

Preparation and Properties of Microcapsule with EVA Core-PU Shell Structure

Hea-in Kim, Soo-min Park

Department of Textile Engineering, College of Engineering, Pusan National University, Pusan 609-735, Korea

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ABSTRACT: Microcapsule with poly(ethylene-co-vinylacetate) (EVA) core-polyurethane (PU) shell structure was synthesized by interfacial polymerization in aqueous polyol dispersion with ethylene diamine as the chain extender of toluene diisocyanate in poly(vinyl alcohol) aqueous solution as the stabilizing agent. The effects of polyol constituent on the average particle size and distributions, morphologies, color strength, and friction fastness of core-

shell particles were investigated to design microcapsule. The friction fastness of printed fabrics with EVA core-PU shell microcapsules became the increase to 4–5 grades. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 893–902, 2007

Key words: EVA core-PU shell microcapsule; microsphere; particle size distribution; friction fastness

INTRODUCTION

Conventional fabric printing systems, the predominant method of printing textiles, are incompatible with the trend in the textile industry toward quick response and demand-activated manufacturing, which requires frequent style and color changes.¹ On the other hand, xerography textile printing systems can improve some of these disadvantages of the conventional screen printing. However, there are numerous processes and material problems that must be resolved before xerographic printing can have an impact on commercial textile printing. Fabrics printed with xerography have poor adhesion and low dyeing fastness, because initial xerographic textile printing studies were conducted using typical paper toner.² Since the initial studies, work has involved the development of polymer-based xerographic toners with the required properties for the xerographic process and the desired printed fabric properties.^{1–4}

In textile applications, the microsphere for xerography printing must have properties compatible with xerography, and at the same time meet several textile requirements. Microsphere contains other materials such as charge controlling agents, crosslinking agents, and flow agents to enhance the xerographic performance. The microsphere material must be convertible into a desired power form, typically having a particle size of 5–20 μm .⁵ There are four major parameters that must be optimized to produce high performance: molecular weight, glass transition temperature (T_g), melt viscosity, and electrical properties.

Especially, microsphere has been typically designed to have a T_g ranging from 50 to 65°C. Additives such as plastisizers and flow aids have been used to enhance polymer properties. So, the selection of a polymer composed most of microsphere is important in microsphere design.^{2,4,5}

From these grounds, the EVA polymers were selected for their potential of meeting the flexibility and color fastness requirements of textile printing since they have good adhesive strength, low T_g , low initial modulus, and good elongation properties. The properties and practical application of prepared EVA microsphere have been reported in previous works.^{6,7} On the other hand, polyurethanes are a group of widely used materials such as coating binder resins and high-performance elastomeric products.^{8,9} Polyurethanes have interactional force for various fibers in contrast to hydrophobic EVA.

Surface treatments of particles to introduce reaction sites include surface coating, coupling agents treatments, and polymer formation by monomers. In the particle production technique, studies of the preparation of microcapsule with core-shell structure, and the different polymer components of core and shell materials has been carried out.^{10–13} To enhance adhesive strength between the backing fabric and the microsphere and to present a new method of particle surface treatment, the introduction of shell portion as the core material is based on an interface polymerization.

This article describes a new method of preparation of microcapsule (up to 15 μm) with a core-shell structure from EVA microsphere synthesized by liquid–liquid thermally induced phase separation (TIPS). The effects of the structure of soft segments in the PU shell as a well-forming material and the effects on particle size distribu-

Correspondence to: S. Park (soominpark@pusan.ac.kr).

TABLE I
Physical Properties of EVA

ASTM test method	Melt index (g/10 min)	Softening temp. (°C)	Hardening temp. (°C)	Density
PET	D1238 1.9	D1525 64	D747 38	D1505 0.938

tion and morphologies of resulting microcapsules were evaluated. The color depth and the rubbing fastness of printed fabrics with the EVA microsphere and the EVA core-PU shell microcapsule were compared.

EXPERIMENTAL

Materials

An EVA polymer with a 15% vinyl acetate content was used in this study to synthesize the core material. Table I shows physical properties of the EVA polymer. C I Pigment Red 112 was used as a pigment in core microsphere.

In addition, commercially available reagent grade reagents used in this study were obtained from Junsei Chemical (Japan), and dried under a vacuum atmosphere for 3 h. The PU shell was prepared with 2,4-toluene diisocyanate (TDI) as a polyisocyanate, poly(propylene glycol) (PPG, M_w 750), poly(tetramethylene glycol) (PTMG, M_w 710), and poly(ethylene glycol)s (PEG, M_w 400, 600, 1000, and 2000) with various molecular weights, and ethylene diamine (EDA) was used as a chain extender. Poly(vinyl alcohol) (PVA, M_w 1500) as a protective colloid and dibutyl tin dilaurate (DBTDL) as a catalyst were used without any further purification. And characteristics of the several types of fabrics used are given in Table II.

Preparation of the EVA core-PU shell type microcapsule

Figure 1 shows the schematic diagram of the preparation of EVA core-PU shell microcapsules.

Synthesis of EVA microsphere

The synthesis of EVA microsphere by TIPS carried out in toluene. The 10 wt % mixed solution of EVA and toluene was poured into a flask at 30°C, heated up, and

added to C I Pigment Red 112 at 100°C to make a homogeneous solution containing pigment. Cooling of the mixture was carried out in a 20°C water bath and gel was prepared. The gel was filtered, washed with acetone, dried, and grounded using an air mill. Then, the EVA microsphere of about 5 μm was prepared.

Conversion to poly(ethylene-co-vinyl alcohol) microsphere

A partially converted EVA microsphere, consisting of an outer ethylene-co-vinyl alcohol (EVAL) shell and an inner EVA, was prepared using a partial saponification of EVA microsphere in a 35% aqueous solution of NaOH/Na₂SO₄/methanol (2:1:1 by weight) at 60°C for 4 h to produce a saponified surface layer of about 50–60% of the original radius.

Formation of PU shell

The formation of a PU shell containing an EVA microsphere was carried out using typical interfacial polymerization. An oily solution with 0.23M TDI and a 1 g EVAL microsphere was prepared by an adequate mixture. The oil-in-water emulsion was formed by pouring 150 g of the organic solution with 0.01M PVA as a protective colloid, and immersed vigorously using a homogenizer. The resulting emulsion was stirred under atmospheric pressure at 25°C for 5 min. DBTDL as a catalyst and polyols with various molecular weights were added into the oil-in-water emulsion. After going up to 70°C, EDA as a chain extender was added into the resultant solution. A reaction time of the subsequent 60 min formed a PU shell containing an EVA microsphere. The EVA core-PU shell microcapsule was decanted and washed with a 30% ethanol aqueous solution to remove unreacted TDI and core microspheres on their surface. The filtered microcapsule was dried at room temperature for 24 h.

Characterization of EVA core-PU shell microcapsule

FTIR spectrophotometer

To identify the reaction, an FTIR spectrometer (Impact 400D, Nicolet) was used. For each sample, 32 scans at 2 cm^{-1} resolution were collected in the adsorption mode.

TABLE II
Characteristics of the Fabrics

Fabric	Weave	Density (warp \times weft/5 cm)	Warp counts	Weft counts	Weight (g/m ²)
Cotton	Plain	141 \times 135	30s	36s	105
Silk	Plain	314 \times 200.5	1.65 D	7.3 D	62.5
PET	Plain	117.5 \times 102.5	7.5 tex/2	20 tex	135

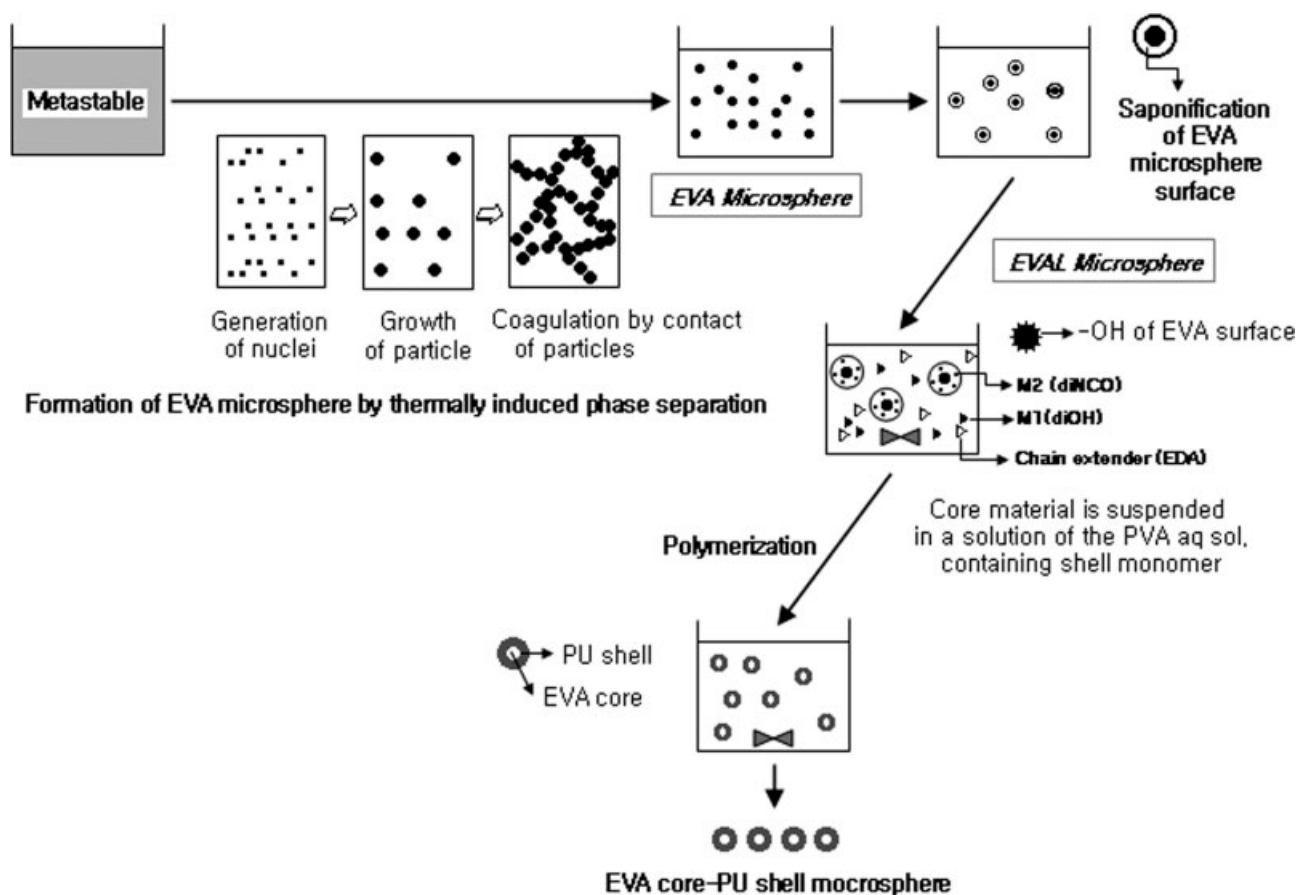


Figure 1 Schematic diagram of preparation of EVA core-PU shell microcapsule.

Particle size

The particle size of the microcapsule should be in the range of 5–20 μm for the use of the xerographic printing toner. A Galai CSI-1 particle size analyzer (Galai Production, Israel) and a laser diffraction particle analyzer were used to measure the particle size distribution and the mean particle size.

Scanning electron microscopy

Morphologies of the microparticles were observed by SEM (Hitachi S-4200, Japan).

Printing and curing

A screen printing machine of 90 \times 90 mesh was used for the printing of the EVA microsphere, and the EVA core-PU shell microcapsule on cotton, silk, and PET fabrics. The curing of printed fabrics was carried out by a press at 198°C for 10 min. The color strength (K/S) of the printed samples was evaluated with a Macbath Coloreye 700 spectrophotometer (illuminant D65, 10° observer).

Friction fastness

The test method for rubbing was obtained by the American Association of Textile Chemists and Colorists (AATCC method 8).

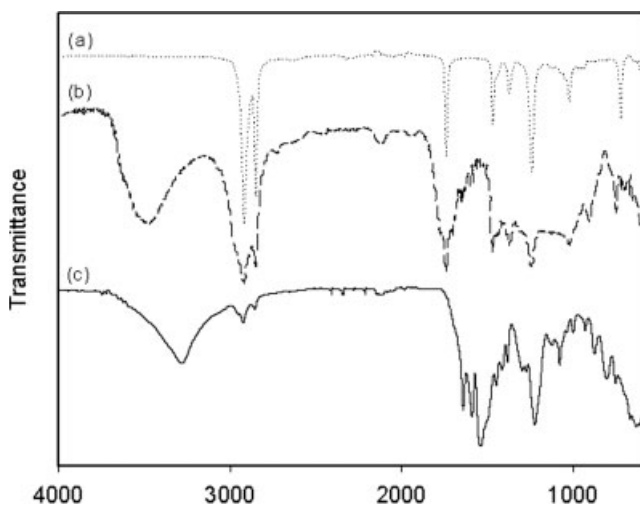


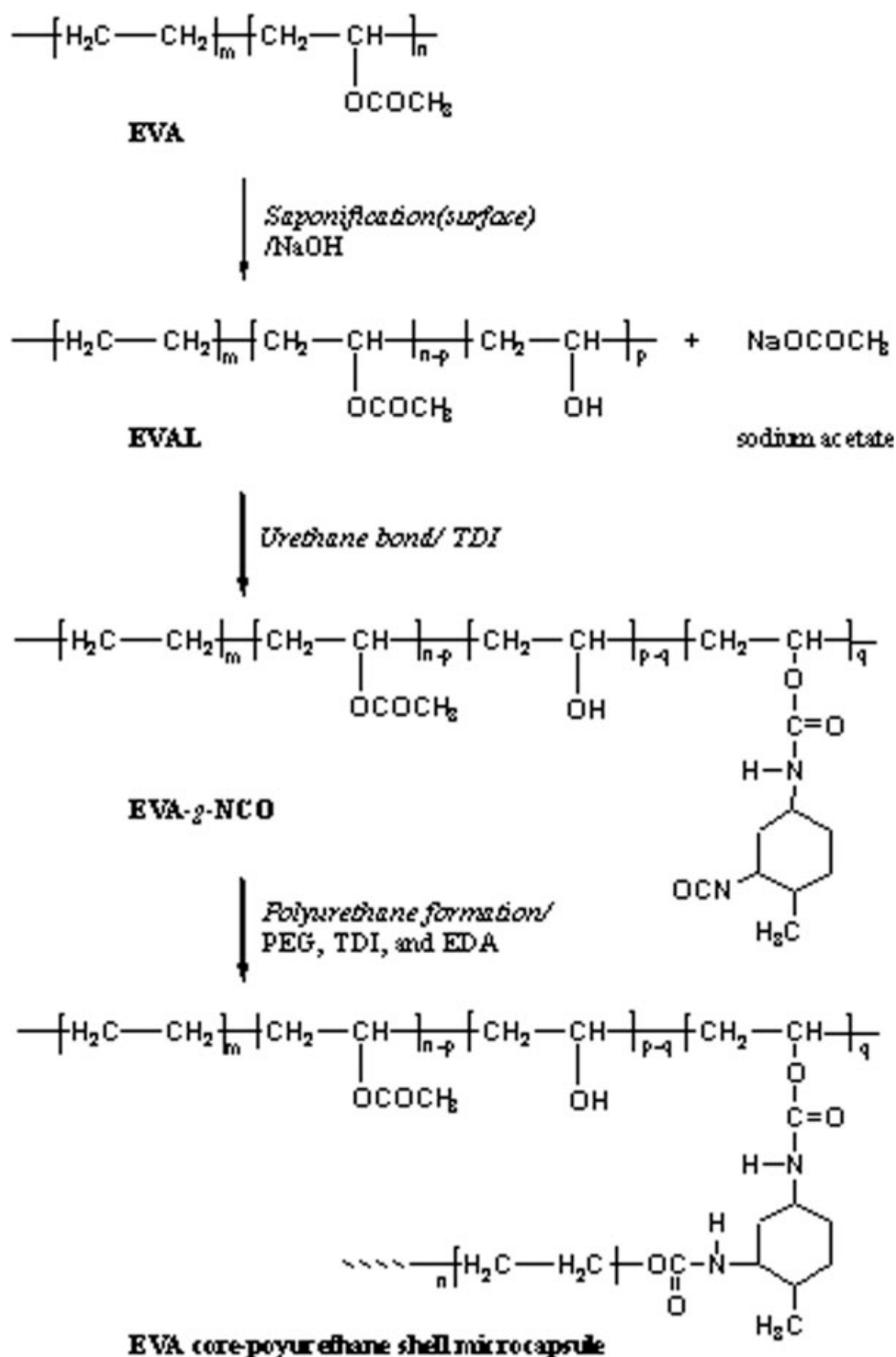
Figure 2 FTIR spectra of PVA microsphere (a), PVAL microsphere (b), and PVA core-PU shell microcapsule (c).

RESULTS AND DISCUSSION

Structure of EVA core-PU shell microcapsule

The FTIR spectra of synthesized EVA microsphere, converted EVAL microsphere, and the prepared EVA core-PU shell microcapsule are presented in Figure 2. As seen in Figure 2(b), the spectrum shows

an appearance of the —OH absorption band at 3500 cm^{-1} . The IR spectrum indicates the introduction of polyol groups on the shell of the EVA microsphere. As seen in Figure 2(c), the spectrum shows absorption bands at $1740\text{--}1710\text{ cm}^{-1}$ for the C=O stretching of urethane and at $1690\text{--}1650\text{ cm}^{-1}$ for urethane-urea formation. The N—H stretching was observed



Scheme 1 Schematic diagram of reaction steps involved in the preparation of EVA core-PU shell microcapsule.

at $3450\text{--}3300\text{ cm}^{-1}$. The IR spectra also indicate the completion of the reaction of diisocyanate and polyol by the disappearance of the NCO absorption band at 2270 cm^{-1} and the appearance of the N—H and C=O absorption bands. Moreover, C—C stretching in the phenylene ring at 1600 cm^{-1} , =C—H stretching at 2850 cm^{-1} , C—O—C stretching at 1100 cm^{-1} , =C—H bending at $80\text{--}750\text{ cm}^{-1}$ were also observed. Thus core and shell materials of the produced microcapsule are composed of EVA and PU, respectively. Scheme 1 shows a schematic diagram of the reaction steps involved in the preparation of an EVA core-PU shell microcapsule.

Particle size

The EVA microsphere, synthesized via TIPS, was spherical and rough, with diameters up to $20\text{ }\mu\text{m}$. The corresponding SEM photographs and mean par-

tle size distribution are shown in Figures 3 and 4. The normal synthetic procedure in converting EVA to EVAL generally involves the alkali or acid hydrolysis of EVA in an alcohol solution.¹³ During such a direct reaction, EVA in the solution phase is rapidly hydrolyzed to EVAL. In the first step of the process, EVA microspheres are saponified mainly on the surface in an alkaline methanolic solution.^{14,15} In the present study, the reaction time and methanol concentration were controlled, such that the thickness of the saponified surface layer was about 40–50% of the original microsphere radius. The conversion ratio of EVAL was measured using a particle size analyzer as the method reported on previous papers.^{6,7,11}

The effects of structure and molecular weight of polyols on particle size are expected because of the decrease in hard segment content by changing the NCO/OH. Figures 5 and 6 show the mean particle size and particle size distribution of the EVA core-

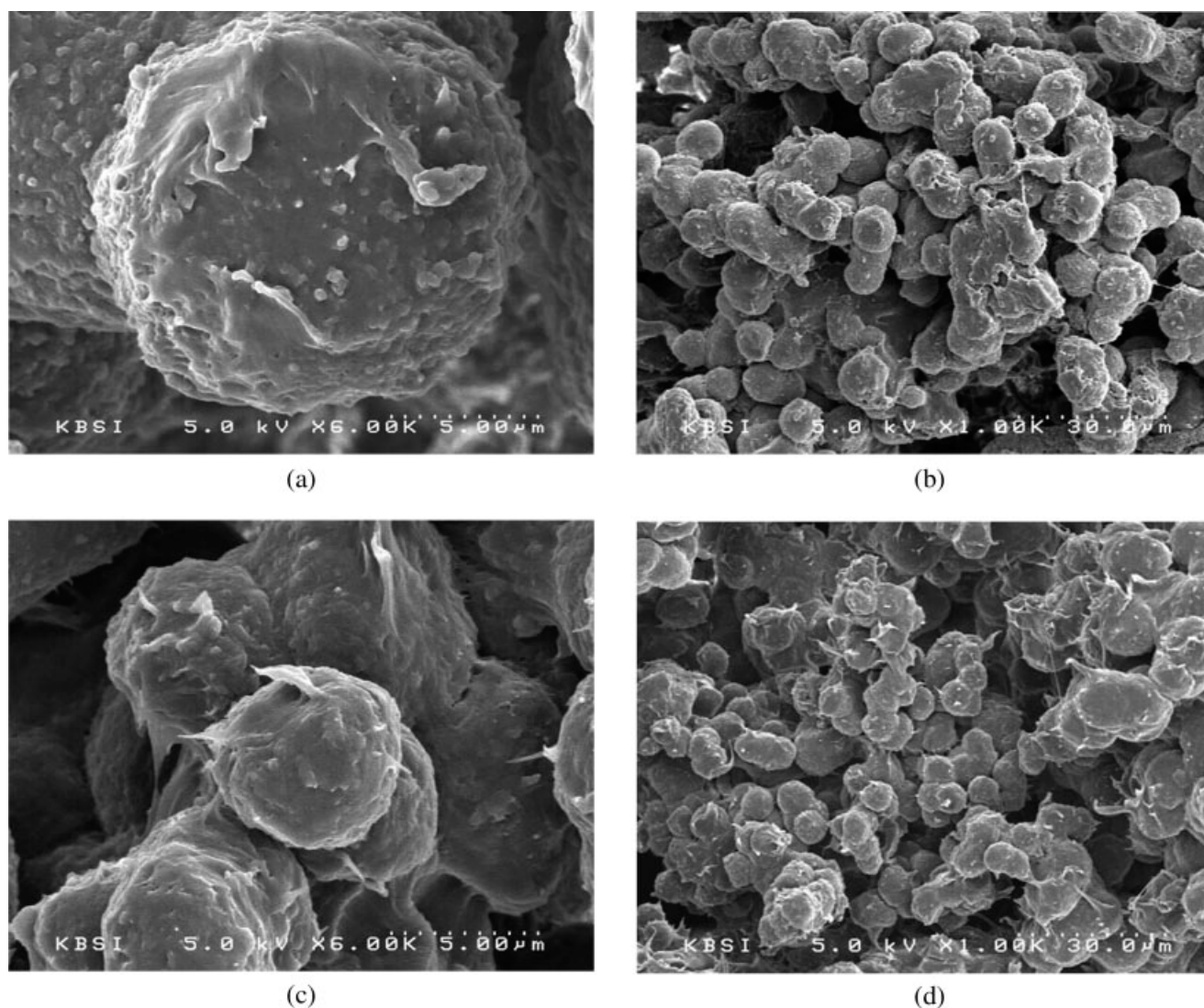


Figure 3 SEM photographs of EVA (a) and EVAL (b) microsphere.

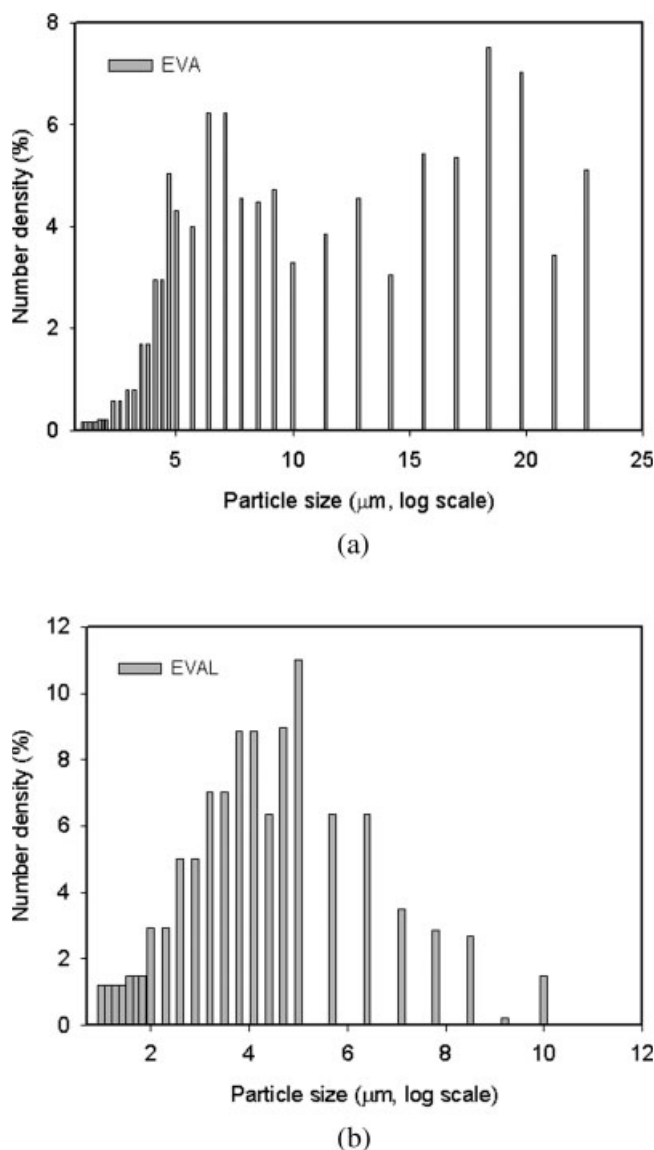


Figure 4 Particle size distribution of EVA and EVAL microspheres.

PU shell microcapsules with the different number of carbon in the repeat unit of polyol. As the increase of the amount of carbon in the repeat unit, the mean size of the synthesized particles increased and the size distribution became wider. In the process of microencapsulation, globules in the first emulsion step would be the same size, but agglomeration could occur between the globules by adding polyol with diverse structure of the aliphatic group into the solution, which resulted from an increase of viscosity in the oil-in-water emulsion.¹⁵ Moreover, particles from PPG and PTMG have bimodal particle size distribution for this reason.

General PU consists of a soft segment with a high molecular weight of polyol, and a hard segment with a low molecular weight of diisocyanate, and chain ex-

tender such as diol or diamine, have been synthesized in the range of 20–50% hard segment. However, in the production of PU microcapsules, elasticity properties are less important than modulus to produce monodispersed particles. Therefore, low molecular polyols ($M_w < 100$) were used to enlarge the content of hard segment related to an elastic modulus.¹⁶

Figure 7 presents the mean particle size of PU microcapsules produced by using different molecular weights of PEG (M_w 400, 600, 1000, and 2000) to obtain a high modulus PU wall. Their mean particle sizes were 6.20, 7.06, 8.36, and 12.19 μm, respectively. When compared with the mean particle size of high molecular weight polyol-based particles, that of low molecular weight polyol-based microcapsules is lower, but the differences are not conspicuous as a result. This result is considered to have to do with the rapid reactivity of polyol with diisocyanate. Moreover, the second crosslinkages such as biuret and allophanate might be accelerated by the reaction of diisocyanate with water, which is possible in emulsion polymerization, in which case the chain of the hard segment would be more complicated by adding EDA as chain extender. Thus, as shown in Figure 7, the mean particle size of microcapsules increased slightly with the molecular weight of polyol.

Morphologies of EVA core-PU shell type microcapsule

Generally, the chemical structure, the molecular weight, and the chemical properties of polyol have an influence on the properties of synthesized PU polymer and affect the morphology of the particle shell.

Figures 8 and 9 show the morphologies of PU microcapsules prepared using different soft segments. In the case of the PU microcapsules with the different

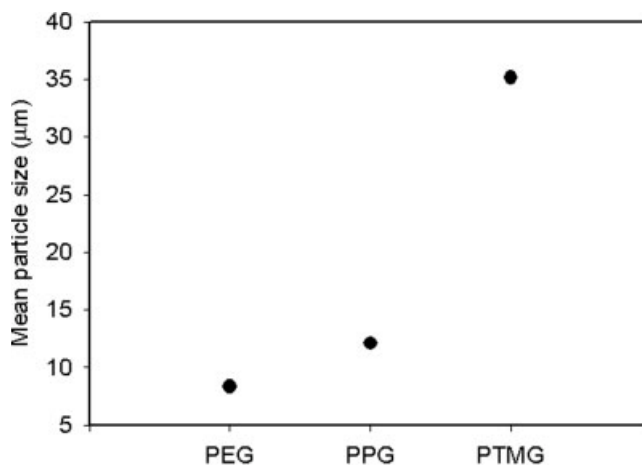


Figure 5 Mean particle size of various polyol-based PU microcapsules.

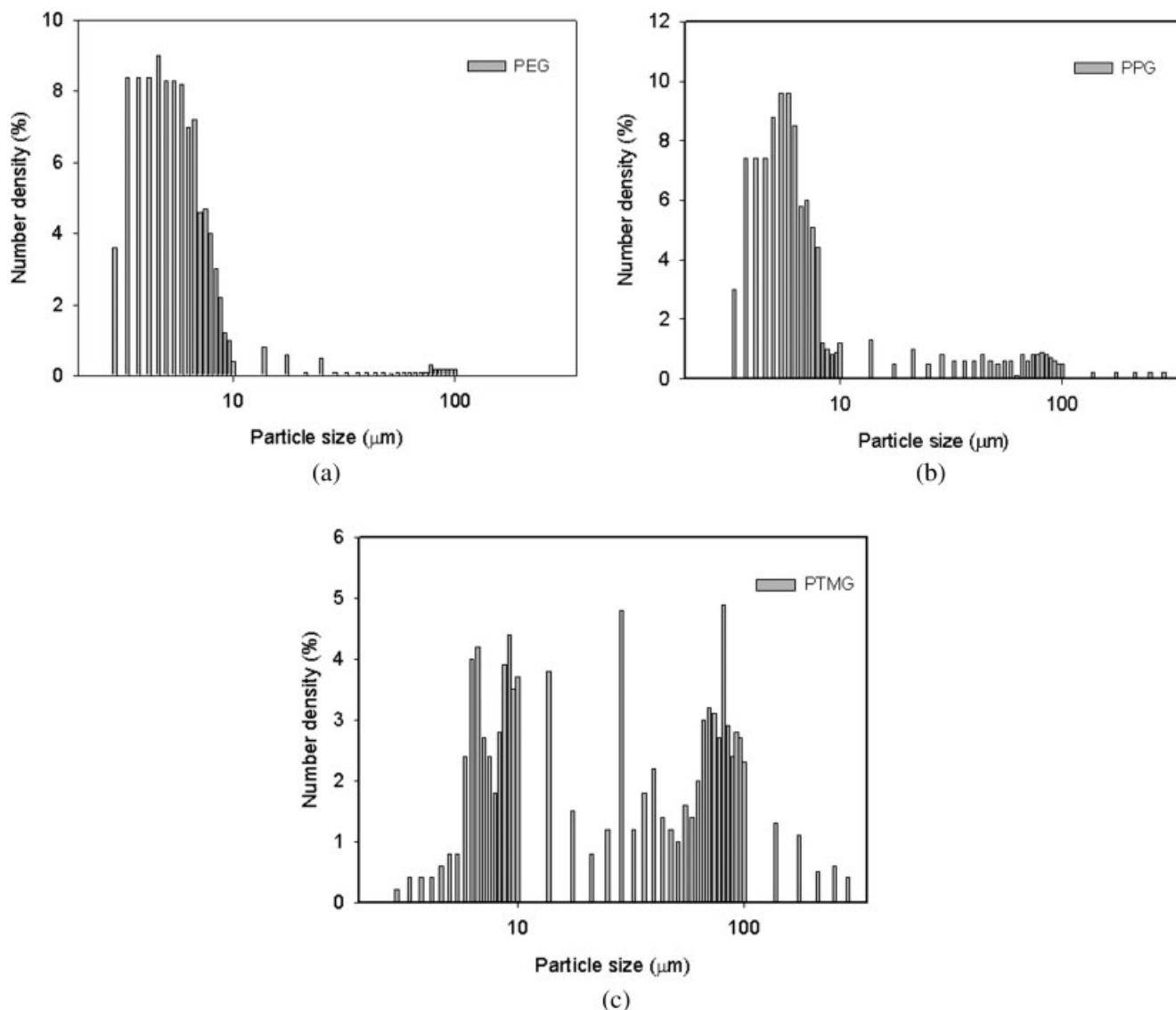


Figure 6 Particle size distribution of various polyol-based PU.

methylene chain of polyol, Figure 8, the more the molecular weight of the repeated chain in polyols increases, the smoother the surface and the bigger the size of the particles seen. It seems that a wider and thicker microcapsule wall results from the adhesiveness among formed chains by means of the reaction between TDI and the stronger hydrophobic polyol. Figure 9 shows the morphologies of the PU microcapsules with different molecular weights of PEG. As a result, the more the molecular weight of polyol increases, the more porous the surface of its capsules seem. The surface of the microcapsules from the PEG 2000 departs from the round shape and appears very coarse and porous, while that from the PEG 400 seems smooth and less permeable. Eventually, the surface of the prepared microcapsules was more and more porous as the molecular weight of the polyol increased. This indicates that the particles from polyol with more

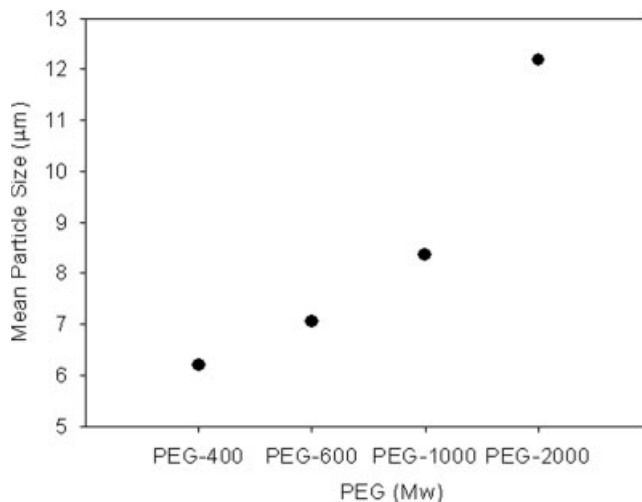


Figure 7 Mean particle size of different molecular weight polyol-based PU microcapsules.

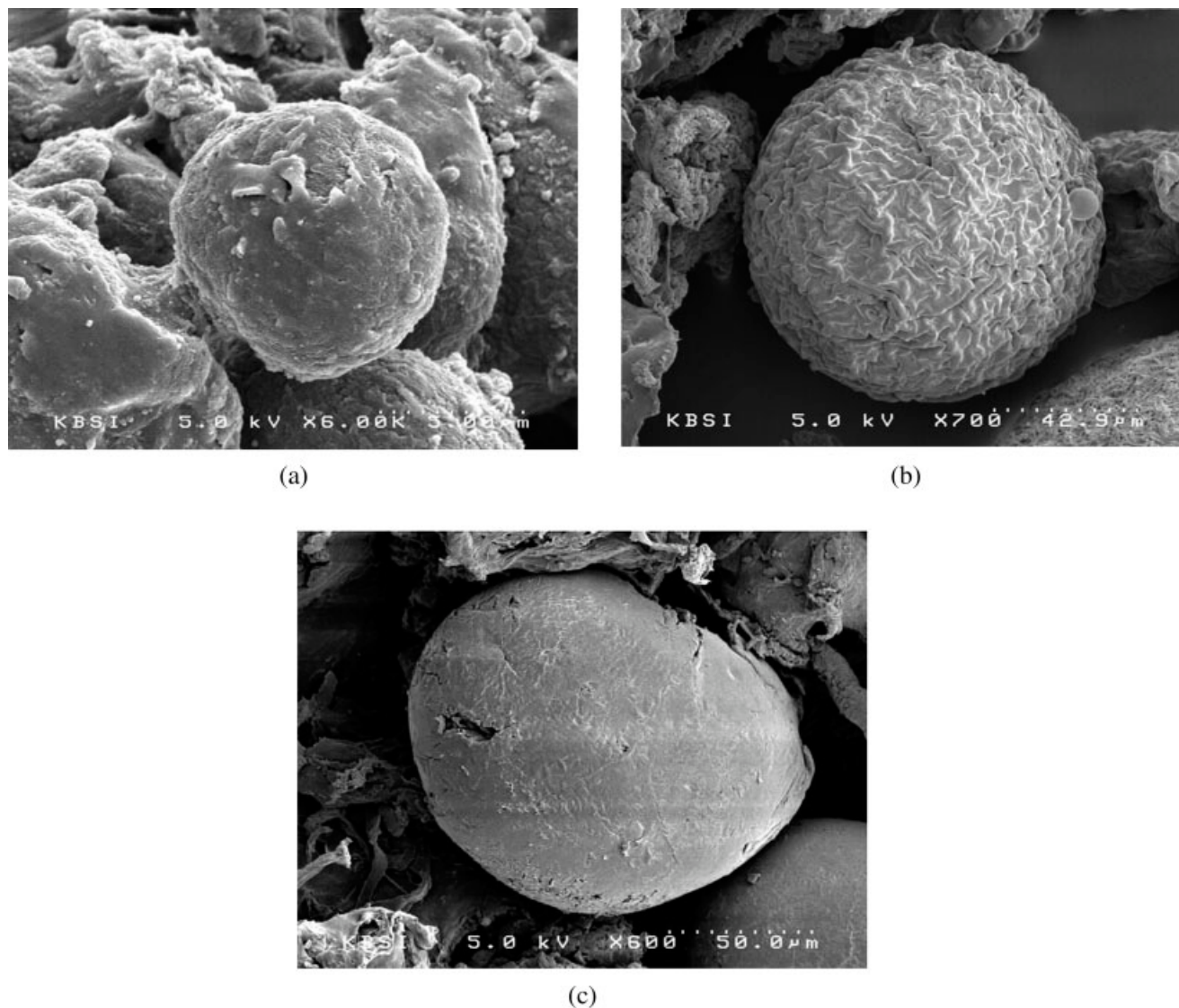


Figure 8 SEM photographs of EVAL core-PU shell microcapsules prepared by PEG (a), PPG (b), and PTMG (c) microsphere.

—OH groups than the other types of polyols consist of a stronger wall membrane.¹⁶

Color strength and friction fastness of printed fabrics

Table III shows the *K/S* values and friction fastness of cotton, silk, and PET fabrics printed using the EVA microsphere and EVA core-PU shell microcapsule. Irrespective of the type of fabric, the surface of the printed fabrics with the EVA core-PU shell microcapsule was more flat, more uniform, and darker than that of fabrics printed with the EVA microsphere. This results from the increase of a chemical attraction between the particles and the fabric because the PU shell is formed around a hydrophobic EVA particle.

When compared with the friction fastness of cotton, silk, and PET fabrics printed using the EVA microsphere, those printed using the EVA core-PU shell microcapsule are better. Sides from the wet friction fastness of silk and PET, fabrics printed using the EVA core-PU shell microcapsule show more enhanced grades than those of the EVA microsphere. Especially, the dry friction fastness of cotton and silk fabrics were enhanced to 4 and 4–5 grades, respectively.

CONCLUSIONS

EVA microspheres were prepared using TIPS. PU microcapsules containing hydrophobic EVA microspheres as the core material, EVA core-PU shell microcapsules, were synthesized by interfacial poly-

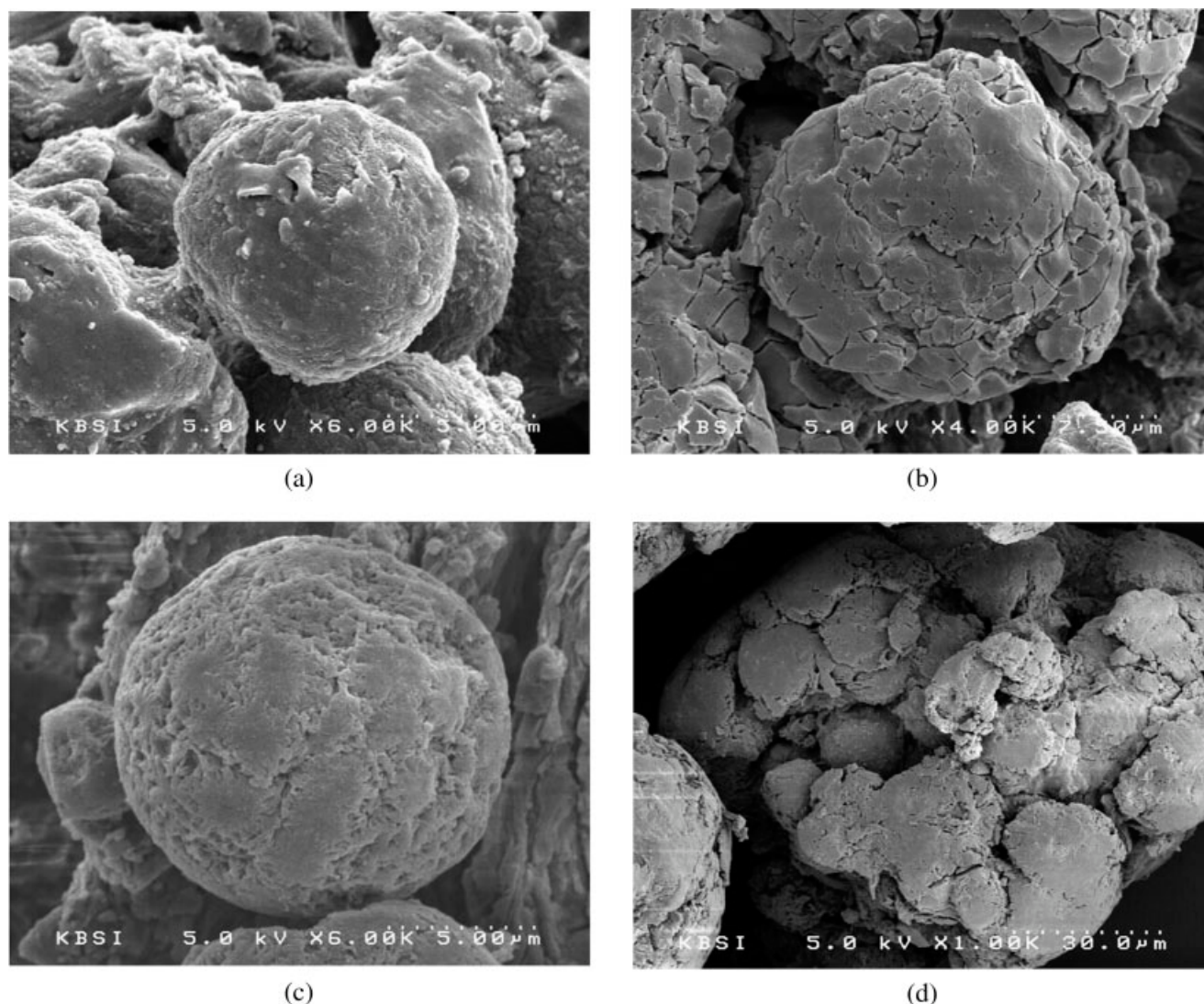


Figure 9 SEM photographs of EVAL core-PU shell microcapsules prepared by PEG 400 (a), PEG 600 (b), PEG 1000 (c), and PEG 2000 (d).

merization using TDI, polyols, and EDA, and were characterized by their particle size distribution, morphologies, color strength, and friction fastness when printed fabrics were produced with polyols of a different chemical structure. An increase in the molecular weight of the repeated chain in the polyols could

give a smoother surface and bigger particle size. An increase of the molecular weight of the polyols gave bigger and more porous surfaces and more permeable micromembranes due to an increase in the hydrophobic hard segment and a thinner wall. In addition, friction fastness of the printed fabrics with

TABLE III
Color Strength and Friction Fastness of Cotton, Silk, and PET Fabrics Printed by EVA Microsphere and EVA Core-PU Shell Microcapsule

Particle	Cotton			Silk			PET		
	K/S	Fastness		K/S	Fastness		K/S	Fastness	
		Dry	Wet		Dry	Wet		Dry	Wet
EVA	1.21	2	3-4	1.40	3	3-4	2.91	3	4
EVA core-PU shell	3.46	4	4-5	3.87	4-5	3-4	3.54	3-4	4

the EVA core-PU shell microcapsule could have more enhanced grades than those of the EVA microsphere.

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