Aqueous Reactive Polyurethane Prepolymer with Poly(ethylene oxide) Monomethyl Ether Side Chains for the Hydrophilic Finishing of Poly(ethylene terephthalate) Fabrics

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ABSTRACT: In this study, a series of aqueous polyurethane (PU) prepolymers were synthesized with 4,4-methylene bis(isocyanatocyclohexane), poly(ethylene glycol) or polycaprolactone diol (PCL), methyl ethyl ketoxime, and dispersing centers produced by isophorone diisocyanate, N-diethanol amine, and poly(ethylene oxide) monomethyl ether (PEO), containing different hydrophobic groups ($—CH_3$ and $—C_6H_4C_9H_{19}$) at the end. The thermal properties of the prepolymers and the characteristics of poly(ethylene terephthalate) (PET)-treated fabrics were investigated. The glass-transition temperature was the highest in the CC prepolymer containing a benzene ring ($—C_6H_4C_9H_{19}$) and a long PEO side chain, and it was the lowest in the CA prepolymer having a longer PEO side chain. The CB prepolymer containing a shorter PEO side chain did not produce a melting point of PEO, although a heat endothermic peak of the PCL crystal appeared. The melting point and enthalpy from PEO of the CA prepolymer were larger than those of the CC prepolymer. With respect to the hydrophilic finishing effects of aqueous PU prepolymers for PET fabrics, the fabric treated with the CB prepolymer had higher add-on and washing durability than the fabrics treated with the CA prepolymer, which was followed by the CC prepolymer with the lowest, but the opposite trend was found for the hydrophilic properties. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 1947–1957, 2007

Key words: hydrophilic polymers; polyesters; polyurethanes

INTRODUCTION

A reactive polyurethane (PU) prepolymer is generally produced by condensation, the reaction of a hard segment and a soft segment, and the isocyanate group (—NCO) at the end is blocked by a capping agent. It has several advantages, including high reactivity, resilience, heat resistance, and frictional resistance in its formation, and it is versatile for adhesives, conductive materials, biomaterials, and finishing agents in textiles.[1–10] The synthesis of prepolymers with respect to environmental protection, conductive stabilization, biocompatibility, and functional improvement of fabrics includes attaching the soft chain, poly(ethylene glycol) (PEG), to the main chain of the prepolymer to increase the hydrophility.[11–14] In previous research, Chen et al.[11] observed that a film that was copolymerized from vinyl ester monomer and a prepolymer and blocked by caprolactam possessed excellent swelling properties, biocompatibility, and heat resistance. Yang and Lee[12] produced a film from an epoxy resin and a PU prepolymer, which was synthesized with toluene diisocyanate, hydrophilic PEG, and 2-dimethylaminoethanol as a capping agent, by an electrocoating system. They reported that this film had high conductivity, hardness, and impact strength. Hydrophobic finishing agents introducing hydrophilic components have usually been employed to improve the hydrophilic properties of naturally hydrophobic fabrics. In the past, the hydrophilic segment, which was connected to the hydrophobic segment in the main chain of the finishing agent, tended to obstruct the affinity of the hydrophobic segment to the fiber. This should be considered for the allocation of the hydrophilic segments in the structures of finishing agents.

In the past, there have been many processing methods proposed to improve the hydrophilic properties of poly(ethylene terephthalate) (PET) fiber, mainly including the copolymerization of hydrophilic monomers,[13] the combination of hydrophilic ingredients and spinning,[14,15] the grafting copolymerization of hydrophilic monomers,[16,17] the cavitation erosion or hollowing of fibers and fluffing of textiles,[18,19] and the covering of hydrophilic resins or adsorption.[20–28] In

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the covering or adsorption of hydrophilic resins, previous researchers generally employed water-soluble polyester, acrylic, silicone, and epoxy resin with fabric-padding or fiber-coating methods;[20-23] alternatively, a dipping process could be carried out to increase the adsorption of PET fabric.[24-28] In a patent, Lark[20] synthesized a hydrophilic polyester from acid anhydride, aromatic poly(carboxylic acid), and PEG to treat PET fabric by a padding method. That process mainly applied the hydrophilic properties of PEG and the affinity of ester groups in the structure to improve the hydrophilic properties and soil repellence of the treated fabrics. Caldwell et al.[21] added a macromolecule containing anionic groups (—COOH, —SO_3H, or —PO_4H_2) to the padding solution. After fiber covering, the hydrophilic properties and soil resistance of the treated fabrics could be improved. Zeronian et al.[24] treated PET fabrics with a nonionic polymeric hydrophile by a dipping method, which allowed the hydrophilic compound to be adsorbed onto the fibers to increase the surface tension and hydrophilic properties of PET fabrics. We previously synthesized an ester type of polyol with dimethyl terephthalate, ethylene glycol, and PEG to study the effects of the benzene ring number and PEG arrangement on the hydrophilic properties and adsorptive behavior of PET fabrics.[25,26] The fabric treated by polyol with PEG connected to only one end of the double benzene ring had better washing durability and hydrophilic effects. Generally, hydrophilic finishing could improve the hydrophilic properties of treated fibers, but the hydrophilic segment connected to the hydrophobic segment in the main chain of the agent tended to decrease the detergent washing durability of treated fabrics. Thus, durable hydrophilic finishing should be investigated.

In this research, reactive aqueous PU prepolymers with hydrophilic groups in the side chain were synthesized by the blending of a soft chain of hydrophobic polycaprolactone diol (PCL) and a hydrophilic dispersing center with a poly(ethylene oxide) monomethyl ether (PEO) side chain and the reaction with a hard segment. As finishing for the fibers, the hydrophilic segment and hydrophobic segment were not on the same main chain to prevent the hydrophilic segment from affecting the attachment of the hydrophobic segment to the fiber. To perform the experiment, a series of aqueous PU prepolymers were synthesized by the hard chain 4,4-methylene bis(isocyanatocyclohexane) (H_{12}MDI), the PCL or PEG soft chain, and a dispersing center produced by isophorone diisocyanate (IPDI), N-diethanol amine (NDEA), and PEO containing different hydrophobic groups (—CH_3 and —$C_6H_4C_9H_{19}$) at the end. This study verifies the types and molecular weights of the soft chains, the kinds and contents of the dispersing centers used to confer the thermal properties of the prepolymer, and the

influence of the durable hydrophilic properties of the treated fabrics.

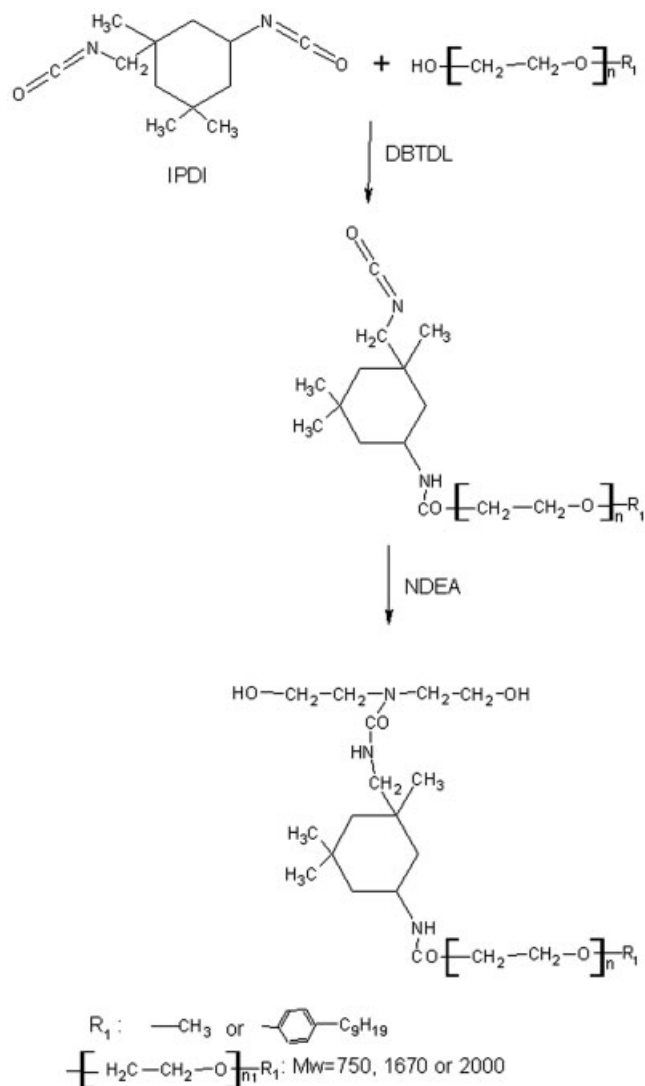## EXPERIMENTAL

Synthesis of the dispersing centers

The dispersing center was synthesized as described by Noll.[27] One mole of PEO with a molecular weight of 2000 (reagent; Aldrich, Milwaukee, WI), PEO with a molecular weight of 750 (reagent; Aldrich), or poly-(ethylene oxide) monononylphenyl ether 1760 (Pannox 140) with a molecular weight of 1760 (purchased from Pan ASIA Chemical Corp., Taiwan) was dissolved in 1-methyl-2-pyrrolidone and dehydrated *in vacuo*. Then, each was added to 1 mol of IPDI (reagent; Aldrich) and 0.01 mol of catalyst di-*n*-butyltin dilaurate (DBTDL; reagent; Aldrich) to react for 4 h at 45°C under ambient nitrogen. While the temperature was increased to 50°C, 1 mol of NDEA (reagent; Acros, Belgium) was added for 1 h to synthesize three kinds of dispersing centers, and the formative products were confirmed by Fourier transform infrared (FTIR) and NCO titration analyses. The reaction is shown in Scheme 1.

Synthesis of the aqueous reactive PU prepolymers

The synthesis of aqueous PU prepolymers was performed as follows. One mole of the soft segment PEG (molecular weight = 600, 1000, or 2000; reagent; Acros) or 1 mol of PCL (molecular weight = 550, 1250, or 2000; Sunko Ink Co., Ltd., Taiwan) was added to 1 mol of the synthesized dispersing center and then dehydrated *in vacuo*. That was then reacted with 4 mol of the hard chain H_{12}MDI (reagent; Aldrich) at 75°C for 5 h under ambient nitrogen. As the temperature dropped to 60°C, methyl ethyl ketoxime (MEKO; reagent; Acros) was used to cap the NCO group for 40 min; this was followed by cooling in a water bath for 15 min. By the addition of water for emulsification, emulsions of aqueous PU prepolymers containing different side chains could be obtained. The reaction is displayed in Scheme 2, and the compositions and code names of the synthesized compounds are shown in Table I.

Analysis of the structure

FTIR analysis proceeded in the scanning range of 400–4000 nm for 16 times at 25°C. NCO titration was performed as described in David.[28] For gel permeation chromatography (GPC) testing, which used polystyrene as the standard, a 100-μm sample at a concentration of 7–8 mg/mL was injected into a Water (Waters, MA)RI-6000 apparatus at a speed of 1 mL/min, which determined the molecular weight and distribution of the prepolymer.

Scheme 1 Synthesis of the dispersing center.

pickup), predrying at 90°C for 5 min, and curing at 150°C for 3 min. Then, the treated fabric was washed with a sodium carbonate solution (2 g/L) at 60°C for 20 min. The add-on and physical properties of the treated fabric were determined as follows. AATCC 135 was used to test the washing durability. The regain, time of drop absorption, vertical wicking height, and half-life were evaluated with ASTM 629-88, CNS12915 water absorption method A (the dropdown standard), CNS12915 water absorption method B (the Byreck standard), and JIS-L1094 A. The bending length and tensile strength were measured according to CNS12915 (stiffness 45° cantilever) and ASTM D 1682-64 (1975).

RESULTS AND DISCUSSION

Identification and analysis of the synthesized PU prepolymers

Figure 1 shows the changes in the NCO residual amount for different reaction times for the aqueous PU prepolymers. The CB prepolymer containing a short PEO without a benzene ring had the fastest reaction speed, the CC prepolymer containing a long PEO with a benzene ring was next, and the CA prepolymer containing a long PEO without a benzene ring was the slowest. The NCO residual amount of the

Thermal properties of the PU prepolymers

Differential scanning calorimetry (DSC) analysis was performed with a differential scanning calorimeter (PerkinElmer, Waltham, MA) to measure the heat variation at an increasing temperature rate of 100°C/min. The range of the measuring temperatures was set between −100 and 100°C.

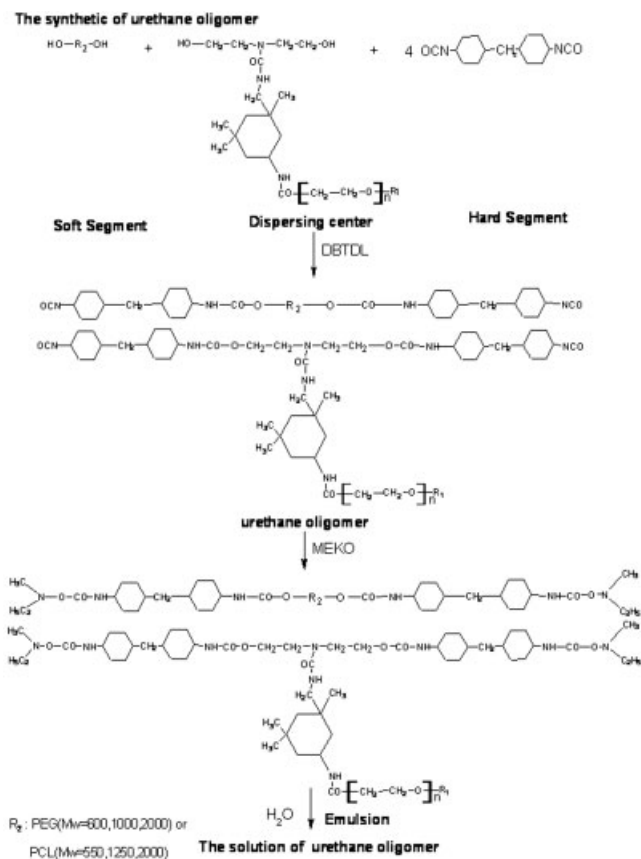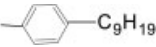## Properties of the finished fabrics

The treatment solution was composed of PU prepolymers with a series of concentrations and catalyst Cat 32 (Chin-yee Chemical Industries Co., Ltd., Taiwan) (0.05% prepolymer). PET fabric (Everest, Taiwan) for finishing was processed by weight reduction with NaOH, and the reduction ratio was 12 wt %. For the pad–dry–cure process, padding of the PET fabric was carried out by the two-dip, two-nip process (85%

Scheme 2 Synthesis of the aqueous PU prepolymer.

TABLE I
Compositions of Aqueous PU Prepolymers Synthesized with Different Soft Segments and Dispersing Centers

| Symbol | Type of soft segment (R_2) | Dispersing center | | H_{12}MDI/soft segment/dispersing center (molar ratio) | Composition of the prepolymer (wt %) | | |
		R_1	M_n of PEO		Hard segment	Soft segment	Dispersing center
EA600-411	PEG600	—CH$_3$	2000 (A)	4:1:1	25.30	14.45	56.6
EA1000-411	PEG1000				23.08	21.97	51.13
EA2000-411	PEG2000				18.92	36.03	41.92
CA550-411	PCL550				26.61	13.41	56.74
CA1250-411	PCL1250				21.88	26.03	48.47
CA2000-411	PCL2000				18.92	36.03	41.92
CA550-621	PCL550	—CH$_3$	2000 (A)	6:2:1	28.51	19.91	42.12
CA550-411				4:1:1	26.61	13.41	56.74
CA550-612				6:1:2	21.57	7.53	63.74
CB550-621		—CH$_3$	750 (B)	6:2:1	29.43	20.55	20.13
CB550-411				4:1:1	34.71	18.17	35.60
CB550-612				6:1:2	32.81	11.45	44.86
CC550-621			1760 (C)	6:2:1	28.53	19.92	42.09
CC550-411		—C$_9$H$_{19}$		4:1:1	24.54	12.85	54.31
CC550-612				6:1:2	21.59	7.54	63.71

M_n = number-average molecular weight.

PU prepolymers reached one-half of the reactants, and it did not decrease with time; this indicated that the synthesizing reaction of the prepolymer was complete at this time.

Figure 2 shows the FTIR spectrum of the dispersing centers and the synthesized PU prepolymers. The absorptions of all groups were illustrated on a graph. The vibration of C—H was shown for all dispersing centers (A–C) at 2850–2940 cm^{-1}. The bending vibration of —CH$_2$— was observed at 1465 cm^{-1}, and the absorption peak of the C—O—C group appeared at 1300–1000 cm^{-1}. In addition, the absorption peaks from —CO— of urethane and —CO— of urea appeared at 1690 and 1600 cm^{-1}, respectively. There was a wide absorption peak of —OH and —NH at 3320 cm^{-1}. The C—O—C absorption at 1300–1000 cm^{-1} increased following the trend A > B > C because of the different contents of —CH$_2$CH$_2$O— (ethylene oxide group) in the three kinds of dispersing centers. The single-substituted benzene of dispersing center C had obvious absorption peaks at 1600, 1475, 690, and 750 cm^{-1}. As shown from the spectrograms of three kinds of aqueous PU prepolymers, all had —NH— absorption at 3323 and 3460 cm^{-1}, and —CO— group absorption of urethane existed at 1690 cm^{-1} and characterized the —NHCOO— group. Furthermore, the —COO— absorption peak of the PCL soft chain appeared at 1750 cm^{-1}. From this spectrum analysis, the structures of the synthesized prepolymers could be identified.

Table II displays the molecular weights and molecular weight distributions of the aqueous PU prepolymers that were synthesized from the different kinds of soft chains and dispersing centers. For both PEG and
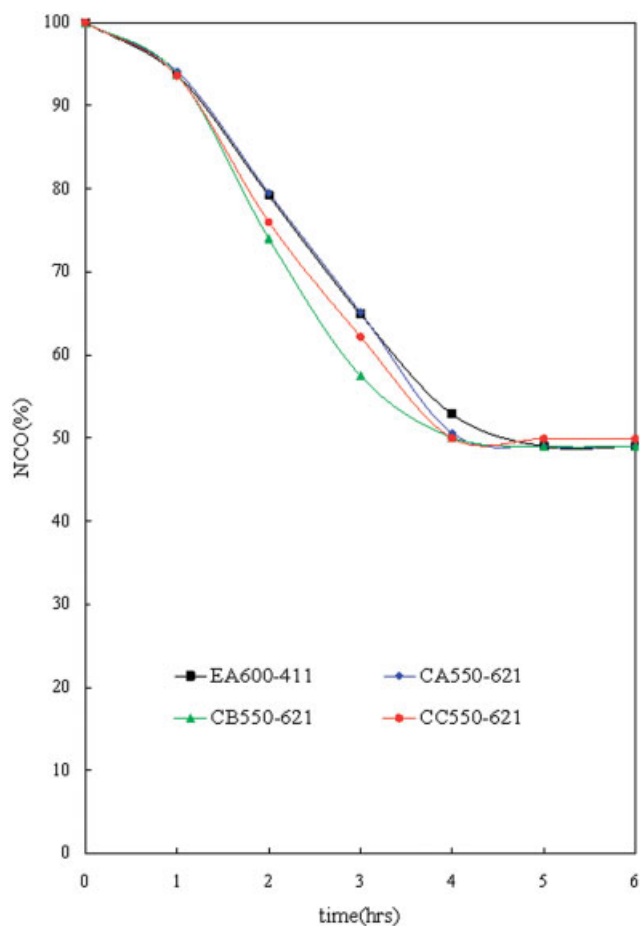

Figure 1 NCO residue ratio of PU prepolymers synthesized for different reaction times. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
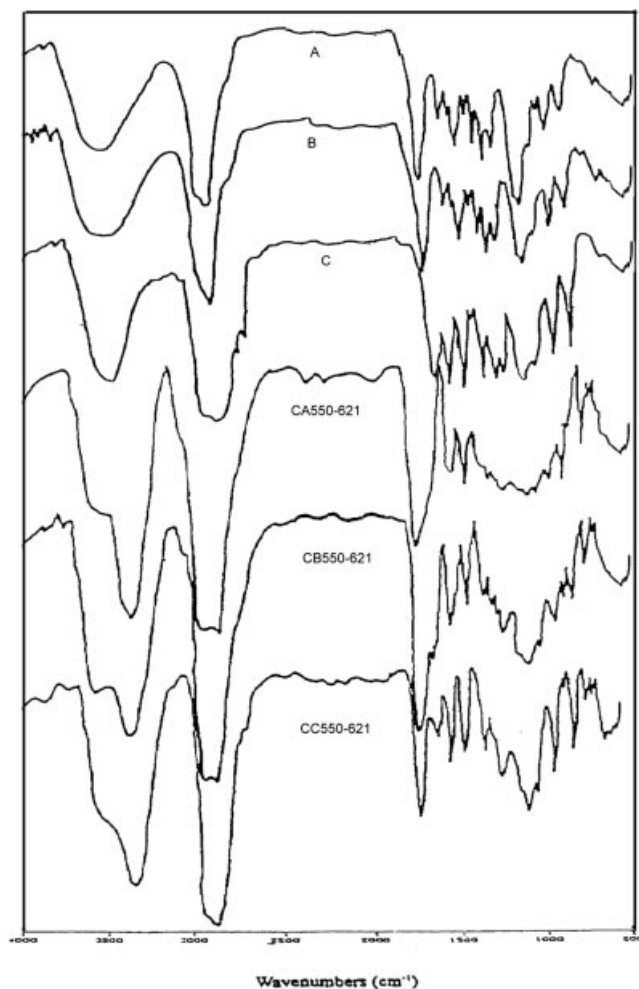
Figure 2 FTIR spectra of dispersing centers and aqueous PU prepolymers.

PCL soft chains, the molecular weight and molecular weight distribution of the synthesized PU prepolymer increased as the molecular weight of the soft chain increased. As for the same PCL soft chain, the molecular weight of the synthesized prepolymer increased in the prepolymer order of CC > CA > CB because the prepolymers contained different side chains. The molecular weight and molecular weight distribution of the synthesized substances increased along with the increase in the dispersing-center content.

Thermal properties of the PU prepolymers

Figures 3 and 4 show a DSC analysis of the PU prepolymers synthesized from different soft segments and dispersing centers; the glass-transition temperature (T_g), melting temperature (T_m), and melting enthalpy (ΔH_m) data are presented in Table II. Figure 3 shows the influence of the thermal properties of the prepolymers with the same dispersing center (A) and the soft chains of different types and molecular

weights. As for T_g, the EA type containing the PEG soft chain did not possess the T_g of the PEO side chain. The CA type containing the PCL soft chain had the T_g of the PEO side chain, and it declined as the PCL molecular weight increased because the high content of the soft chain was less constrained by the hard chain; this caused the increase in the molecular mobility. As for T_m and ΔH_m, in the case of the EA type, PEG was too short to produce a crystal as the molecular weight of the PEG soft chain was 600 (EA600), and the endothermic peak at 30–50°C was from the PEO side chain (number-average molecular weight = 2000). When the molecular weight of PEG was 1000 (EA1000), the enlarged PEG molecules enhanced the interaction and agglutination between the PEG molecules and the partial PEG soft chain and cocrystallized with PEO of the dispersing center, causing T_m and ΔH_m to slightly rise. When the molecular weight of PEG was 2000 (EA2000), most PEG molecules produced cocrystallization with PEO, causing T_m and ΔH_m to substantially rise. In the case of the CA type, CA550 had higher T_m and ΔH_m than EA600. PCL 550 in the CA550 prepolymer was too short to produce a crystal, and the crystal was mainly from the PEO 2000 side chain. The uncrystallized and unattractive PCL 550 molecules could aggregate the PEO molecules to

TABLE II
Molecular Weights and Thermal Properties of Aqueous PU Prepolymers Synthesized with Different Soft Segments and Dispersing Centers

Symbol	Molecular weights[a]			Thermal properties		
	$M_w \times 10^4$	$M_n \times 10^4$	M_w/M_n	T_g (°C)[b]	T_m (°C)[d]	ΔH_m (J/g)[c]
EA600-411	0.947	0.512	1.85	—	28	52
EA1000-411	1.263	0.638	1.98	—	32	61
EA2000-411	1.852	0.908	2.04	—	55	117
CA550-411	1.125	0.583	1.93	−56	59	68
CA1250-411	1.385	0.689	2.01	−72.1	21	32
CA2000-411	2.401	1.132	2.12	−91.6	34, 61	63
CA550-621	0.923	0.507	1.82	−56	60	55
CA550-411	1.125	0.583	1.93	−56	59	68
CA550-612	1.697	0.893	2.14	−40	59	83
CB550-621	0.839	0.482	1.74	−45	—	—
CB550-411	0.903	0.496	1.82	−35	—	—
CB550-612	1.489	0.752	1.98	−30	—	—
CC550-621	1.042	0.582	1.79	−67	48	30
CC550-411	1.436	0.704	2.04	−42	48	38
CC550-612	2.042	0.924	2.21	−29	50	51

M_w = weight-average molecular weight; M_n = number-average molecular weight.
[a] Measured by GPC and referred to a polystyrene standard.
[b] Soft-segment glass-transition temperature determined from the midpoint of the change in the baseline height.
[c] Melting enthalpy of the soft-segment crystal determined from the area of the endothermic peak.
[d] Melting temperature of the soft-segment crystal indicated by the temperature at the endothermic peak.
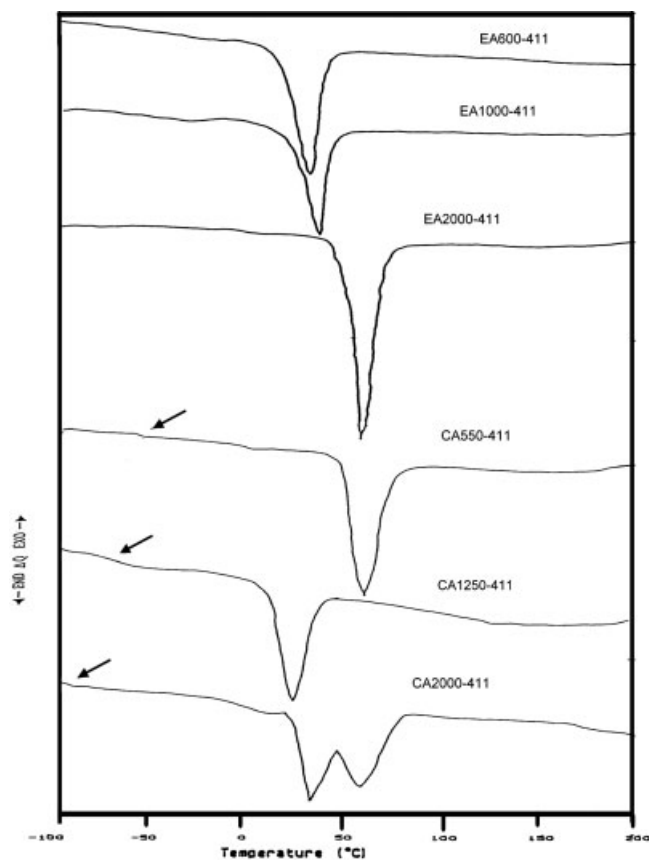
Figure 3 DSC thermograms of aqueous PU prepolymers synthesized with soft segments of different types and molecular weights.

crystallize so T_m and ΔH_m of CA550 were higher than those of EA600. T_m and ΔH_m of PEO 2000 in CA1250 decreased and were lower than those of CA550. PCL 1250 still did not crystallize in CA1250; the reason for decreasing T_m and ΔH_m of PEO 2000 may be that the attraction between the PCL 1250 molecules was strong enough to interfere with the crystallinity of PEO 2000. When the molecular weight of PCL reached 2000 (CA2000), two significant endothermic peaks appeared at 34.3 and 61.3°C from the PEO side chain and the PCL 2000 soft chain, respectively. The greater molecule of PCL was able to produce a crystal itself, and the stronger bonding of the ester group made its endothermic peak appear at a higher temperature. According to our previous research of aqueous PU, T_m of the PCL type appeared at a higher temperature than that of the PEO type according to DSC and X-ray analyses.[29,30]

Figure 4 indicates the influence of the thermal properties of the prepolymers with the same soft chain of PCL 550 and dispersing centers of different types and contents. As for the comparison of the dispersing-center types, the prepolymers had T_g of the PEO side chain at −30 to −50°C. T_g of the CC prepolymer containing a benzene ring was higher than that of the

CA prepolymer without a benzene ring, but T_m and ΔH_m followed the opposite tendency because the CC prepolymer contained a hard benzene ring to hinder the movement and attraction of PEO molecules. T_g of the CB prepolymer with a short PEO was lower than that of the CA prepolymer with a long PEO, and the CB prepolymer did not have the T_m value of PEO but had an endothermic peak of the PCL 550 crystal at 20°C because the PEO molecular weight ($M_n = 750$) of the CB prepolymer was too short to produce a crystal. With respect to the comparison of the dispersing-center contents, T_g increased as the dispersing-center content increased. Except for the CB prepolymer, T_m and ΔH_m of all the other prepolymers increased as the side-chain content increased. The increase of T_g, T_m, and ΔH_m caused by more side-chain content strengthened the interaction of the PEO molecule. The endothermic peak of the PCL soft chain from the CB prepolymer at 20°C gradually vanished as the side-chain content increased because the increase in the PEO content interfered with the PCL crystallinity.
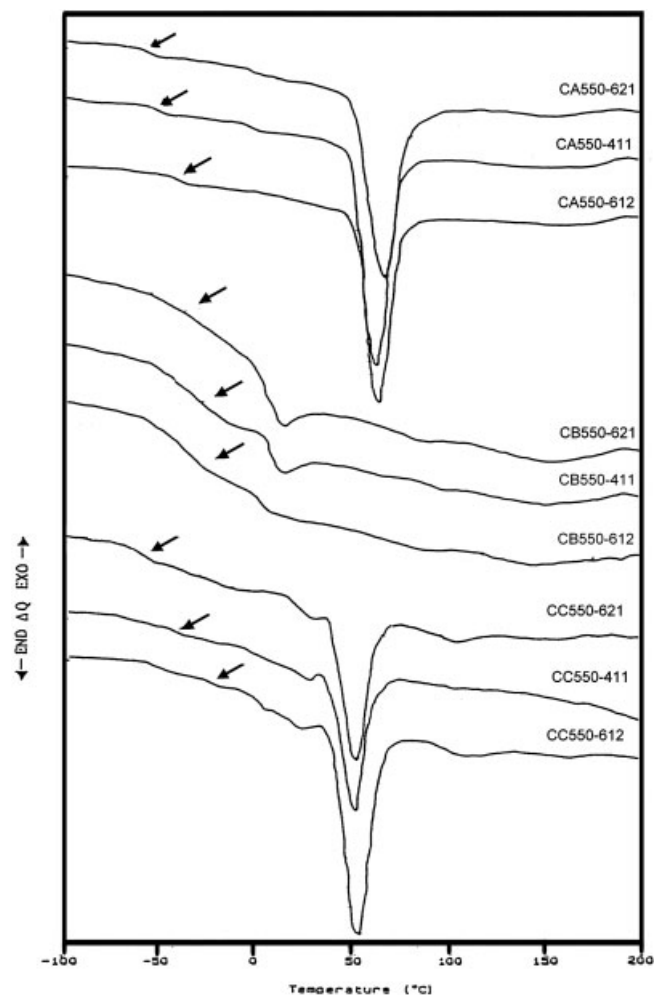

Figure 4 DSC thermograms of aqueous PU prepolymers synthesized with dispersing centers of different molar ratios and types.

TABLE III
Physical Properties of PET Fabrics Treated with Aqueous PU Prepolymers Synthesized with Different Soft Segments and Dispersing Centers

	Fixation rate (%)		Physical properties					
Symbol	Add-on	Washing 15 times with Marseilles soap	Vertical wicking height (mm)	Moisture regain (%)	Drop absorption time (s)	Half-life of static electricity (s)	Breaking strength (kgf)	Bending length (mm)
Untreated	—	—	54	0.35	68	1.8	25.66	33
EA600-411	0.38	0.23 (61)	62	0.42	24	1.3	25.23	40
EA1000-411	0.42	0.35 (80)	66	0.46	21	1.2	25.31	38
EA2000-411	0.44	0.36 (82)	72	0.46	17	1.2	25.58	39
CA550-411	0.89	0.85 (95)	65	0.53	20	0.9	23.66	45
CA1250-411	1.02	0.96 (95)	60	0.58	38	2.4	24.49	49
CA2000-411	1.15	1.11 (97)	56	0.59	42	3.2	23.88	50
CA550-621	1.22	1.13 (93)	60	0.55	45	1.7	24.87	51
CA550-411	0.89	0.85 (95)	65	0.53	20	0.9	23.66	45
CA550-612	0.65	0.57 (88)	63	0.48	20	0.9	23.66	45
CB550-621	1.72	1.69 (99)	50	0.48	112	8.6	24.26	56
CB550-411	1.71	1.55 (91)	56	0.46	98	8.4	25.41	60
CB550-612	1.38	1.27 (92)	58	0.42	75	8.3	23.33	62
CC550-621	0.80	0.29 (37)	60	0.43	28	1.3	25.46	49
CC550-411	0.84	0.39 (47)	65	0.44	20	1.2	25.73	48
CC550-612	0.92	0.57 (62)	66	0.54	21	1.2	25.65	46

The finishing agents were waterborne PU prepolymers (2%), and the catalyst was Cat 32 (0.1%). The finishing conditions were two-dip and two-nip (85% pickup); drying was performed at 80°C for 5 min. Curing was performed at 170°C for 3 min. The Na_2CO_3 washing conditions were 60°C and 20 min. The durability was determined with the AATCC 135 standard method for 15 cycles.

Physical properties of the PET-treated fabrics

Table III shows the hydrophilic finishing results of PET fabrics treated with PU prepolymers. Figure 5 shows the influence on the add-on and washing durability of the fabrics treated with aqueous PU prepolymers with the same dispersing center (A) and soft chains of different types and molecular weights. In terms of the soft-chain types, the fabrics treated by the CA type had better add-on and durability than the fabrics treated by the EA type because PCL and PET possessed the same hydrophobic characteristics and the CA type had stronger crystallinity (Fig. 3), which were both advantageous to the firmness of the PET fiber. With respect to the molecular weight of the soft chain, the CA-type fabrics had an increase in the add-on and washing durability as the PCL molecular weight increased, but the fabrics with respect to the EA type did not change obviously because PCL of a higher molecular weight enhanced the hydrophobic characteristics and crystallinity of the CA type. The greater hydrophilic PEG content of the EA type provided poor entanglement with the hydrophobic PET fiber as the PEG molecular weight of the prepolymer increased, but strengthening the crystallinity (Fig. 3) reduced the effects of the add-on and durability. Figure 6 shows the effects on the vertical wicking height and drop absorption time of treated fabrics. In terms of the soft-chain types, the fabric of the EA type had a low add-on because of the hydrophilic soft chain, but
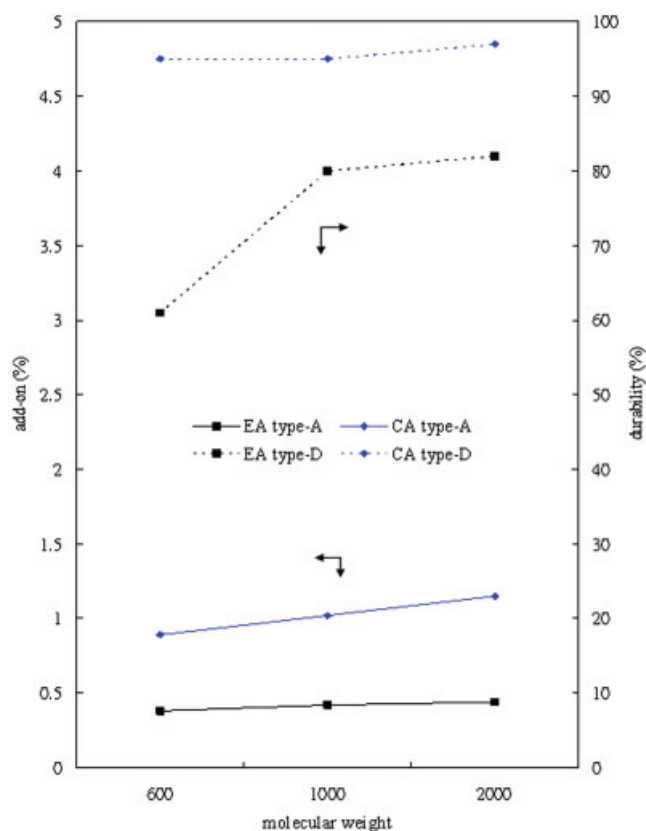

Figure 5 Durability and add-on of PET fabrics treated by PU prepolymers with dispersing center A and soft segments of different types and molecular weights. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
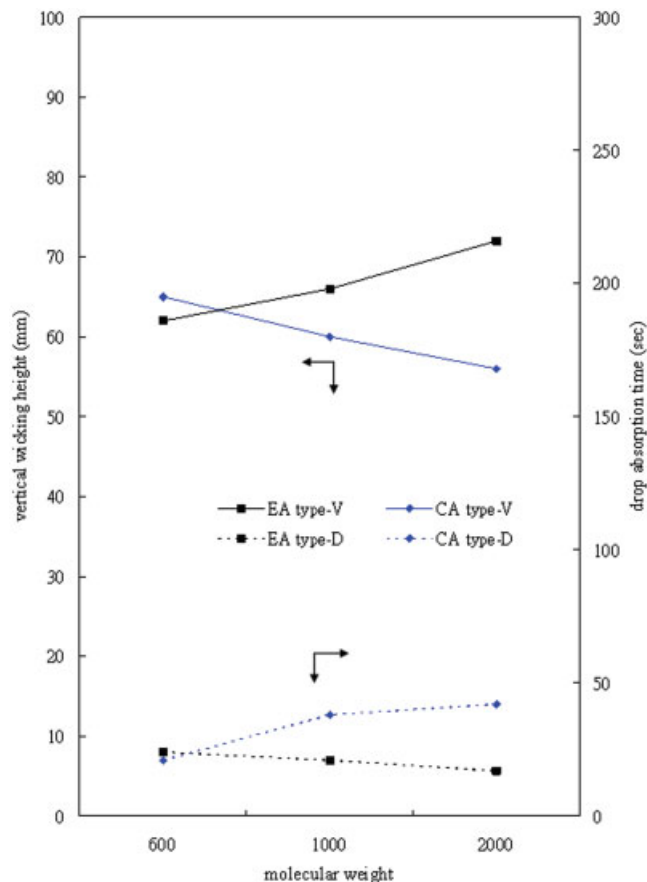
Figure 6 Vertical wicking height and drop absorption time of PET fabrics treated by PU prepolymers with dispersing center A and soft segments of different types and molecular weights. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

it had a better vertical wicking height and drop absorption time than the fabric treated by the hydrophobic CA type. In terms of the molecular weight of the soft chain, the hydrophilic properties of the fabric treated by the CA type were enhanced as the PEG molecular weight of the prepolymer increased, but the case of the PCL type showed an opposite trend. The hydrophilic properties of the fabric treated by the EA type increased as the PEG molecular weight increased because more hydrophilic PEG conferred more hydrophilic properties of the EA type. The hydrophobic PCL of the CA type produced a crystal when the molecular weight of PCL was large, and the hydrophilic properties of the CA type could rely only on the PEO of its dispersing center. As shown in Table III, the moisture regain of the fabric treated by the CA type was higher than that of the fabric treated with the EA type because the CA type had a greater add-on than the EA type. The EA type had a shorter half-life of static electricity in the treated fabric than the CA type; that is, the fabric of the EA type could not attract static electricity because of the better hydrophilic properties

of the treated fabric. As for the other properties of the finished fabrics, the strength and softness of the treated fabrics showed less influence.

Figure 7 shows the add-on and washing durability of fabrics treated by prepolymers with the same soft chain (PCL 550) and different types and contents of dispersing centers. With respect to the types of dispersing centers, the fabric treated by the CB prepolymer with a short PEO side chain had higher add-on and washing durability than the fabric of the CA prepolymer with a long PEO side chain. The CB prepolymer containing less hydrophilic PEO was easily adsorbed by hydrophobic PET fibers. Furthermore, the CB prepolymer of smaller molecules, which allowed it to diffuse into the fiber interior, was also an advantage for the durability after the adsorption of the prepolymer. The treated fabric of the CC prepolymer with a benzene ring had poorer add-on and washing durability than the fabric of the CA prepolymer without a benzene ring. The benzene ring at the side chain reduced the crystallinity of PEO (see Fig. 3) and so increased the hydrophilic characteristics of CC the prepolymer, and the CC prepolymer with a high mo-
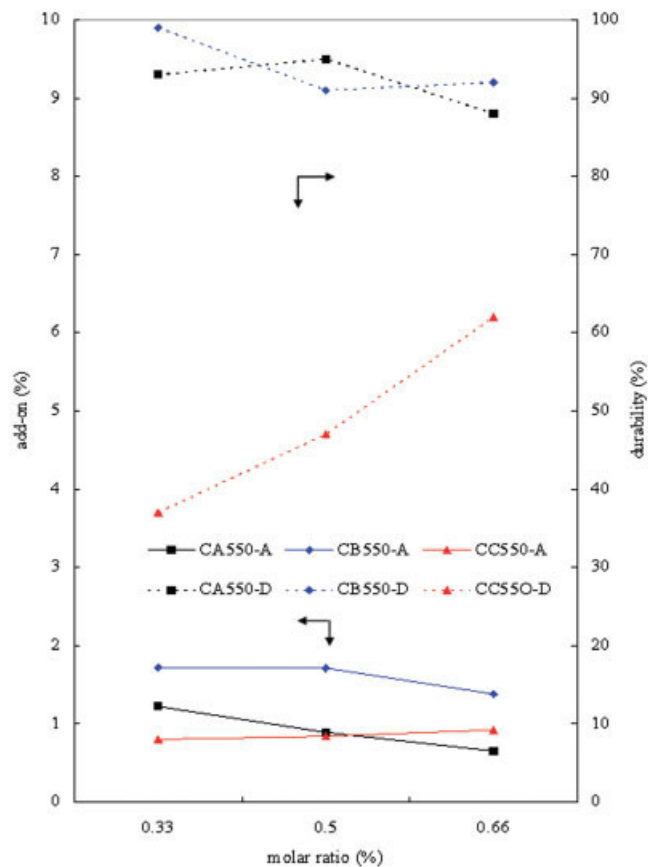

Figure 7 Add-on and durability of PET fabrics treated by PU prepolymers with soft segments of PCL 550 and dispersing centers of different types and molar ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
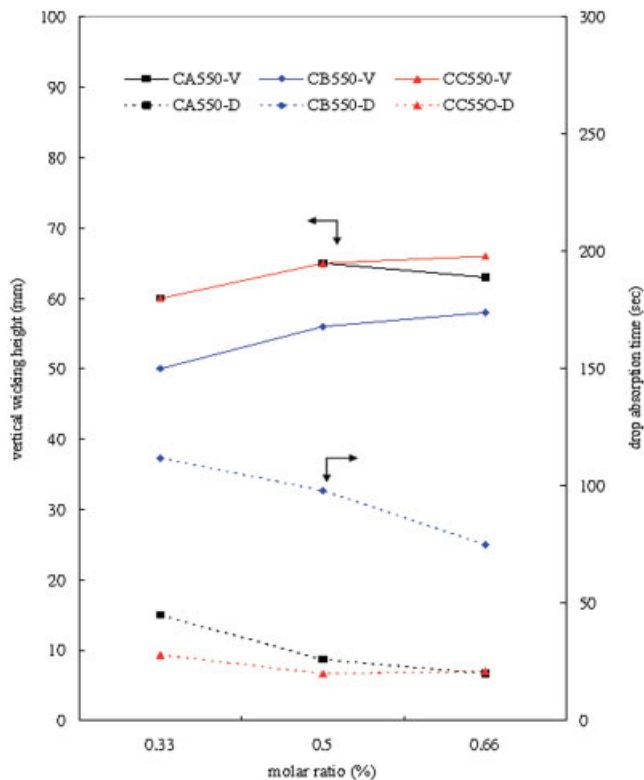
Figure 8 Vertical wicking height and drop absorption time of PET fabrics treated by PU prepolymers with soft segments of PCL 550 and dispersing centers of different types and molar ratios. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

lecular weight was not easy to diffuse into the fiber interior. With respect to the content of the dispersing centers, the add-on and washing durability of treated fabrics of the CA and CB prepolymers were reduced as the content of dispersing centers decreased because of the increase in the hydrophilic properties. On the contrary, fabrics of the CC prepolymer increased with respect to the add-on and durability as the dispersing-center content increased because the increase in the dispersing centers was advantageous to the crystallinity of the PEO side chain. The add-on of the CC fabric could be maintained, and the durability of the CC fabric was improved. Figure 8 shows the influence of the vertical wicking height and drop absorption time of PET-treated fabrics. In terms of the dispersing-center types, the hydrophilic properties of the fabric treated by the CA prepolymer were better than those of the fabric of the CB prepolymer because the side chain of the CA prepolymer had a longer hydrophilic PEO molecule and the CB fabric had a higher add-on, but hydrophilic PEO was surrounded by the soft chain of PCL, so the PEO could not supply hydrophilic characteristics. The CC fabric possessed better hydrophilic properties than the CA fabric because the benzene ring interfered with the crystallization of PEO,

causing more hydrophilic characteristics for the CC prepolymer than for the CA prepolymer with a stronger PEO crystallinity. In terms of the dispersing-center content, the treated fabric, which had enhanced vertical wicking height as the content rose in the particular fabric of the CB prepolymer, had the greatest increase. The increase in noncrystalline PEO reduced the crystallinity of PCL and was advantageous for the hydrophilic properties. Figure 9 shows the relationship between the add-on and vertical wicking height of the treated fabrics. The fabric of the CC prepolymer had a higher efficiency for hydrophilic finishing than the other prepolymers; that is, less add-on of the CC prepolymer could improve the hydrophilic properties of the fabrics. Figure 10 displays the relationship between the washing durability and vertical wicking height of the treated fabrics. The CA prepolymer achieved both the best washing durability and vertical wicking height. As indicated by the other physical properties of the treated fabrics in Table III, the absorption time and moisture regain of the treated fabrics were consistent with the trend of the vertical wicking height, and the half-life of static electricity
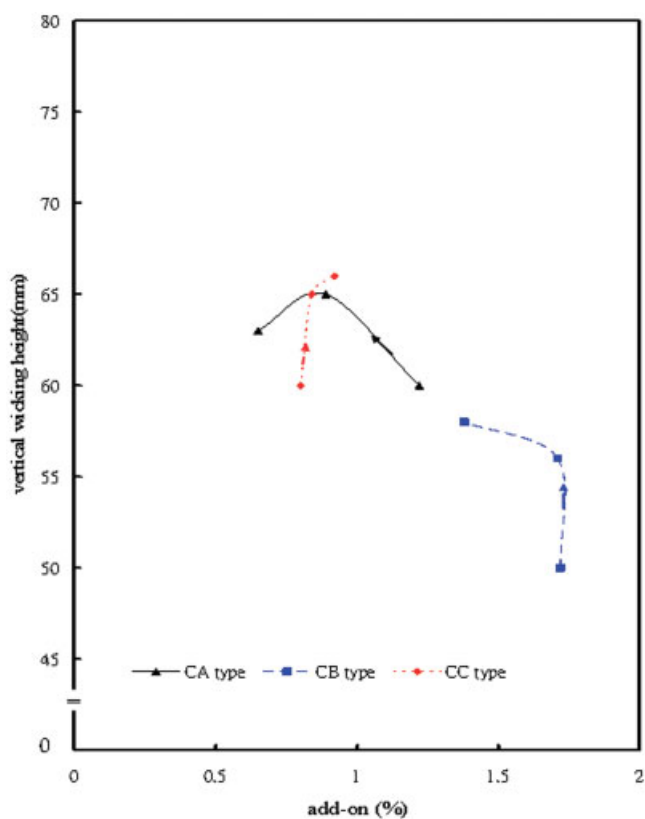

Figure 9 Vertical wicking height and add-on of PET fabrics treated by PU prepolymers with soft segments of PCL 550 and dispersing centers of different types and molar ratios (an arrow represents an increase in the molar ratio). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Figure 10 Vertical wicking height and durability of PET fabrics treated by PU prepolymers with soft segments of PCL 550 and dispersing centers of different types and molar ratios (an arrow represents an increase in the molar ratio). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
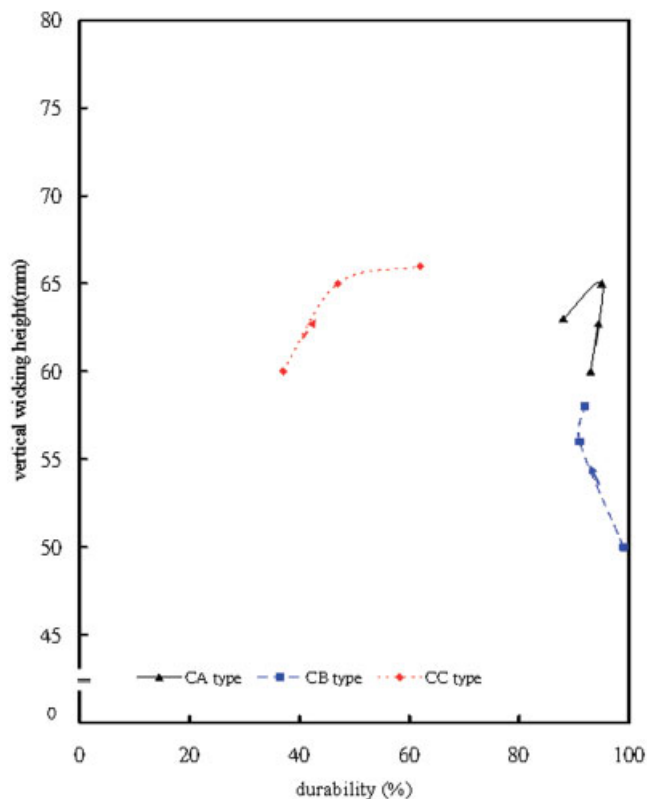
decreased after the hydrophilic properties of the treated fabric were enhanced.

CONCLUSIONS

In this research, a series of aqueous PU prepolymers were synthesized with H_{12}MDI, PCL or PEG, MEKO, and dispersing centers containing PEO side chains. Subsequently, the thermal properties of the prepolymers and characteristics of the PET-treated fabrics were investigated. The results were as follows.

With respect to the thermal properties, within the different types and molecular weights of the soft chains, the EA type did not produce any T_g, and T_m and ΔH_m of the PEO side chain increased as the molecular weight of the PEG soft chain increased. The CA type reduced T_g, T_m, and ΔH_m of the PEO side chain as the molecular weight of the PCL soft chain increased. When the molecular weight of PCL reached 2000, two significant endothermic peaks appeared at 34.3 and 61.3°C from the PEO side chain and the PCL soft chain. Within the various kinds and contents of dispersing centers, T_g was the highest in the CC prepolymer and lowest in the CA prepolymer. The T_m of the

PEO side chain in the CA prepolymer was larger than that in the CC prepolymer, and the CB prepolymer did not produce a T_m of PEO, but a heat endothermic peak of the PCL crystal appeared. T_g and ΔH_m of the prepolymers rose as the dispersing-center content increased, and T_m had no significant difference.

In the hydrophilic finishing effects of aqueous PU prepolymers, within the different types and molecular weights of soft chains, the fabrics of the CA type had better add-on and durability than those of the EA type, and as expected, the durability of the EA type and the add-on and durability of treated fabrics of the EA and CA types were unchanged clearly as the molecular weight of the soft chain increased. The hydrophilic properties of the fabric treated by the EA type were higher than those of the fabric treated by the CA type; the hydrophilic properties of the EA type were enhanced, but those of the CA type decreased, as the molecular weight of PEG increased. With respect to the different dispersing centers and contents, the fabric of the CB prepolymer resulted in the best add-on and washing durability, whereas the fabric of the CC prepolymer gave the poorest results. The durability and add-on of the fabrics treated by the CA and CB prepolymers declined as the contents of the dispersing centers increased, but the CC prepolymer showed the opposite trends. The hydrophilic properties of the CA-treated fabric were the best, whereas those of the CB-treated fabric were the poorest. The hydrophilic properties of the treated fabric increased with an increase in the dispersing-center content. Better efficiency of hydrophilic finishing could be obtained with the CC prepolymer, and the CA-treated fabric could achieve both the best washing durability and hydrophilic properties.

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