained WPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



intensity of peaks for PU4, PU5 and PU6 gradually increases. PU5 and PU6 have relatively sharp peaks. Varying intensity of XRD peaks indicates decreased crystallinity of the soft segment from PU1 to PU3 and increased crystallinity from PU4 to PU6 with the content of glycolized oligoesters increasing constantly from PU1 to PU6.

Because of the ester group (C=O) in glycolized oligoesters, the more introduction of glycolized oligoesters in WPU is, the stronger hard-soft hydrogen bonding in WPU is. Therefore, more hard segments are dispersed in the soft matrix and the degree of microphase separation becomes smaller. In addition, compared to PPG, the obtained glycolized oligoesters have a rigid benzene ring and lower molecular weight. After reaction with diisocyanate, small rigid molecular chain segments can mix in the soft phase easily. Thus, the flexibility of molecular chain reduces and the neat arrangement of soft segments when crystallizing is hindered. So the crystallization capacity decreases from PU1 to PU3. However, for PU5 and PU6, the molar ratio of glycolized oligoesters to PPG is higher and they have more ester group. Two kinds of the soft segments (glycolized oligoesters and PPG) cannot completely mix at the molecular level, and phase separation of PPG and glycolized oligoesters may occur. That is also verified by two decomposition peaks in the second decomposition in TGA. Besides, according to Howard,<sup>39</sup> PPG can crystallize and glycolized oligoesters may facilitate crystallization of PPG in soft segments, which causes more microphase separation. This is reflected in the high crystallinity observed in XRD for PU5 and PU6.

#### Particle Size and Viscosity Analysis of WPU

Figure 7 shows particle size distribution of all samples. Comparing PU1 with PU2, the mean particle size from 0.044 to 0.134  $\mu\text{m}$  is both 68 nm. Only the volume of PU2 is slightly increased (from 78.6% in PU1 to 84.3% in PU2) by seldom introduction of glycolized oligoesters to WPU. Nevertheless, with the increased introduction of glycolized oligoesters, the mean particle size of WPU increases from 68 nm (PU1) to maximum 1.14  $\mu\text{m}$  (PU6). PU3, PU4, PU5, and PU6 show larger particle sizes compared to PU1. It may be due to the presence of aromatic ring on its backbone, which decreases the flexibility of soft segment. As known flexible particles are more deformable in shear field, and thus at the dispersion stage, the dispersed phase can be broken into smaller particles more easily.<sup>40</sup> Besides, according to Lee<sup>41</sup> the larger the molecular weight is, the better the flexibility of soft segment is. GPC results show that the molecular weight decreases from PU1 to PU6 (except for PU4). Thus, with the increased molar ratio of glycolized oligoesters to PPG (from PU1 to PU6), the flexibility decreases and the particle size increases (except for PU4). According to Feng<sup>41</sup> WPU synthesised from branched polyol has a larger particle size than that synthesised from linear polyol. Therefore, PU1 shows a smaller particle size compared to other samples. Compared with other samples, PU6 has a relatively larger particle size, which could be attributed to excessive viscosity of the prepolymer during the dispersion step in the synthesis procedure. It makes the dispersion of prepolymer more difficult, and then inhibits the polymer from fragmenting into smaller particles in water.

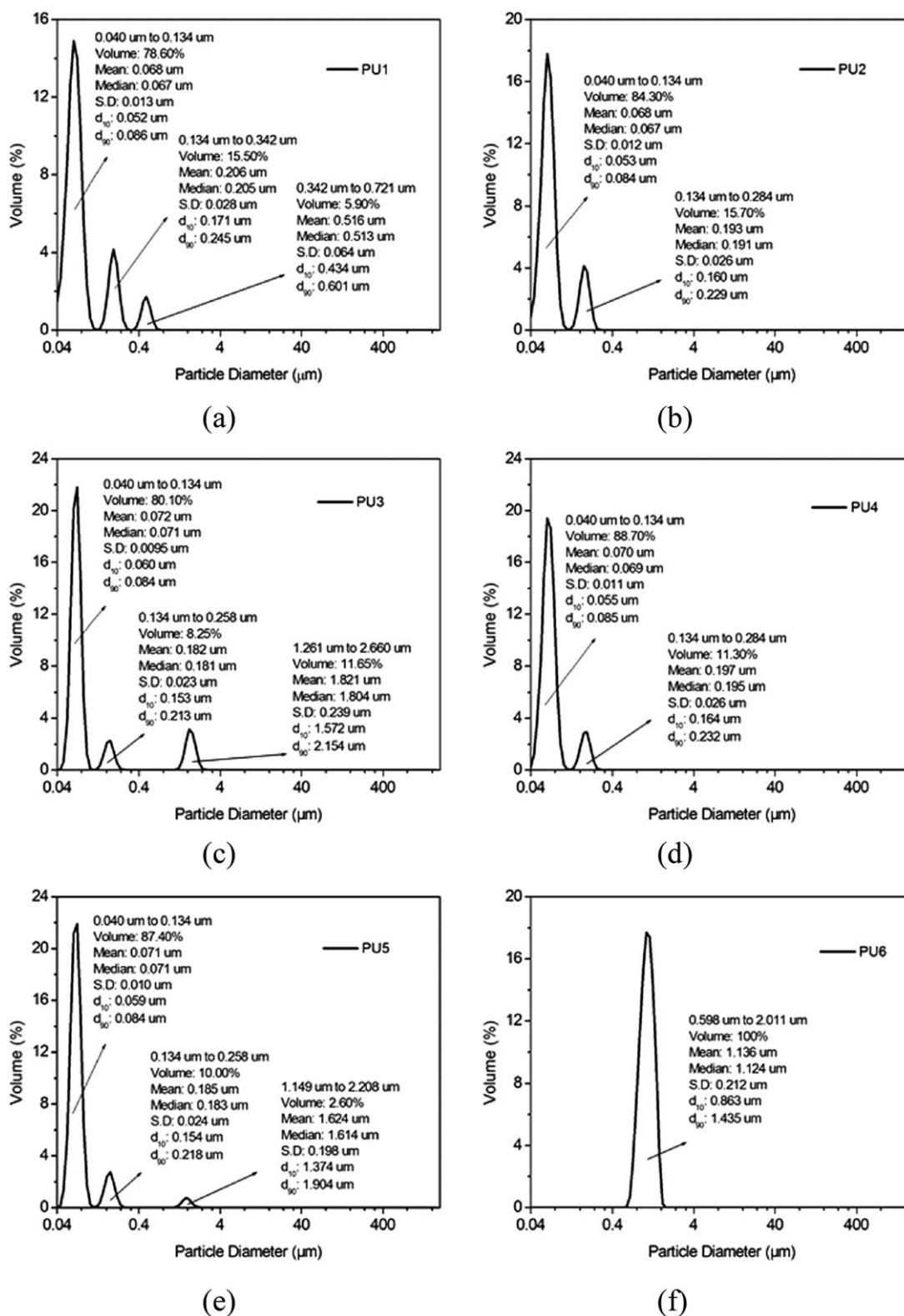
Generally, small latex particles are used to obtain films with better appearance and mechanical property. Small WPU particles are desirable when deep penetration of the dispersion into a substrate is essential.<sup>42</sup> In the printing procedure, printing substrates absorb ink to accelerate the speed of drying. When used as an ink binder, the smaller the WPU size is, the faster the drying processing is, and the better the printing results are. Hence, nanosized WPU particles are more attractive in both research and for end-use applications.<sup>42</sup> In this study, nanosized PU3 (72 nm), PU4 (70 nm) and PU5 particles (71 nm) with a good size distribution were synthesized, which is promising for application in water-borne ink binder.

Viscosity is one of the most important performance indexes of WPU, and it directly affects the storage stability of WPU. In general, different viscosity is needed in different applications. Figure 8 shows the viscosity of WPU versus time. It can be seen that PU2, PU3, PU4, PU5, and PU6 exhibit lower viscosity and their values are all below 20 mPa·S, even decreasing to approximately 5 mPa·S (PU5), while the viscosity of PU1 is up to 21 mPa·S. According to the previous study, the smaller the particle size of the dispersion is, the higher the viscosity is. The particle size analysis proves that particle size of PU1 is the smallest among all samples. Thus, PU1 has a relatively higher viscosity than other samples. Moreover, with the increased molar ratio of PET-glycolized oligoesters to PPG, the viscosity increases (except for PU5). This may arise from the stronger inter/intramolecular hydrogen bonding resulting from the carbamate groups in WPU, which limits the molecular mobility. Meanwhile, the free volume decreases with the increased inter/intramolecular hydrogen bond force. However, for PU5, the lowest viscosity is probably attributed to various reasons, such as decreased content of DMPA, lower neutralization or incorrect amount of acetone, which may arise from artificial errors. As seen, WPU synthesized from pure PPG has a stable viscosity within 180 s, while the viscosity of WPU in synthesis of PET glycolized oligoesters and PPG is relatively unstable, especially for PU4 and PU6. This may be caused by excessive introduction of glycolized oligoesters to soft segment. Once the content of glycolized oligoesters increases, PPG and glycolized oligoesters cannot mix well at the molecular level and be embedded in the main chain of WPU. Thus, the stability is bad, which is also reflected in TG and DSC results.

#### Thermal Analysis of WPU

Thermal stability is an important parameter for end-use product application. Therefore, thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) was conducted to analyse the decomposition behaviour of cured films of polyurethane dispersion. It is proposed that the thermal degradation of polyurethane is primarily a process of depolycondensation, which starts at about 200°C and presents a multimodal profile. Polyurethane with different backbone structures has different thermal stability.<sup>43</sup>

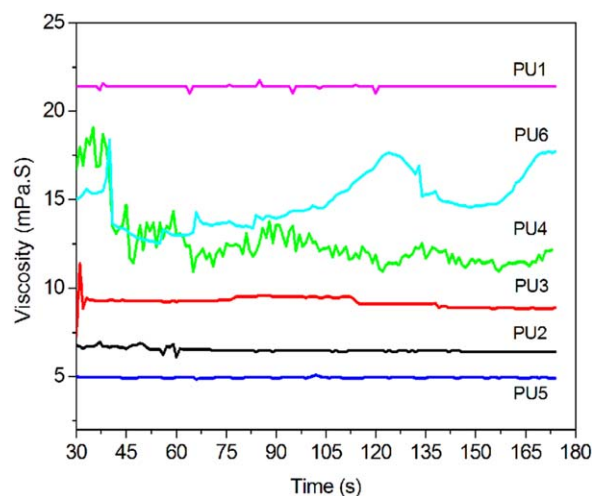
TGA curves of glycolized oligoesters and WPU are given in Figure 9 and Figure 10 shows TG and DTG curves of PU1. The detailed data of thermal decomposition are summarized in Table III. As depicted in Figure 9, glycolized oligoesters show



**Figure 7.** Particle size and particle size distribution of the obtained WPU in synthesis of glycolized oligoesters/PPG blends with different molar ratios. (a) PU1; (b) PU2; (c) PU3; (d) PU4; (e) PU5; (f) PU6.

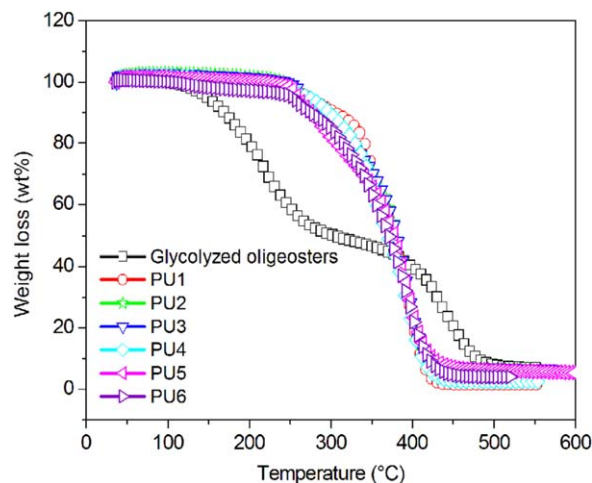
two main stages of degradation. The initial stage of degradation at 116°C may be due to the EG formed during the glycolysis reaction. The later stage occurring at 341°C may be ascribed to

the glycolized oligoesters. For aqueous polyurethanes, two stages of decomposition over the range 220–430°C appear in TGA curves of all samples. The first stage, between 220°C and

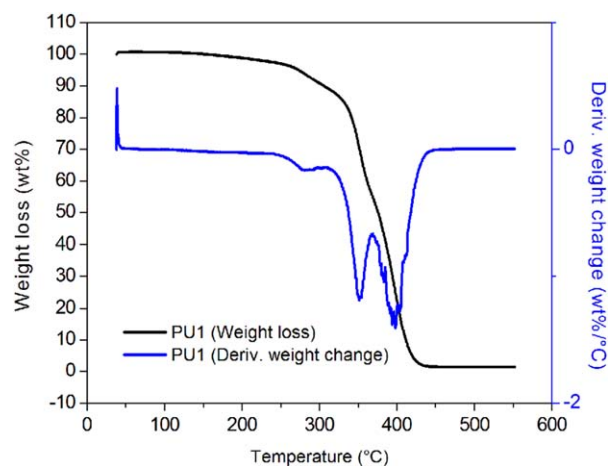


**Figure 8.** Viscosity of the WPU in synthesis of glycolysed oligoesters/PPG blends with different molar ratios. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

320°C, corresponds to the decomposition of the hard segment, which results in the formation of isocyanate and alcohol, primary or secondary amine and olefin and carbon dioxide. The second stage, between 320°C and 430°C, corresponds to the decomposition of polyol segments. The onset decomposition temperature ( $T_1$ ) of the first decomposition stage increases only slightly from PU1 to PU3 with a small weight loss, and PU4 has almost the same onset decomposition temperature but more weight loss than PU1. However, compared with PU1, the onset decomposition temperature of PU5 and PU6 is much lower and the weight loss is relatively more. This indicates that PU2 and PU3 possess higher thermal stability while PU5 and PU6 have a lower stability, in contrast to PU1. This is ascribed to the introduction of glycolysed oligoesters in comparison with PPG. Generally, the ester group is more difficult to thermally decompose because of larger cohesive energy than that of the ether group. For another, the introduced ester group makes the hydrogen bonding stronger in WPU. Yet, introduction of a cer-



**Figure 9.** TG curves of glycolysed oligoesters and the obtained WPU. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10.** TG and DTG curves of PU1. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

tain amount of glycolysed oligoester to WPU can improve thermal stability of the product. As seen in the second stage, PU2 and PU3 show lower onset decomposition temperatures ( $T_2$ ) but also less weight loss, and PU4 has a higher onset decomposition temperature but also more weight loss than PU1, so it is difficult to determine thermal stability. Nevertheless, at 364°C (the onset decomposition temperature of PU1), PU2 and PU3 have less weight loss, but PU4 has more weight loss than PU1. It is obvious that the order of thermal stability is  $PU3 > PU2 > PU1 > PU4$ . Therefore, with increased amount of glycolysed oligoester, thermal stability of WPU increases. Though thermal stability of PU4 is worse than PU2 and PU3 and it is nearly similar to PU1. Moreover, when the molar ratio of PET glycolysed oligoesters to PPG is 3 : 3 (PU4), glycolysed oligoesters and PPG can react completely, which is demonstrated by  $^1\text{H}$  NMR result. It not only reduces the wastage of raw materials but also increases the production of WPU. Therefore, PU4 is more significant for end-use applications. At the same time, double peaks appear at 275°C and 335°C for PU5 and at 282°C and 364°C for PU6. These may be attributed to decomposition of glycolysed oligoesters and PPG, respectively. Thus, the results show that PU3 is the most stable sample while PU5 and PU6 are the most unstable samples among all WPUs (from PU1 to PU6).

Further information about phase structure and thermal property of the obtained polyurethane dispersions can be obtained from analysis of the DSC traces. Figure 11 shows transition temperature of glycolysed oligoesters and WPU in synthesis of pure PPG, and glycolysed oligoesters–PPG blends with different molar ratios. According to Fang<sup>42</sup> glass transition temperatures ( $T_g$ ) of PPG ( $M_n = 2000$ ) and glycolysed oligoesters are approximately  $-69^\circ\text{C}$  and  $-43.1^\circ\text{C}$ , respectively. However, all samples from PU1 to PU6 have different  $T_g$  compared to PPG and glycolysed oligoesters, indicating that a certain number of hard segments are dispersed in soft segments. It also suggests that the reaction among PPG, glycolysed oligoesters and other raw materials disturbs the structured chain of PPG and glycolysed oligoesters, indicating generation of polyurethane. The  $T_g$  for PU1, PU2, PU3, PU4, PU5, and PU6 are observed to be  $-43.7$ ,

**Table III.** TGA Data of Polyurethane Films

Samples	First decomposition		Second decomposition		367°C
	T1 (°C)	Weight loss (wt %)	T2 (°C)	Weight loss (wt %)	Weight loss (wt %)
PU1	242	2.57%	367	43.73%	43.73%
PU2	245	2.01%	344	27.81%	38.35%
PU3	244	1.00%	329	21.80%	39.15%
PU4	241	3.17%	369	49.56%	48.32%
PU5	223	3.01%	275	10.11%	-
			335	28.53%	-
PU6	220	3.09%	282	10.98%	-
			364	45.27%	-

−46.7, −41.5, −47.0, −53.4, and −60.1°C respectively (Figure 9,  $T_g$  order: PU3 > PU1 > PU2 > PU4 > PU5 > PU6), which is almost the same order as the results obtained from TGA (thermal stability: PU3 > PU2 > PU1 > PU4 > PU5 > PU6), except for PU2. According to Howard<sup>39</sup> PPG can crystallize and glycolized oligoester may facilitate the crystallization of PPG in soft segments, which causes larger degree of microphase separation and lower  $T_g$  for PU2. From PU1 to PU3 (except for PU2), with the increased molar ratio of glycolized oligoesters to PPG, the hard-soft hydrogen bonding becomes stronger because of the ester group (C=O) in glycolized oligoesters, and more hard segments are dispersed in soft matrix and the degree of microphase separation is smaller. Hard segments are able to reduce the room for movement of molecular chains of soft segments, and then restrict mobility of soft segments, which makes  $T_g$  higher. Besides, the molecular weight of glycolized oligoester is smaller than PPG, as obtained from GPC results, and glycolized oligoesters have a rigid benzene ring. After reaction with diisocyanate, small molecule chain segments mix in the soft phase easily, which reduces the flexibility of molecular chains and makes  $T_g$  higher. On the other side, the ester group (C=O) has a stronger polarity and more cohesive energy than the ether group (C—O). With the increased molar ratios of glycolized oligoesters to PPG, more ester groups are introduced into WPU and then make it more difficult for soft segments to move, namely higher  $T_g$  values. For PU5 and PU6, although the molar ratios of glycolized oligoesters to PPG are higher and they have more ester groups, two kinds of soft segments (glycolized oligoesters and PPG) cannot mix completely at the molecular level, and phase separation of glycolized oligoesters and PPG may occur. That is also verified by two decomposition peaks in the second decomposition in TGA. Hence, the hard segment cannot dissolve well in the soft segment, and the soft segment can move more easily, namely lower  $T_g$  values.

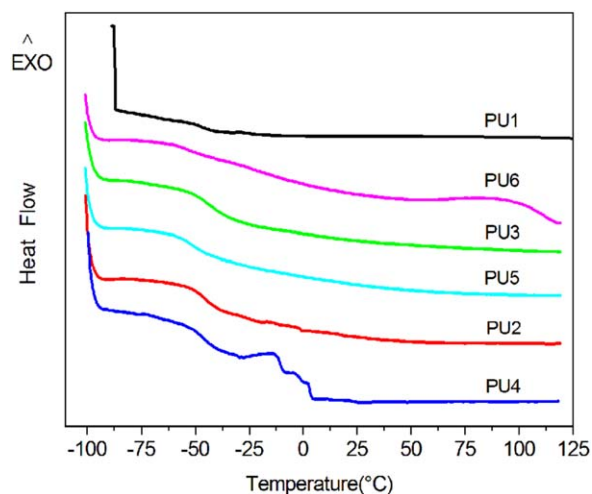
#### TEM Analysis

The morphology of colloidal particles can be observed by transmission electron microscopy. TEM images of WPU synthesised from pure PPG and glycolized oligoesters–PPG blends are shown in Figure 12. The dark dots or dark regions, which resulted from the coagulation of particles, are WPU particles. Figure 12 shows that PU1, PU2, PU3, PU4, and PU5 disper-

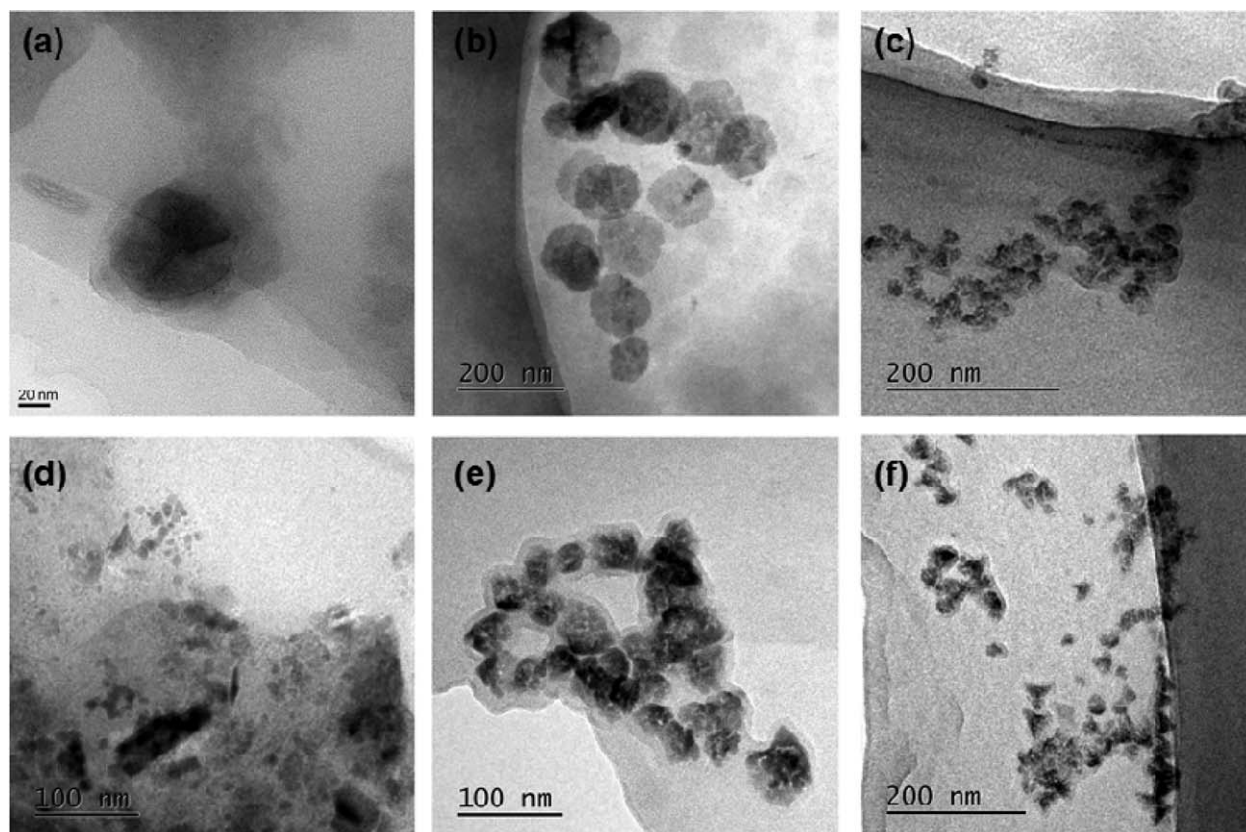
sions are composed of spherical particles with diameter of 67–300 nm, while the PU6 dispersion is different from others. Coagulation of particles could be obviously recognized in almost every TEM image, except in Figure 12(a), namely PU1. In other words, coalescence of particles occurs when glycolized oligoesters are incorporated in WPU, and then larger particles form because of particle coalescence. Thus, PU2, PU3, PU4, PU5, and PU6 have larger particle sizes than PU1, which is confirmed by the results of particle size and particle size distribution. Therefore, differences among these samples indicate that molar ratios of glycolized oligoesters to PPG in this study play a role in influencing the particle morphology.

#### DMA Analysis

The dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) of all obtained WPU are shown in Figures 13 and 14. Figure 13 shows that the storage modulus  $G'$  of all samples is maintained constant in the glassy plateau region, and then it is rapidly decreased due to the glass transition of the soft segment of WPU. Figure 13 also shows that from −80°C to −30°C the more introduction of glycolized oligoesters to WPU is, the lower storage modulus  $G'$  WPU possesses. However, after −5°C



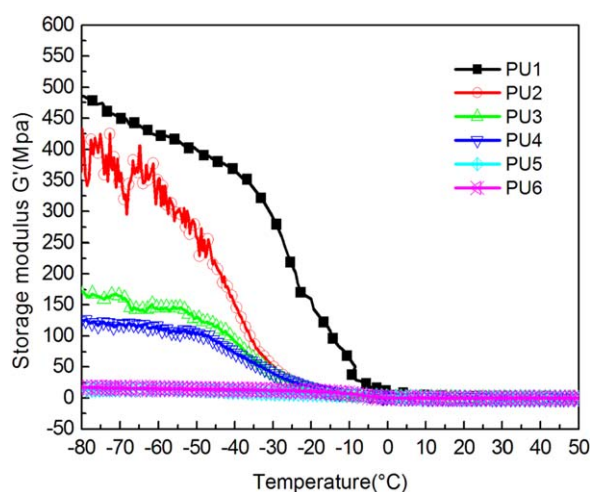
**Figure 11.** DSC thermograms of WPU in synthesis of glycolized oligoesters/PPG blends with different molar ratios. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



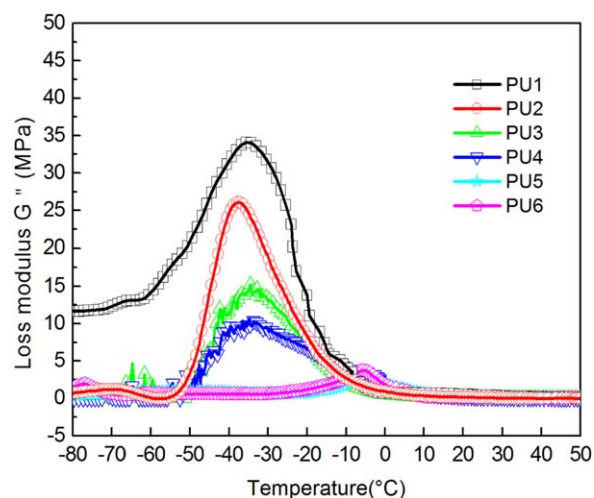
**Figure 12.** TEM images of WPU in synthesis of glycolized oligoesters/PPG blends with different molar ratios. (a) PU1 (b) PU2 (c) PU3 (d) PU4 (e) PU5 (f) PU6.

all obtained WPUs have nearly the same storage modulus  $G'$ . The loss modulus  $G''$  peaks of all samples from  $-45^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$  in Figure 14 are assigned to the glass transitions of WPUs. As seen glass transition temperatures of PU1, PU2, PU3, PU4 are approximately  $-35.1^{\circ}\text{C}$ ,  $-36.3^{\circ}\text{C}$ ,  $-33.8^{\circ}\text{C}$ ,  $-36.8^{\circ}\text{C}$ . Although the glass transition temperatures are slightly higher than that measured by DSC, the variation tendency from PU1

to PU4 is almost the same ( $\text{PU3} > \text{PU1} > \text{PU2} > \text{PU4}$ ). From  $-50^{\circ}\text{C}$  to  $-30^{\circ}\text{C}$ , with more introduction of glycolized oligoesters to WPU, namely from PU1 to PU6, the loss modulus  $G''$  can be observed to decrease from maximal 34 MPa to 0.4 MPa. It also means the viscosity from PU1 to PU6 becomes lower. Because of lower viscosity and better liquidity PU5 and PU6 can easily flow during DMA experiment, it is hard to take



**Figure 13.** Storage modulus ( $G'$ ) of WPU in synthesis of glycolized oligoesters/PPG blends with different molar ratios. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 14.** Loss modulus ( $G''$ ) of WPU in synthesis of glycolized oligoesters/PPG blends with different molar ratios. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

glass transition temperatures, and loss modulus  $G''$  peaks around glass transitions are also hardly seen. Yet, at 25°C PU1 has larger loss modulus  $G''$  while from PU2 to PU6 the loss modulus  $G''$  waves little difference, that proves that at room temperature PU1 has the highest viscosity and the viscosity from PU2 to PU6 waves in a small range, which is coordinated with particle size and viscosity analysis.

## CONCLUSIONS

PET bottles used for soft drinks were depolymerized by glycolysis using a 1 : 3 molar ratio of PET repeating unit to glycols like NPG and DPG. A series of WPU was synthesized in different molar ratios of glycolized oligoesters and PPG blends as soft segment. The main purpose of this paper is to investigate performances of WPU synthesized from glycolized oligoesters.

The results of FT-IR and  $^1\text{H}$  NMR indicate that the ketone carbonyl and hydrazine have reacted and glycolized oligoesters have been successfully introduced into the soft segment of polyurethanes. According to TGA and DSC data, the introduction of a certain amount of glycolized oligoester to soft segment, such as PU2, PU3 and PU4, can make glass transition temperature,  $T_g$ , of WPU increase, and thermal stability of these WPU samples has also been improved. However, thermal stability becomes worse with the increased content of oligoester. It may be caused by introduction of ester group (C=O) into WPU, which makes hard-soft hydrogen bonding stronger, and the degree of hard-soft domain microphase separation smaller. This corresponds to XRD results. XRD also shows that when the molar ratio of glycolized oligoester and PPG is excessively high like PU5 and PU6, two kinds of soft segments (glycolized oligoesters and PPG) could not mix completely at molecular level and the phase separation may occur. And this can be verified by two decomposition peaks in the second decomposition in TGA, and also by the crystallization of glycolized oligoesters and PPG. GPC shows that by using PET waste the molecular weight of WPU is decreased, and the introduction of different amounts of glycolized oligoester increases the possibility of forming varying chain lengths of polyurethane dispersions. Furthermore, in contrast with pure WPU, WPU synthesized from glycolized oligoesters and PPG blends possess larger particle size and relatively lower viscosity, especially PU2 and PU3, which have a lower and more stable viscosity. Nanosized PU3 (72 nm) and PU4 particles (70 nm) with a good size distribution are promising for application in water-borne ink binders. Thus, in contrast to other samples, PU3 has a better combination of properties such as better thermal stability and particle size distribution, lower and more stable viscosity.

In conclusion, it is believed that glycolized oligoesters obtained from recycled PET would be applicable for synthesis of environment-friendly WPU. And WPU incorporated with a certain amount of glycolized oligoester can show good performances, especially glycolized oligoesters and PPG blends in a molar ratio of 2 : 4, namely PU3.

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