

Single-Pack, Self-Curable, Aqueous-Based Polyurethane Dispersion Containing a Disperse Dye

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ABSTRACT: An organic-solvent-soluble disperse dye was introduced into an aqueous phase by a reaction with a self-emulsified, aqueous-based polyurethane (PU), and this resulted in the formation of a homogeneous, aqueous polymeric dye dispersion. This aqueous polymeric dye was stable in a water phase with excellent color extension upon application. It was formulated with a latent curing agent, polyaziridine (e.g., TMPTA-AZ), as a single-component, self-curable, aqueous polymeric dye. The curing reaction took place between PU carboxylic acid and the latent curing

agent upon drying. A self-cured polymeric dye was obtained with excellent color extension and fastness and resistance to organic solvents and water after drying. This single-component, self-curable, aqueous-based PU system containing a dye has potential for printing, writing, and dyeing applications. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 3741–3747, 2006

Key words: curing of polymers; dyes/pigments; polyurethanes

INTRODUCTION

Most disperse dyes are soluble only in organic solvents. Therefore, organic solvents as media are needed for their applications. Because of environmental, safety, and hygienic requirements, organic solvents for practical applications are gradually being phased out and replaced by water. A self-curing, aqueous-based polyurethane (PU) system with a latent curing agent was prepared that self-cured upon drying.¹ A self-emulsified, aqueous-based PU was designed to bring a disperse dye into an aqueous phase and resulted in a homogeneous, aqueous polymeric dye. This aqueous polymeric dye was formulated with a latent curing agent (e.g., polyaziridine) and resulted in the formation of a self-curable, aqueous polymeric dye.² This self-cured polymeric dye had not only excellent color extension but also high color fastness upon application with respect to its original disperse dye or a conventional polymeric dye without curing prepared from acrylate³ or PU oligomers.^{4,5}

A carboxylic acid containing and NCO-terminated PU prepolymer was prepared by the addition of isophorone diisocyanate (IPDI), poly(propylene glycol)-1000 (PPG-1000), and dimethylolpropanic acid (DMPA). A disperse dye consisting of an amino group that reacted with the PU NCO terminal group resulted in a self-

emulsified, aqueous PU-based polymeric dye after it was neutralized and dispersed into water.

A polyaziridine, such as an addition adduct of aziridine with trimethylol tri-acrylate (TMPTA-AZ), was chosen as a latent curing agent for this self-emulsified, aqueous polymeric dye dispersion and resulted in a single-component, stable, aqueous PU-based polymeric dye dispersion when its pH remained at 8.0 or higher. It was self-cured with a curing agent, TMPTA-AZ, upon drying and became a solvent-resistant and waterproof polymeric dye. This self-curable system of an aqueous polymeric dye dispersion has potential applications in printing, writing, and dyeing.

EXPERIMENTAL

Instruments

Thermogravimetric analysis (TGA) data were measured with a TGA 2950 high-resolution thermogravimetric analyzer (TA, United States). The appearance color strength of the polymeric dye was measured with an X-Rite (United States) SP62 sphere spectrophotometer. The UV absorption spectrum of the acetone solution of the disperse dye or polymeric dye was measured with an HP (United States) UV Agilent 8453 ultraviolet–visible (UV–vis) spectrophotometer.

Materials

Triethylamine (TEA), DMPA, C.I. Disperse Blue 56, C.I. Disperse Red 4, and C.I. Disperse Yellow 9 were obtained from Aldrich Chemical Co., Inc. (Milwaukee,

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WI). IPDI and PPG-1000 were supplied by Dow Chemical Co. (Midland, MI). All the materials were used as received without further purification.

Preparation of the NCO-terminated PU prepolymer

PPG-1000 (0.2 mol) and DMPA (0.1 mol) were dried at 110°C overnight before being mixed with IPDI (0.4 mol) in a 1-L, four-necked resin flask. The resin flask was equipped with a mechanical stirrer, a thermometer, a nitrogen inlet, and a condenser with a CaCl₂ drying tub. The reaction mixture was kept at 110°C for about 4 h under nitrogen until NCO% dropped below 3.5 (ASTM D 1638 NCO determination method), remained constant for another half-hour, and then was cooled to the ambient temperature for the polymeric dye preparation process (Scheme 1).^{1,6}

Preparation of the latent curing agent TMPTA-AZ

Aziridine (ethylene imine) was prepared and modified according to the published literature.^{1(a-c)} A quantitative amount of freshly prepared aziridine was added slowly to an acetone solution of trimethylolpropane triacrylate in an ice bath and then raised to the ambient temperature for 5 h until the absorption peak of the acrylate double bond in the IR spectrum disappeared.^{1,7}

Preparation of the aqueous PU-based polymeric dye dispersion

An acetone solution of 0.03 g of the disperse dye with two drops of dibutyl tin dioctoate (T-12) (catalyst) was added to an acetone solution of the prepared NCO-terminated PU prepolymer (41.0 g) slowly through an addition funnel. Then, TEA (0.15 mol) was added to neutralize PU carboxylic acid before it was dispersed with 100 mL of deionized water.⁸ An aqueous PU-based polymeric dye dispersion was obtained with a 20% solid concentration after water mixing. A disperse dye was chosen, such as C.I. Disperse Blue 56, C.I. Disperse Red 4, or C.I. Disperse Yellow 9, to prepare the aqueous PU-based polymeric dye dispersion.

UV absorption of the disperse dye and polymeric dye

The maximum UV absorption of each disperse dyes or its polymeric dyes in an acetone solution was measured with a UV-vis spectrophotometer.

Single-pack, self-cured, aqueous PU-based polymeric dye

The aqueous PU-based polymeric dye dispersion was formulated with a latent curing agent, polyaziridine

(e.g., 5 phr TMPTA-AZ); a stable and homogeneous, aqueous PU-based polymeric dye dispersion was formed at pH values of 8.0 and greater. It was self-cured upon drying, and a waterproof and solvent-resistant film with the polymeric dye was obtained at the ambient temperature.¹

Physical properties of the self-cured polymeric dyes

Gel content

A known weight of the dried polymeric dye was placed in a Soxhlet extractor for continuous extraction with tetrahydrofuran (THF) for 24 h. The polymer gel remaining after extraction was dried and calculated according to the test results. Three tests were carried out and averaged for each sample.

Water uptake

A known weight (W_0) of an oven-dried polymeric dye sample was immersed in a deionized water bath for a week. The towel-wiping-dry polymeric dye weight (W_1) and oven-dried PU sample weight (W_2) were obtained. The water uptake (W_w) and weight loss (W_x) of the polymeric dye in water were calculated according to the following equations:

$$W_w(\%) = [(W_1 - W_2) / W_2] \times 100\%$$

$$W_x(\%) = [(W_0 - W_2) / W_0] \times 100\%$$

Ethanol swelling

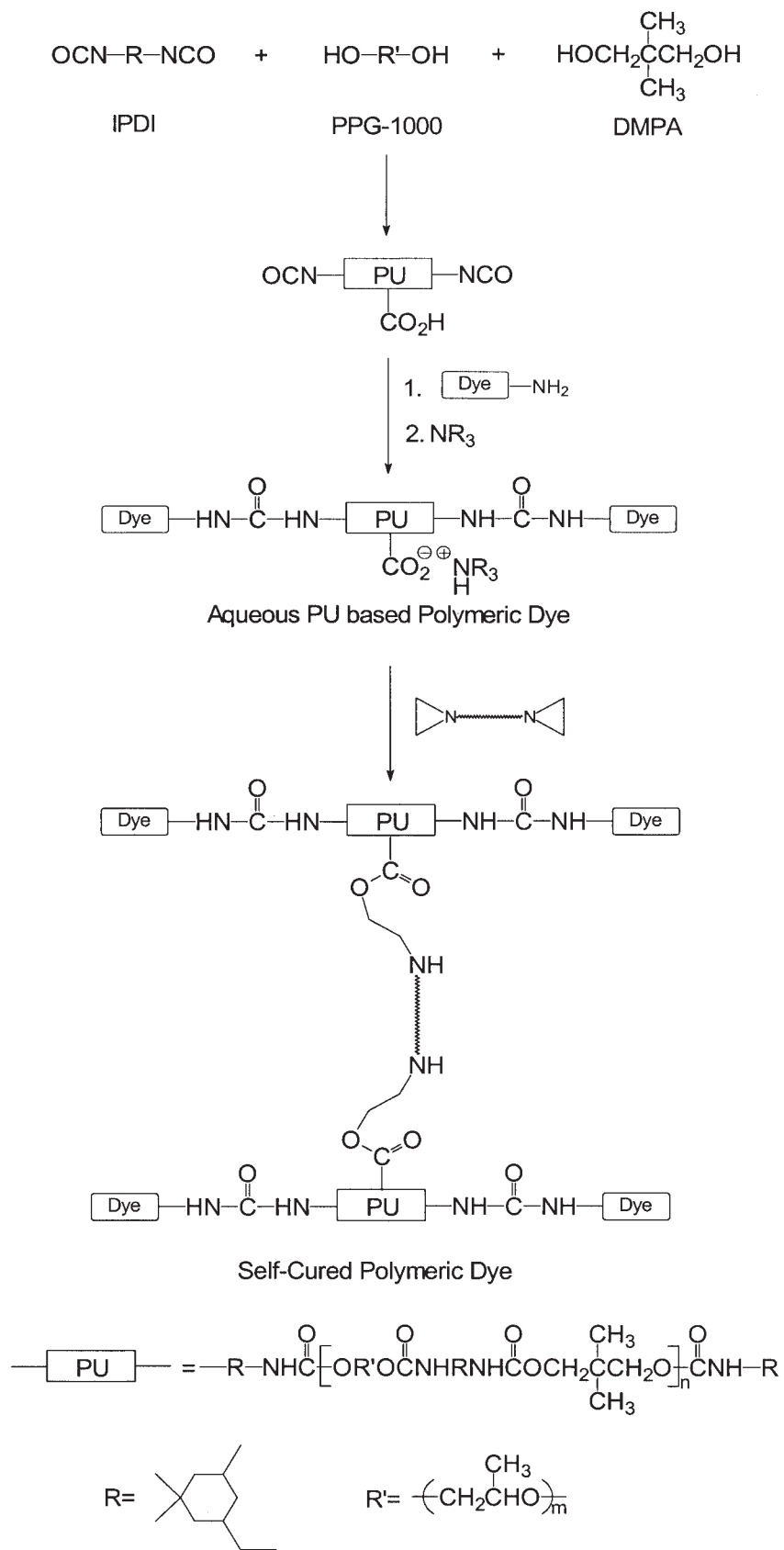
A known weight (W_0) of a dried PU film sample was immersed in a 95% ethanol bath for 24 h. The towel-down-dry PU sample weight (W_1) and oven-dried PU sample weight (W_2) were obtained. The ethanol absorption (W_e) and weight loss (W_y) of the polymeric dye in ethanol were calculated according to the following equations:

$$W_e(\%) = [(W_1 - W_2) / W_2] \times 100\%$$

$$W_y(\%) = [(W_0 - W_2) / W_0] \times 100\%$$

TGA

The conditioned samples were measured with a thermogravimetric analyzer at a heating rate of 10°C/min from the ambient temperature to 500°C. This was performed under a nitrogen or air atmosphere for the measurements of the thermal stability of the polymeric dyes.



Scheme 1 Self-curable, aqueous-based PU containing a dye.

TABLE I
Properties of the Self-Cured PU Polymeric Dyes

Property	TMPTA-AZ (5 phr)/dosage of disperse dye (phr) ^a								
	Red 4/ aqueous-based PU			Blue 56/ aqueous-based PU			Yellow 9/ aqueous-based PU		
	0.5	1.0	2.0	0.5	1.0	2.0	0.5	1.0	2.0
Gel content (%) ^b	85.7	86.9	88.5	85.1	87.6	89.4	85.3	86.7	88.2
Water uptake (%) ^c	7.7	8.9	9.5	8.6	9.8	10.5	8.1	9.2	10.1
Polymer weight dissolved in water (%)	0.8	0.9	1.8	4.2	5.0	5.5	3.2	4.4	5.3
Ethanol swelling (%) ^d	83.9	93.6	117.4	69.7	74.4	80.8	28.3	33.7	41.6
Polymer weight dissolved in ethanol (%)	6.5	5.0	4.4	6.8	5.6	4.1	6.6	4.8	4.1

^a Disperse dye dosage (phr) with 100 g of the PU prepolymer.

^b The gel content was obtained from a known weight of dried polymeric dye placed in a Soxhlet extractor for continuous extraction with THF for 24 h.

^c The water uptake was measured by a known weight of an oven-dried polymeric dye sample immersed in a deionized water bath for a week.

^d The ethanol swelling was measured by a known weight of a dried PU film sample immersed in a 95% ethanol bath for 24 h.

Appearance color strength of the polymeric dye film

Each self-cured polymeric dye film was dipped in a water bath for 24 h and then dried. The appearance color strength of the treated polymeric dye film (after it was dipped in water), in comparison with that of the original sample (without dipping), was measured with a sphere spectrophotometer.⁹

RESULTS AND DISCUSSION

A self-emulsified, aqueous-based PU dispersion was prepared from an NCO-terminated PU prepolymer

that consisted of a carboxylic-ion-stabilizing, homogeneous, aqueous polymeric dispersion with an average particle size of 75 nm.¹ The amino-group-containing disperse dye (C.I. Disperse Dye Red 4, Disperse Dye Blue 56, or Disperse Dye Yellow 9) reacted with the NCO terminal groups of the PU prepolymer and formed a urea-bonded polymeric dye. This polymeric dye was dispersed into an aqueous phase through mixing with water after it was neutralized with TEA. This preparation process brought a water-insoluble disperse dye into a homogeneous, aqueous polymeric dye dispersion.

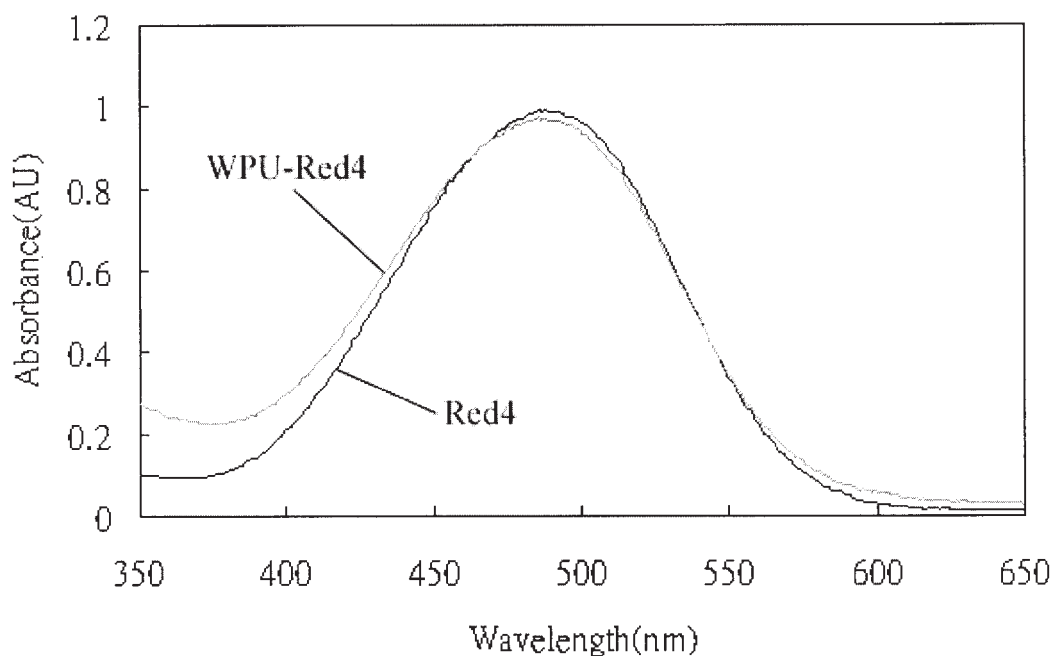


Figure 1 UV-vis spectra of the disperse dye (Red 4) and self-curable, aqueous-based PU containing Red 4 (WPU/Red 4) in an acetone solution.

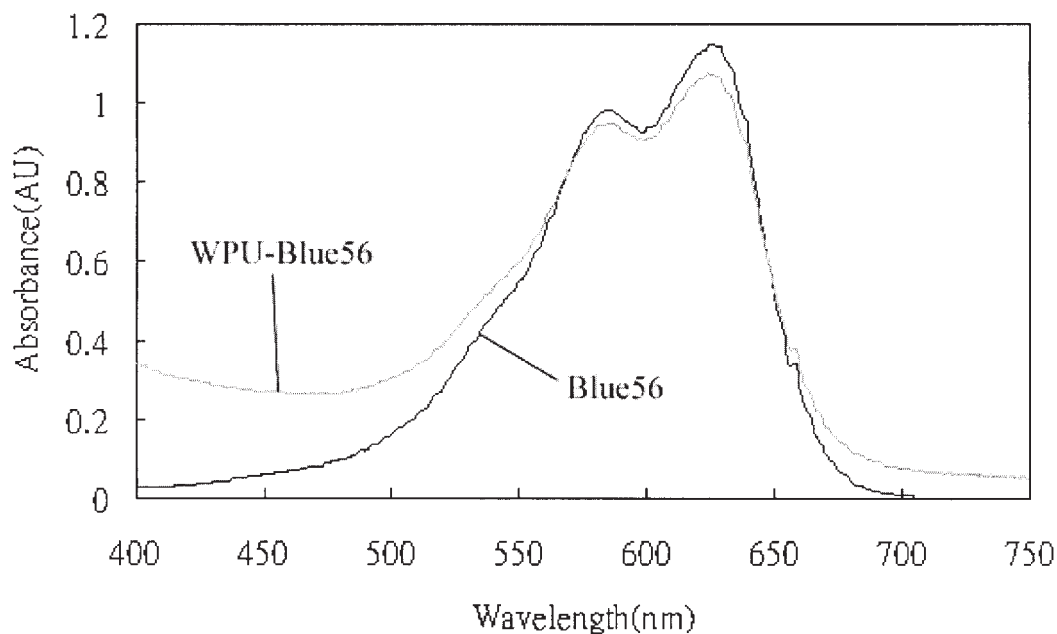


Figure 2 UV-vis spectra of the disperse dye (Blue 56) and self-curable, aqueous-based PU containing Blue 56 (WPU/Blue 56) in an acetone solution.

Polyaziridine (e.g., 5.0 phr TMPTA-AZ) was formulated with this aqueous PU-based polymeric dye dispersion as a latent curing agent and formed a single-pack, self-curable system of the aqueous-based polymeric dye dispersion, which was stable at pH values

of 8.0 and higher. A self-curing reaction took place between the aziridinyl group of TMPTA-AZ and PU carboxylic acid of the polymeric dye upon drying, and this resulted in a polymeric dye with a polymeric networking structure.¹

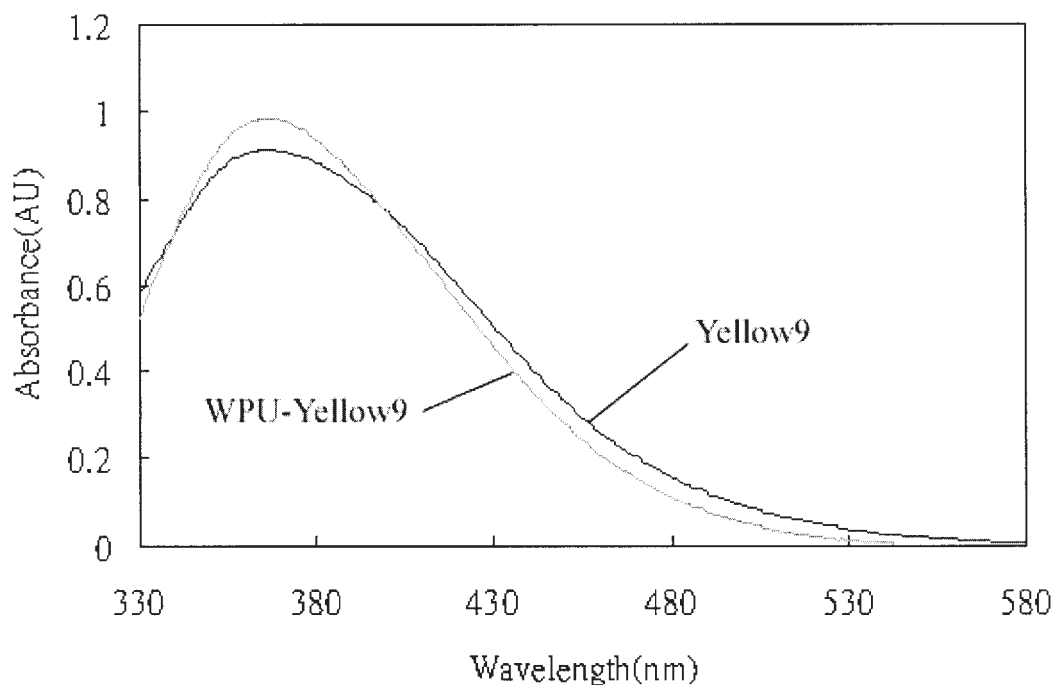


Figure 3 UV-vis spectra of the disperse dye (Yellow 9) and self-curable, aqueous-based PU containing Yellow 9 (WPU/Yellow 9) in an acetone solution.

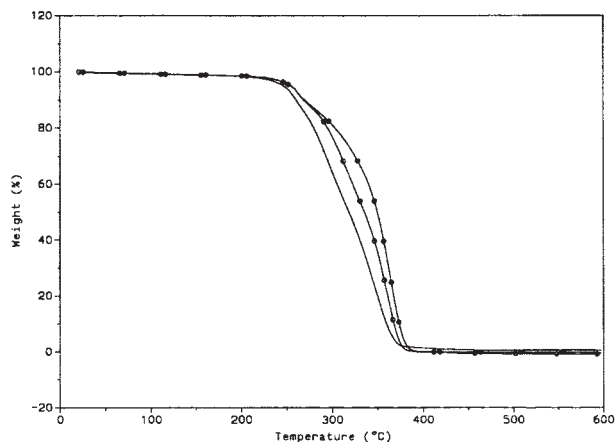


Figure 4 TGA of self-cured, aqueous-based PU (WPU) and its polymeric red dye under nitrogen (1.0 phr Red 4 disperse dye): (—) original WPU, (○) original WPU/dye, and (●) self-cured WPU/dye.

Properties of the self-cured, aqueous PU-based polymeric dye

The gel concentrations of the self-cured, aqueous PU-based polymeric dyes were more than 85%, and this indicated that the relative degree of the polymer crosslinking density of the polymeric dyes, in comparison with that of the original polymeric dye (without curing), was soluble in most organic solvents (e.g., THF and ethanol). The weight loss of these self-cured polymeric dyes after dipping in water was less than 5.5%. This proved that a curing reaction took place between the aqueous polymeric dye and the latent curing agent, TMPTA-AZ, upon drying (Table I). This was due to the formation of an amino ester bond networking structure¹ between the curing agent and PU backbone of the polymeric dye.

The UV maximum absorption peaks were almost at an identical wavelength for the acetone solution of each disperse dye and that of the polymeric dye. The maximum absorption wavelengths of disperse dyes C.I. Red 4, C.I. Blue 56, and C.I. Yellow 9 were 488, 625, and 366 nm and those of their relative polymeric dyes were 487, 624, and 366 nm, respectively (Figs. 1–3). This indicated that the chromophore of each dye and that of its polymeric dye remained identical; the polymeric dye only had urea bond formation between each disperse dye molecule and PU prepolymer.

Thermal behavior

The TGA thermogram indicated that each self-cured polymer dye with a latent curing agent had better thermal stability than the original aqueous-based PU and its polymeric dye without curing (Figs. 4–6). The self-cured polymeric dye resulted in a networked PU

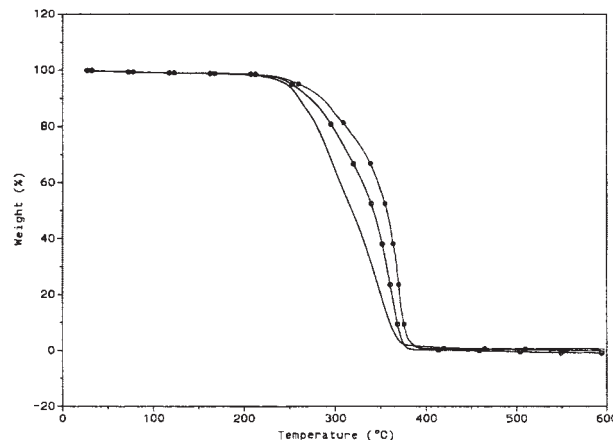


Figure 5 TGA of self-cured, aqueous-based PU (WPU) and its polymeric blue dye under nitrogen (1.0 phr Blue 56 disperse dye): (—) original WPU, (○) original WPU/dye, and (●) self-cured WPU/dye.

structure bonded with disperse dye C.I. Red 4, C.I. Blue 56, or C.I. Yellow 9.

Appearance color strength

These disperse dyes were soluble in ethanol but were water-insoluble. However, the self-cured polymeric dyes were resistant to water and ethanol. The color strength of each polymeric dye before dipping in water or ethanol was set at 100%. The color strength of the original (without curing) and self-cured polymeric dyes (PU with 1.0 phr Red 4) decreased to 95.0 and 95.8%, respectively, after dipping in water for 24 h. Their color strengths were 93.1 and 94.6%, respectively, after a treatment with ethanol. The other polymeric dyes (blue and yellow) demonstrated results similar to those of the polymeric red dye after dipping

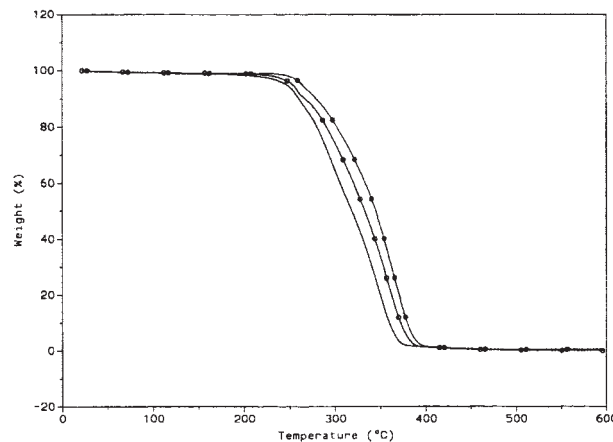


Figure 6 TGA of self-cured, aqueous-based PU (WPU) and its polymeric yellow dye under nitrogen (1.0 phr Yellow 9 disperse dye): (—) original WPU, (○) original WPU/dye, and (●) self-cured WPU/dye.

TABLE II
Appearance Color Strength^a of Self-Cured
Polymeric Dyes

Polymeric dye ^b	Polymeric dye color strength (%) ^c	
	Water treatment	Ethanol treatment
Original Red 4/WPU	95.0	93.1
Self-cured Red 4/WPU	95.8	94.6
Original Blue 56/WPU	96.4	94.2
Self-cured Blue 56/WPU	98.3	95.5
Original Yellow 9/WPU	90.5	85.8
Self-cured Yellow 9/WPU	91.8	87.0

^a The original color strength was 100% of each polymeric dye before treatment.

^b Each polymeric dye was aqueous-based PU (WPU) treated with 1.0 phr disperse dye (dye/WPU = 1/100 w/w)

^c Each dried polymeric dye was dipped in a water or ethanol bath for 24 h and then dried in a 50°C oven.

in water or ethanol. The self-cured samples of the polymeric dyes had a higher appearance color strength than the original polymeric dye after water or ethanol treatment (Table II). This improvement in the color fastness was also due to the polymeric network formation of the self-cured polymeric dye.

CONCLUSIONS

An organic-solvent-soluble disperse dye was introduced into a water phase with a self-emulsified, aqueous-based PU ionomer as a carrier and became a reactive, aqueous polymeric dye dispersion. That was

formulated with a latent curing agent (polyaziridine, e.g., TMPTA-AZ) and formed a single-pack, self-curable system of the aqueous polymeric dye. It was self-cured with TMPTA-AZ upon drying and resulted in the formation of a polymeric dye that was organic-solvent-resistant and waterproof. This self-curable system of an aqueous polymeric dye dispersion became a water- and organic-solvent-insoluble dye instantly when its pH value dropped to 6.0 or upon drying and has the potential for printing, writing, and dyeing applications.

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