

# Water Remaining Properties of Nonwoven Fabrics Treated with the Polyurethane Polymers Containing Carboxylic Acid Group and the Thermal and Structural Characterization of the Polymers

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Received 17 May 2006; accepted 5 September 2007

DOI 10.1002/app.27365

Published online 13 November 2007 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Three low-molecular-weight polyurethanes (LMWPU) containing various amounts of carboxylic acid were synthesized and applied on the nonwoven fabric for the improvement of water remaining property. The chemical structure of the LMWPU was confirmed with <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. The molecular weights of those three LMWPU ranged from 3100 to 4200 g/mol. The results showed that the add-on values were increased with the increasing of the content of 2,2-bis(hydroxymethyl)propionic acid in LMWPU at a same resin concentration in padding bath. However, the water remaining values were decreased with the increasing of the content of 2,2-bis(hydroxymethyl)propionic acid in LMWPU for a given add-

on value. The thermal properties, such as thermo-degradation and the values of  $T_g$  and  $T_m$  of the polymers, could not affect the water remaining property of the treated fabrics. The analyses of X-ray diffraction patterns and polarizing microscope observations showed that LMWPU with higher content of polytetramethyleneglycol had higher amorphous region. This phenomenon clearly supported that the values of water remaining were strongly affected by the amorphous region of the LMWPU polymers. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2618–2625, 2008

**Key words:** NMR; glass transition; melting point; polyurethanes; thermal analysis; nonwoven fabric

## INTRODUCTION

In recent decennium, the grassing of gardening is becoming a very important factor for the sale of a house in the area of Asia. On the other hand, the engineering of river and road<sup>1–4</sup> also need a huge amount of reinforcing and grassing to prevent the washout of ground or soil. Nonwoven fabric is a well-known material to achieve those jobs because of its high porosity and entanglement. The porosity contributes to high water permeation while entanglement prevents disintegration which makes nonwoven fabric an ideal candidate to prevent soil washout.

Another interesting field for the use of nonwoven fabric is the arboricultural engineering, such as planting of vegetation. Some investigations<sup>5–7</sup> focused on the degradation of grid materials, which would not astrict the upgrowth of vegetation and could improve the trouble of environmental pollution.

Some reports<sup>8,9</sup> revealed that the inclusion of gemination improving agent within the nonwoven could enhance the seeding of cultivation. Wang<sup>10</sup> pointed out that the well structure of vegetation planting block could improve the growth of vegetation. This structure of vegetation planting block was formed with five layers. Those layers were original soil, first nonwoven, grid of plastic, second nonwoven, and soil containing small stone particle layers. The grid of plastic layer was used as drainage. The roots of the vegetation in the soil layer will penetrate through the first nonwoven layer and also the second nonwoven layer. If the nonwoven layer is highly hydrophobic, the penetration of the roots of the vegetation will be undesired. The higher water remaining property and larger pore structure of the nonwoven layer could provide the more suitable environment for the penetration of the roots of vegetation. This will have the higher benefit for the upgrowth of vegetation on the layer of original soil. In general, the methods for improving the water remaining of polyester (PET) nonwoven fabrics are the blending of hydrophilic cellulose fibers to PET

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fibers or the addition of hydrophilic surfactant onto the surface of the PET fibers. However, the former has the significant decrease on the strength of the nonwoven fabrics and the latter has only the temporary effect. In another case, the use of alkali agents could hydrolyze PET fibers to create the rough concavity on the fiber surface, but they decrease the strength of nonwoven fabric significantly. Wang<sup>11</sup> used the pad-baking after-treatment of the emulsions of water dissoluble PU to treat the nonwoven fabric for improving the water remaining properties of the treated PET nonwoven fabrics. The results pointed out that there is no significant effect on the strength of the nonwoven fabric. Wang revealed that the water remaining property of the after-treated nonwoven fabrics with water dissoluble polyurethane (PU) containing citric acid could significantly improve the water remaining property. The addition of citric acid could also improve the degradation of PU molecules to further increase the water remaining values.<sup>11</sup>

In this study, 2,2-bis(hydroxymethyl)propionic acid (DMPA) was used as a hydrophilic monomer to coreact with diphenylmethane diisocyanate (MDI) and polytetramethyleneglycol (PTMG) under various ratios of MDI/DMPA/PTMG to form the PU prepolymer. Then, those prepolymers were terminated with methanol (excess) and neutralized with sodium hydroxide (NaOH) to obtain the various LMWPU emulsions. Finally, the various LMWPU emulsions were used to treat (pad-baking process) the nonwoven fabric for improving the water containing property. However, the detailed information about the improvement of the water remaining property of nonwoven by using the LMWPU emulsions is lacking. The values of water remaining of the treated nonwoven fabrics and the effects of thermal and structural characterization of the various LMWPU on the water remaining properties of the treated nonwoven fabrics were investigated.

## EXPERIMENTAL

### Materials

In this study, the PET nonwoven fabric (350 g/m<sup>2</sup>) was employed. The polyester fiber was about 3 denier and 51 mm long. One side of the nonwoven fabric was melting treatment to match the standard of CNS 1128 A2183. This nonwoven fabric passed the determination of the method of 5610 L3080. It met the standard level of 60 kg.

2,2-bis(hydroxymethyl)propionic acid (DMPA), diphenylmethane diisocyanate (MDI), and polytetramethyleneglycol (PTMG, 1000 g/mol) were all obtained from the Aldrich Co., Milwaukee, USA. Other reagents were all chemical grade.

### Preparation of LMWPU containing carboxylic acid group

MDI (400 mmol) was mixed with acetone (50 mL) in a 1000-mL reactor (a three-necked flask), then the mixture of DMPA (50 mmol), *N*-methyl-2-pyrrolidine (NMP, 20 mL), and PTMG (150 mmol) was added into the reactor gradually under mechanical stirring. A N<sub>2</sub> flow rate of 50 mL/min was passing through the reactor to avoid the hydrolysis of the isocyanate group of MDI. The polymerization was kept at 80°C for 3 h. After polymerization, 10 mL (excess) of methanol was added into the reactor and stirred for 3 h to block the isocyanate group at the end of the prepolymer. Subsequently, suitable amounts of NaOH (equal to the mole of DMPA) were added into the reactor to neutralize the carboxylic acid group partially. Finally, distilled water was added in the reactor to form the 30 wt % of low-molecular-weight PU emulsions. In this study, there are three sets of mole ratio of MDI : DMPA : PTMG (4.0 : 1.5 : 0.5; 4.0 : 1.0 : 1.0; and 4.0 : 0.5 : 1.5, respectively) were employed. The three emulsions were defined as EPU1, EPU2, and EPU3, respectively. The chemical structure of the LMWPU was confirmed with <sup>1</sup>H nuclear magnetic resonance spectroscopy (<sup>1</sup>H-NMR), <sup>13</sup>C nuclear magnetic resonance spectroscopy (<sup>13</sup>C-NMR), and gel-permeation chromatography (GPC).

### Nuclear magnetic resonance spectroscopy (NMR)

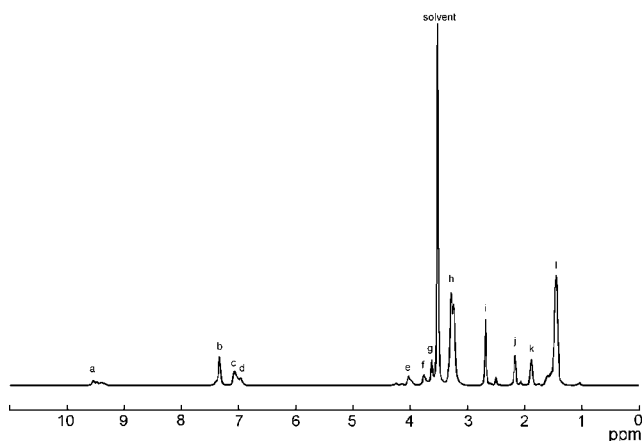
The 600 MHz <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded with a Bruker Avance spectrometer (Bruker Co., Germany) and performed at 30°C with 5% (w/v) polymer solution in deuterated dimethyl sulfoxide (*d*<sub>6</sub>-DMSO).

### Gel-permeation chromatography (GPC)

Firstly, 0.3 g of LMWPU (30 wt % solid content) was added into 50 mL of tetrahydrofuran (THF), and stirred vigorously. After that, the LiCl was added slowly into the mixer until a clear solution was obtained. Then, a GPC (Model 500, Analytical Scientific Instruments, CA) was used to measure the molecular weight distribution. This instrument contained a reflection index (RI) detector (Schambeck RI2000) and two columns in a series of Jordi gel divinyl benzene (DVB) mixed bed and 10,000 Å bed. The relative standard was polystyrene and the measured temperature was 30°C. The calibration curve was obtained by eight standards from molecular weight 3420 to 2.7 × 10<sup>6</sup>. The carrier solvent was THF at a flow rate of 1 mL/min.

### After-treatment of nonwoven fabrics

PET nonwoven fabric samples were padded with padding machine under the roller pressure of



**Figure 1**  $^1\text{H}$ -NMR spectrum obtained from the low molecular weight of polyurethane (LMWPU). The mole ratio of MDI : DMPA : PTMG is 4 : 1.5 : 0.5.

$2.0 \text{ kg/m}^2$ . The padding procedure was carried out two times to obtain an even pickup from the freshly prepared PU emulsions. Padding emulsions contained various concentrations (1, 2, 4, 7, 10, and 12 wt %) of EPU1, EPU2, and EPU3, respectively. Padded fabric samples were then baked at  $135^\circ\text{C}$  for 30 min, washed with tap water to wash out the unfixed PU resin, and finally dried.

#### Water remaining and add-on test

The values of water remaining of the treated fabrics were determined using the method of CNS L3233. The values of add-on were calculated by the following equation.

$$\text{Add-on}(\%) = (A - B)/B \times 100\% \quad (1)$$

where, the values of  $A$  and  $B$  are the weight after and before treatment, respectively.

#### Thermal properties

The thermogravimetric analysis (TGA) was performed using a Du Pont TGA-2050 (TA Instrument, New Castle, DE). All samples were carried out at a heating rate of  $10^\circ\text{C}/\text{min}$  and under flowing nitrogen of a flow rate of  $100 \text{ mL}/\text{min}$ . The samples ( $10$ – $15 \text{ mg}$ ) were placed on the plate of platinum for each experiment.

The thermal properties of the various polyurethanes were determined using a differential scanning calorimetry (DSC, Du Pont DSC Q 10 TA Instruments, New Castle, DE). All scans were carried out at a heating rate of  $10^\circ\text{C}/\text{min}$  and under flowing nitrogen of a flow rate of  $50 \text{ mL}/\text{min}$ . The instrument was calibrated using the pure indium. Samples weighing about  $5 \text{ mg}$  were placed in standard aluminum sample pans for each DSC experiment.

#### Wide angle X-ray diffraction

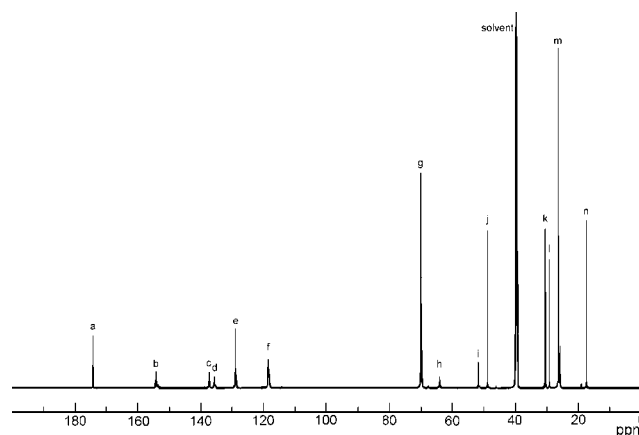
The wide angle X-ray diffraction (WAXD) was determined using a X-ray Powder Diffractometer XRD (MXP18, MAC Science, Yokohama, Japan) equipped with a Ni-filtered  $\text{CuK}\alpha$  radiation and operated at  $40 \text{ kV}$  and  $30 \text{ mA}$ . Each sample with  $3.0\text{-mm}$  thickness was maintained stationary and scanned in the reflection mode from  $2^\circ$  to  $35^\circ$  at a scanning rate of  $2^\circ/\text{min}$ .

#### Polarizing microscope observation

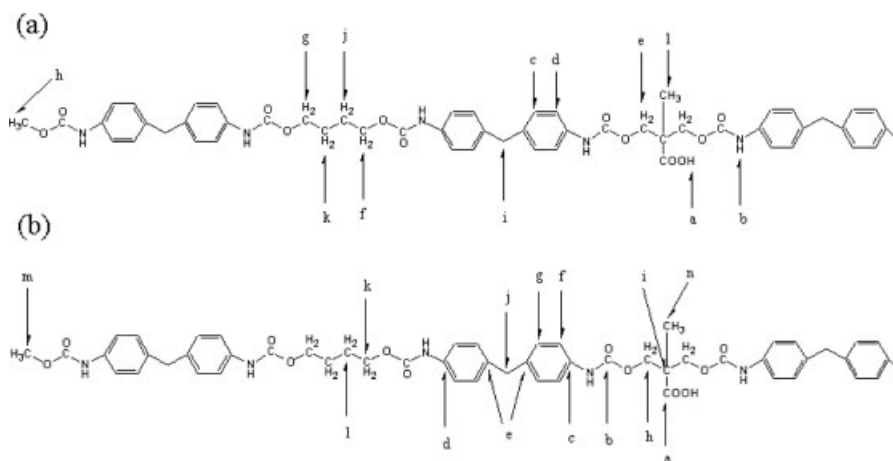
Three synthesized LMWPU (30 wt % solid content) were coated on a piece of glass, respectively, and dried at  $60^\circ\text{C}$ . Then, those samples were observed on a polarizing microscope of Lux 12pols (Leica, Germany) for 500 times.

### RESULTS AND DISCUSSION

In this study, three sets of mole ratio of MDI : DMPA : PTMG ( $4.0 : 1.5 : 0.5$ ;  $4.0 : 1.0 : 1.0$ ; and  $4.0 : 0.5 : 1.5$ , respectively) were employed to synthesize the low-molecular-weight polyurethane (LMWPU). The emulsions of the three LMWPU were defined as EPU1, EPU2, and EPU3, respectively. The chemical structure of the LMWPU is confirmed with the analyses of the patterns of  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR. The patterns are shown in Figures 1 and 2, respectively. From the two figures, the skeleton of the polymer materials of LMWPU is suggested as Scheme 1. The chemical structures of the three LMWPU are the same for the three LMWPU. Therefore, only the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra obtained from the LMWPU (MDI : DMPA : PTMG =  $4 : 1.5 : 0.5$ ) is selected to explain the chemical structures of the LMWPU. The  $^1\text{H}$ -NMR spectrum in Figure 1 reveals the interesting and important peaks



**Figure 2**  $^{13}\text{C}$ -NMR spectrum obtained from the low molecular weight of polyurethane (LMWPU). The mole ratio for MDI : DMPA : PTMG is 4 : 1.5 : 0.5.



**Scheme 1** (a) Various hydrogens assigned on the skeleton of LMWPU and (b) various carbons assigned on the skeleton of LMWPU.

for  $-\text{COOH}$  at about 9.6 ppm (assigned as a),  $-\text{NH}-$  at about 7.3 ppm (assigned as b), aromatic hydrogen at about 6.9–7.1 ppm (assigned as c and d), and the various H on alkyl group at about 2.0–4.0 ppm (assigned as e ~ l). Those peaks of chemical shift (Scheme 1) for the various hydrogen are confirmed with the publication of Silverstein et al.<sup>12</sup> Meanwhile, the interesting and important peaks in Figure 2 ( $^{13}\text{C}$ -NMR spectrum) for  $-\text{COOH}$  at about 175 ppm (assigned as a),  $-\text{NHCOO}-$  at about 154 ppm (assigned as b), aromatic ring carbons at about 70–138 ppm (assigned as c–g), and the various carbon on alkyl group at about 17–65 ppm (assigned as h–n). They (Scheme 1) are also confirmed with the publication of Silverstein et al.<sup>12</sup> The experimental values and literature values<sup>13–17</sup> are listed in Table I for comparison. The literature values again support the results in this study. In this study, the moles for MDI are the sum of DMPA and PTMG. It is expected that the polymerization reaction of the mixtures of MDI, DMPA, and PTMG is a regular/random copolymerization. MDI is expected to react with DMPA and PTMG, respectively, to form a MDI–

(PTMG–MDI–DMPA–MDI)<sub>x</sub> copolymer. After reacting with methanol (Me), a stable end product is expected to be the Me–MDI–(PTMG–MDI–DMPA–MDI)<sub>x</sub>–Me. The possible segment is suggested in Scheme 1(a,b). The higher content of carboxylic acid group is expected to improve the water remaining property of the Me–MDI–(PTMG–MDI–DMPA–MDI)<sub>x</sub>–Me treated nonwoven fabrics. From the analyses of  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR (Figs. 1 and 2), the major skeleton of the synthesized LMWPU can be certified.

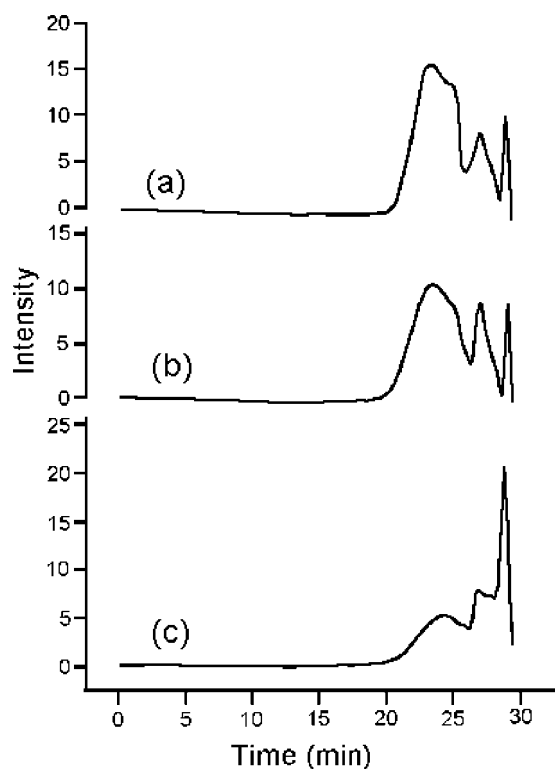
To further realize the molecular weight of the three synthesized polymers, they were dissolved in LiCl/THF and examined with GPC. The results are shown in Figure 3 (a–c), respectively. The average molecular weights ( $M_n$ ) of the three LMWPU are in the range from 3100 to 4200 g/mol (Table II) and the molecular sizes are in the series of EPU1 > EPU2 > EPU3. From the comparison, it can be seen that there are three types of polymers for each LMWPU sample. That is, three peaks appear on the elution time of GPC pattern. It is thought that the three types of LMWPU are Me–MDI–(DMPA–MDI)<sub>y</sub>–Me, Me–MDI–(PTMG–MDI–DMPA–MDI)<sub>x</sub>–Me, and Me–MDI–(PTMG–MDI)<sub>n</sub>–Me, respectively. The higher molecular weight for EPU1 probably causes by the higher reactivity of DMPA than that of PTMG. Under the ratio of MDI : DMPA : PTMG equaling to 4 : 1.5 : 0.5, the main peak (elution time at about 23 min) is Me–MDI–(DMPA–MDI)<sub>y</sub>–Me [Fig. 3(a)]. Meanwhile, under the ratio of MDI : DMPA : PTMG equaling to 4 : 0.5 : 1.5, the main peak (elution time at about 27.5 min) is Me–MDI–(PTMG–MDI)<sub>n</sub>–Me [Fig. 3(c)]. The above results ensure that those three types of polyurethane are low molecular weight containing  $-\text{COOH}$  and  $-\text{COONa}$  groups.

Table II shows that the add-on values are increased with the increasing of DMPA contained in

**TABLE I**  
The Chemical Shift Values in this Study and Literature Values of  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR for Low-Molecular-Weight PU

Type of NMR	Functional group	Experimental values (ppm)	Literature values (ppm)
$^1\text{H}$ -NMR	$-\text{COOH}$	9.6	7.7, <sup>16</sup> 12.7 <sup>13</sup>
	$-\text{NH}$	7.3	6.8 <sup>17</sup>
	Aromatic ring	6.9–7.1	7.0–7.2 <sup>14</sup>
	Alkyl group	2.0–4.0	1.8–4.0 <sup>17</sup>
$^{13}\text{C}$ -NMR	$-\text{COOH}$	175	174 <sup>17</sup>
	$-\text{NHCOO}-$	154	157.2 <sup>17</sup>
	Aromatic ring	70–138	118.1–143.7 <sup>15</sup>
	Alkyl group	17–65	23.0–58.9 <sup>17</sup>

LMWPU for a given agent concentration in padding bath. It is natural that DMPA has the lower affinity with PET fibers. Therefore, the higher add-on value for EPU1 is conflicting to the general knowledge. In general, the hydrophilic group, especially the water soluble group such as  $-\text{COO}^-$ , has lower affinity with the PET fibers and hence polymer containing hydrophilic group have lower add-on value on PET fibers. Clearly, there is other factor affecting the adhesion between PET fiber and LMWPU. This factor might significantly affect the water remaining property of the after-treated nonwoven fabrics. Table II also shows the data of water remaining of pristine nonwoven fabric and the various LMWPU treated nonwoven fabrics with the various concentrations. From the table, it can be found that the water remaining of pristine nonwoven fabric has higher water remaining value. At the same time, the application of LMWPU on/within the nonwoven fabric decreases the water remaining values of the after-treated nonwoven fabrics. This phenomenon is attributed to the blocking effect of the LMWPU on/within the nonwoven fabric. The previous study<sup>11</sup> distinctly showed that this blocking effect was caused by the occupation of the gaps among fibers by the treating agents. The blocking effect will certainly decrease the water remaining ability of nonwoven fabric. However, the water remaining values of the after-treated nonwoven fabrics in this study



**Figure 3** Gel-permeation chromatography (GPC) patterns of (a) EPU1, (b) EPU2, and (c) EPU3, respectively.

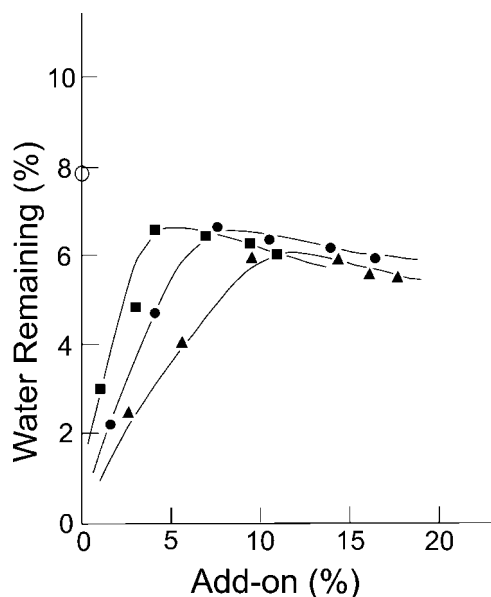
**TABLE II**  
The Values of Add-On and Water Remaining values for the PET Nonwoven Fabrics After-Treated with Low-Molecular-Weight PU Emulsions Under 135°C for 30 min and the Molecular Weight of Low-Molecular-Weight PU Obtained from GPC

Agent	Agent concentrations (%)	Add-on (%)	Water remaining (%)	Average molecular weight (g/mol)
EPU1	0	0	7.98	4148
	1	3.02	2.50	
	2	5.63	4.03	
	4	9.61	5.90	
	7	14.76	5.81	
	10	15.94	5.47	
EPU2	12	17.64	5.37	3966
	1	1.98	2.34	
	2	3.87	4.9	
	4	7.39	6.47	
	7	10.23	6.30	
	10	14.04	6.18	
EPU3	12	16.36	5.95	3144
	1	1.32	3.02	
	2	2.65	4.62	
	4	4.38	6.52	
	7	6.96	6.32	
	10	9.45	6.26	
	12	10.78	6.04	

have higher water remaining percentage than that of the previous study.<sup>11</sup> This result is probably caused by the higher water remaining ability of carboxylic acid group ( $-\text{COOH}$ ) and carboxylic ion group ( $-\text{COO}^-$ ) contained in LMWPU.

On the other hand, the water remaining values for the three types of LMWPU are ranked in the series of  $\text{EPU3} > \text{EPU2} > \text{EPU1}$  for a given add-on value (Fig. 4). Again, this result is dramatically different from that of our prediction. It is known that the functional groups of  $-\text{COOH}$  and  $-\text{COONa}$  (DMPA) have the higher hydrophilic property than that of the functional group of ether (PTMG). To confirm the factor that affects the mechanism of water remaining in this study, the following thermal and structural characterizations are used to explain this phenomenon.

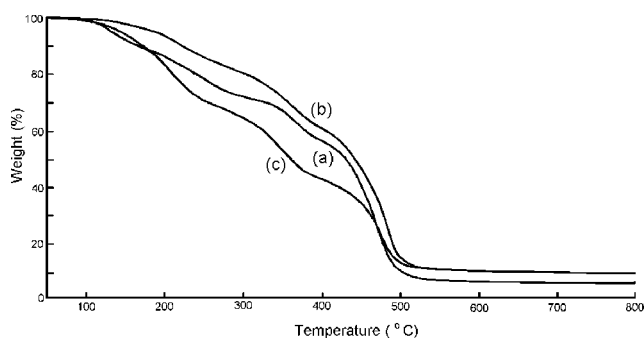
Firstly, those patterns of TGA diagrams for the LMWPU films are shown in Figure 5. Those patterns reveal that the amounts of char yield for EPU2 and EPU3 are significantly higher than that for EPU1. The lower value of char yield for EPU1 is clearly caused by the higher carboxylic acid, which will increase the hydrolysis of PU molecules under higher temperature or a longer time period usage.<sup>11</sup> From Figure 5, the values of char yield, the char yield temperature, and the temperatures having 20% weight loss can be obtained and are listed in Table III, in which char yield temperature is the temperature that the char is formed under test and the char yield value is the weight % of char formed. The



**Figure 4** The relationships between water remaining values and add-on values of the after-treated nonwoven fabrics for the (▲) EPU1, (●) EPU2, and (■) EPU3, respectively.

weight % of char yield for EPU2 is the same with that for EPU3 and is significantly higher than that for EPU1. The char yield temperature for EPU2 is slightly higher than that for EPU3 and is significantly lower than that for EPU1. It is interesting to find that the temperature having 20% weight loss for EPU2 is significantly higher than that for EPU1 and EPU3. This result clearly reveals that the construction of the polymer of EPU2 in solid state is different from that the simple mixtures of EPU1 and EPU3. It probably attributes to the interaction between the EPU molecules.

To confirm the structural difference of solid state among the three synthesized low-molecular-weight polyurethanes, the DSC thermograms ( $-100$  to  $50^{\circ}\text{C}$ ) of the three polymers for (a) EPU1, (b) EPU2, and (c) EPU3 are presented in Figure 6. From those figures,



**Figure 5** Patterns of thermogravimetric analysis (TGA) obtained from the (a) EPU1, (b) EPU2, and (c) EPU3, respectively.

**TABLE III**  
The Values of Char yield, Char yield temperature, and  $Td0.2$  of the Various Low-Molecular-Weight Polyurethane, Respectively

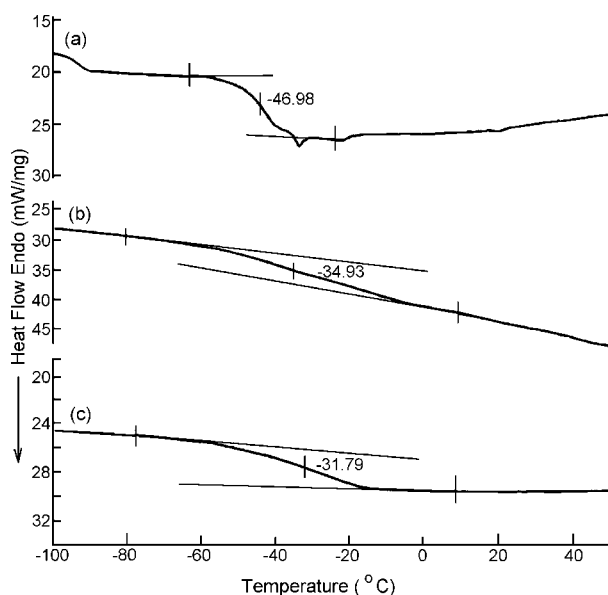
PU	Char yield (%[w/w]) <sup>a</sup>	Char yield temperature ( $^{\circ}\text{C}$ ) <sup>b</sup>	$Td0.2$ ( $^{\circ}\text{C}$ ) <sup>c</sup>
EPU1	6.5	530	240
EPU2	10.6	517	301
EPU3	10.6	513	210

<sup>a</sup> Char yields were obtained at  $800^{\circ}\text{C}$ .

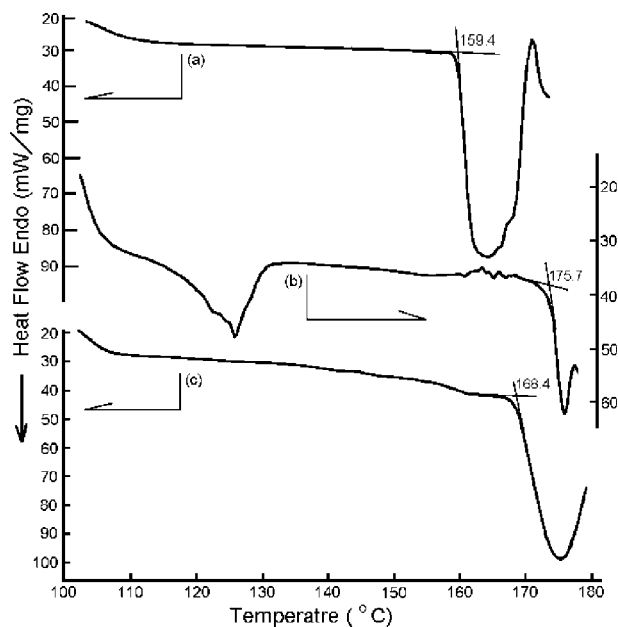
<sup>b</sup> The temperatures that char were beginning to yield.

<sup>c</sup> The temperatures that had 20% weight loss.

the glass transition temperatures ( $T_g$ ) of soft segment are obtained. As predicated, the values of  $T_g$  for the three LMWPU are in the rank of  $\text{EPU1} < \text{EPU2} < \text{EPU3}$  ( $-46.98$ ,  $-34.93$ , and  $-31.79^{\circ}\text{C}$ , respectively). This is caused by the structural factor of higher branch of polymer<sup>18</sup> for EPU1. Because the thermogravimetric property of the hard segment is concerned to the part of crystal, the DSC thermograms of the higher temperature range ( $100$ – $180^{\circ}\text{C}$ ) for the three polymers of (a) EPU1, (b) EPU2, and (c) EPU3 are also employed to observe the thermal properties and are shown in Figure 7. These figures show that the values of  $T_m$  obtained from the peaks of the patterns for the three LMWPUs are in the order of  $\text{EPU3} > \text{EPU2} > \text{EPU1}$ . This result is agreeing with the series of the char yield obtained from Figure 5. This series is certainly attributed to the density of crystal. As discussed earlier, the branch structure cannot build the higher density of crystal; therefore, EPU1 can only have lower value of  $T_m$ . On the other hand, the  $T_m$  values obtained from the initial part of



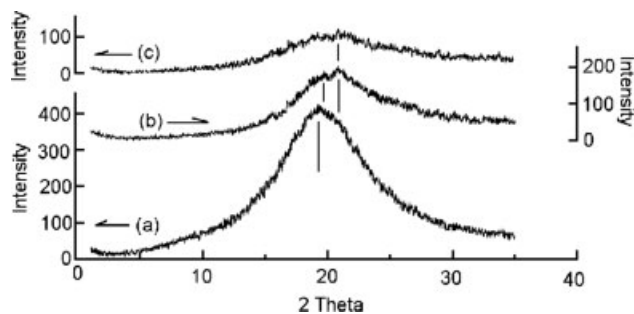
**Figure 6** DSC thermograms (from  $-100$  to  $50^{\circ}\text{C}$ ) obtained from the (a) EPU1, (b) EPU2, and (c) EPU3, respectively.



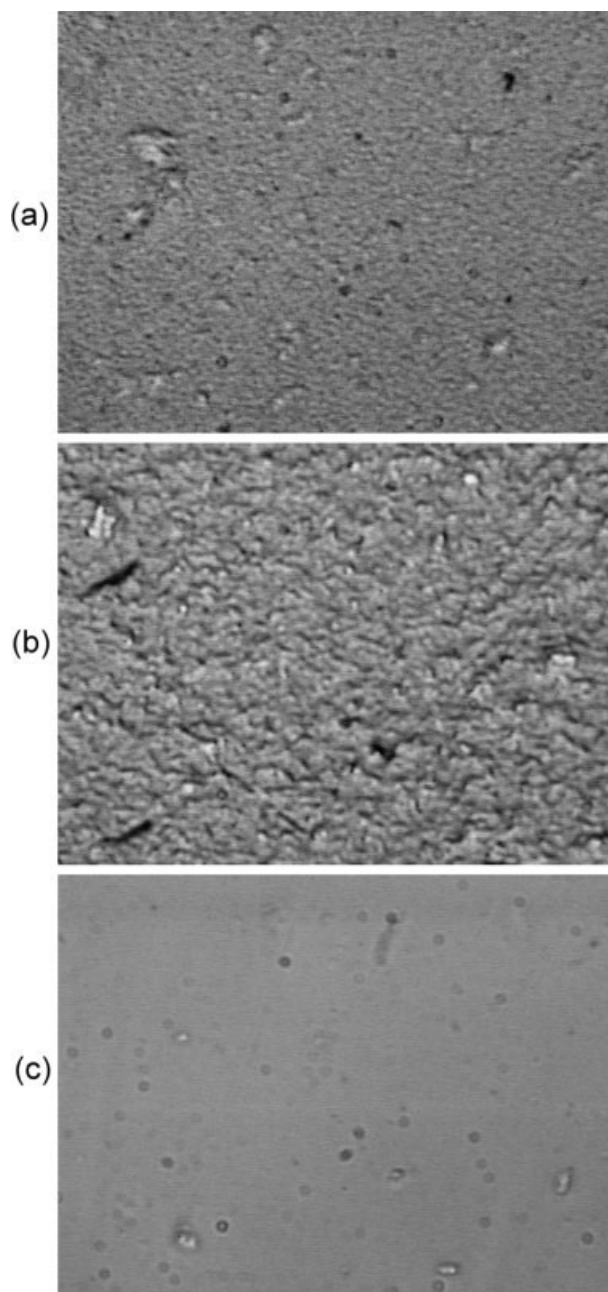
**Figure 7** DSC thermograms (from 100 to 180°C) obtained from the (a) EPU1, (b) EPU2, and (c) EPU3, respectively.

the heat flow endothermic curves are ranked as EPU2 > EPU3 > EPU1 (175.7, 168.4, and 159.4°C, respectively). Significantly, the interaction between EPU molecules is existent. However, it is still not clear that the water remaining value for EPU3 is higher than that for EPU1 and EPU2.

The wide angle X-ray diffraction (WAXD) pattern is the most reliable method, which can clearly distinct the difference of crystalline structures among EPU1, EPU2, and EPU3. They are shown in Figure 8 (a–c), respectively. It is interesting to find that there is a new diffraction peak appears in the pattern of EPU2, which has larger  $2\theta$  value than that of EPU1. According to Bragg's equation, the layer distance of crystal for EPU2 is smaller than that for EPU1. The value of  $T_m$  for EPU2 is certainly higher than that for EPU1. Another interesting phenomenon is that the intensity of X-ray diffraction for EPU3 is significantly lower than that for EPU1 and EPU2. This



**Figure 8** Patterns of wide angle X-Ray diffraction obtained from the (a) EPU1, (b) EPU2, and (c) EPU3, respectively.



**Figure 9** Polarization microscope observations for the films of (a) EPU1, (b) EPU2, and (c) EPU3, respectively.

reveals that EPU3 is a highly amorphous material as compared with EPU1 and EPU2.

To confirm the results observed from X-ray diffraction method, the polarizing microscope pictures are utilized for comparison and are revealed in Figure 9 (a–c) for EPU1, EPU2, and EPU3, respectively. Figure 9(a) shows that EPU1 is a highly crystalline material, which has relatively smaller size of crystal. Figure 9(b) shows that EPU2 is a crystalline material having relatively larger size of crystal. However, EPU3 [Fig. 9(c)] shows a lower crystalline material having only few crystals in the material.

From earlier observations, it can be concluded that the kinds of hydrophilic groups or water soluble groups are not the main factors to affect the water remaining property of the after-treated nonwoven fabrics. Whereas, the larger amount of amorphous region of polymers within/on the after-treated nonwoven fabrics is the major factor that will affect the water remaining property. This result is probably caused by that the hydrophilic carboxylic acid group of DMPA was involved in the crystalline region of the LMWPU film. It is well known that the water molecules cannot penetrate through the crystalline regions to be adsorbed in the polymer materials. Therefore, the effect of the hydrophilic carboxylic acid group of DMPA on the water remaining property is lower and the water remaining value for EPU1 is relatively lower than that for EPU3 under a same add-on value in this study (Fig. 4). Also, the add-on values are decreased with the increasing of the component of PTMG contained in LMWPU for a given agent concentration in padding bath (Table II). This phenomenon is caused by the lower crystalline ability of polymer (EPU3), which increases the amount of the unfixed EPU3 to be washed out on the process of after-treatment.

### CONCLUSIONS

In this study, three low-molecular-weight polyurethanes (LMWPU) containing various amounts of carboxylic acid group were synthesized and were treated on the nonwoven fabrics to examine the effects of those polymers on the water remaining property. The chemical structure of the LMWPU was confirmed with  $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$  analyses. Their molecular weights were in the range from 3100 to 4200 g/mol and were increased with the increasing of the content of DMPA. It is also found that the add-on values were decreased with the increasing of the component of PTMG contained in LMWPU for a given agent concentration in padding bath. However, the water remaining values were

increased with the increasing of the component of PTMG contained in LMWPU for a given value of add-on. The values of  $T_g$  and  $T_m$  of the polymers within/on the treated nonwoven fabrics could not affect the water remaining property of the treated fabrics. The results of X-ray diffractions and polarizing microscope observations clearly revealed that the values of water remaining of the treated fabrics were increased with the increasing of the component of PTMG contained in LMWPU. The water remaining property was mainly affected by the amounts of the amorphous region in those polymers on/within treated nonwoven fabrics.

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