



New washing-free printing binder based on organosilicon-modified polyacrylate for polyester fabric printing of disperse dyes



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ABSTRACT

Based on the disperse dye washing-free printing technology, a new washing-free printing binder was prepared through organosilicon modification of polyacrylate (PA) by mini-emulsion polymerization to achieve high color yield and color fastness of the printed fabric. The washing-free printing properties, structure, thermal behaviours, and surface characteristics of organosilicon-modified polyacrylate (PDMEMA) were intensively investigated. The migration-diffusion-fixation mechanisms of disperse dyes (DD) from PDMEMA film to polyester fiber (PET) were tentatively explored. Results showed that using PDMEMA with vinyl terminated polysiloxane 4313 g/mol at 4 wt %, the washing-free printed polyester fabric obtained the best washing-free printing properties. The color yield, color fastness and handle of PDMEMA surpassed those of commercial printing binders. The organosilicon modification of PA widened the differences of solubility parameters between DD and PDMEMA, contributing to the migration-diffusion of DD from PDMEMA film to PET and the fixation into PET. The decrease of the glass transition temperature of PDMEMA accelerated the migration-diffusion process of DD towards PET. Meanwhile, the organosilicon chain-segments of PDMEMA shifted onto the film surface in baking, which realized the directional transfer of DD from film to PET.

1. Introduction

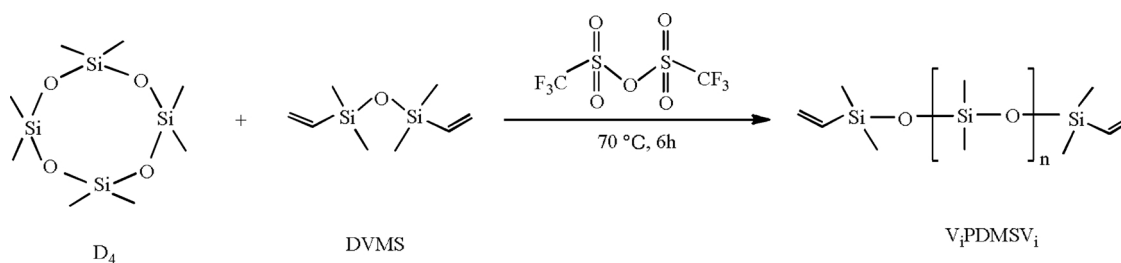
Textile printing is a key link in the textile industry to improve the clothing quality and additional value. In the worldwide, the printed textiles account for about 30%–40% of all textiles. Especially, synthetic fabrics have the unique advantages on the easy-care, comfort, functionality and high-fidelity, which makes the proportion of disperse printing up to 85% of the whole printing [1]. However, after the traditional disperse printing, the reduction cleaning and several washing procedures are necessary to remove unfixed dyes, residual thickeners and chemical auxiliaries, accompanying with high water consumption and large pollutant discharge with hard recycling. In the dyeing and printing industry in China, the effluent volume was 14.13×10^8 ton per year, accounting for 80% of total textile wastewater discharge [2]. The dyeing and printing wastewater greatly burdened the ecological environment, becoming the primary obstruction for the sustainable development of textile industry. Consequently, it is urgent to develop the environmental-friendly auxiliaries and clearer production technology [3].

Disperse dye washing-free printing technology has been emerging as the times require. It makes use of the film-forming characteristics of

polymer binder (PB) and the sublimation dyeing of disperse dye (DD) to realize the migration-diffusion of DD in PB film and the fixation into polyester fiber (PET). The similar short process (printing, drying and curing) as pigment printing is adopted to achieve the high efficiency, energy saving and wastewater-zero discharge. PB plays a crucial role in the washing-free printing paste. The adhesivity, film-forming ability of PB and the migration of DD in PB film directly determine the color yield, color fastness and handle of the printed fabric. So far, researches on washing-free printing mainly concentrated on the compositions of printing paste and the application techniques [4,5]. There were little studies on the development of new PB and the migration of DD between PB and PET.

Nonetheless, the migration-diffusion-fixation behaviours of DD from PB film to PET determine the color brightness and fastness of washing-free printing, which has tight relations with the solubility parameters (δ) and the glass transition temperatures (T_g) of PB [6–9]. The dyeing of PET with DD conforms to Nernst adsorption model. It can be considered as the formation of “solid solution”, namely above the PET's T_g , DD ($\delta_{DD} = 22.11\text{--}22.06 \text{ J}^{0.5}/\text{cm}^{1.5}$) on the surface of PET ($\delta_{PET} = 21.90 \text{ J}^{0.5}/\text{cm}^{1.5}$) diffuses by single-molecule and dissolves into the pores of amorphous region [10]. According to the solubility parameter similar

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Scheme 1. Reaction between Octamethylcyclotetrasiloxane and 1, 3-divinyl-1, 1, 3, 3-tetramethyldisiloxane.

principle, PB which had the similar δ with δ_{DD} would make DD dissolve into the polymer film. As a result, not-all DD in the conventional washing-free printing dyed the PET. The partial DD dissolved into film and simultaneously migrated onto/outside the film surface in baking. Under the external mechanical forces (as repeated rubbing, agitation, washing and so on) and environmental stimuli (as light, heat, chemicals and so on) in wearing, the residual/undyed DD on the surface will separate from the film easily, resulting in color change and undesirable color fastness.

To solve the above-mentioned problems, it is the key to fabricate a new PB that could minimize the dissolution of DD into film and promote the directional migration-diffusion-fixation towards PET. Theoretically, the larger differences of δ between PB and DD and the lower of PB's T_g will contribute to the migration of DD away from PB film and the dyeing of PET [11–13]. In our previous research, using traditional printing on the PB film, PB of greater difference with δ_{DD} had lower color yield while that of smaller differences with δ_{DD} had higher color yield. Polyacrylate (PA) has been the most widely used binder in pigment printing [14]. But PA had the higher δ_{PA} 18.00–23.00 $\text{J}^{0.5}/\text{cm}^{1.5}$ and T_g , leading to the weak migration of DD towards PET and more residual DD in PA film [15]. It was found that polydimethylsiloxane (PDMS) possesses the low δ_{PDMS} 15.60 $\text{J}^{0.5}/\text{cm}^{1.5}$, soft chain segments and low surface energy [16,17]. The introduction of PDMS segments into PA structure will decrease T_g of PA film to reduce the diffusion resistance of DD. Meanwhile, it will enlarge δ differences between DD and PB and make use of Si-migration in baking to realize the directional migration-diffusion of DD towards PET. Furthermore, organosilicon-modified polyacrylate (PDMEMA) has comprehensive advantages of PA and PDMS: Improve the hot-sticking and cold-brittleness, weather-resistance and water-proofing properties of PA; greatly increase the softness, abrasion-resistance and staining-resistance of the printed fabrics [18,19].

In this study, vinyl terminated polysiloxane (ViPDMSVi_n) with different molecular weights were used to modify PA. A series of PDMEMA were successfully prepared by mini-emulsion polymerization. The washing-free printing properties of PDMEMA were associated with the solubility parameter and the glass transition temperature. The structure and thermal behaviours of PDMEMA were investigated by Fourier Transform Infrared Spectroscopy (FTIR-ATR), Differential Scanning Calorimeter (DSC) and Thermogravimetric Analysis (TGA). The surface characteristics of PDMEMA were analyzed by X-ray Energy Dispersive Spectroscopy (XPS) and Contact Angle Goniometer (CAG). Combined with disperse dye diffusivity in PB film, the migration-diffusion-fixation mechanisms of DD from PDMEMA film to PET were tentatively explored.

2. Experimental

2.1. Materials

Polyester woven fabrics were obtained from Hangzhou Jinjing Textile Dyeing & Printing Co., Ltd (China). Fabric specification: weight 156 g/m^2 , warp 28 threads/cm, weft 24 threads/cm.

Three disperse dyes used were C. I. Disperse Red 92, C. I. Disperse

Yellow 211, C. I. Disperse Blue 183, provided by Zhejiang Lonsen Group Co., Ltd (China).

Octamethylcyclotetrasiloxane (D_4) was supplied by Zhejiang Xin'an Chemical Group Co., Ltd (China). 1, 3-divinyl-1, 3, 3-tetramethyldisiloxane (DVMS) was supplied by Guangzhou Longkai Chemical Co., Ltd (China). Triflic acid (TfOH) was supplied by Ruifeng Chemical Co., Ltd (China). Sodium carbonate was supplied by Sinopharm Chemical Reagent Co., Ltd (China). 2-Ethylhexyl acrylate (EHA), methyl methacrylate (MMA) and acrylic (AA) were supplied by Tianjin Kemiou Chemical Reagent Co., Ltd (China). Hexadecane (HD) and Methylol acrylamide (NMA) were supplied by Aladin Reagent Co., Ltd (China). Sodium lauryl sulfate (SDS), fatty alcohol polyoxyethylene ether (O-10), propylene oxide propyl alkyl phenyl polyether ammonium sulfate (V-20S) were supplied by Shanghai Zhongcheng Fine Chemical Co., Ltd (China). Ammonium persulphate (APS) was supplied by Tianjin Yongda Chemical Reagent Co., Ltd (China). Commercial thickener PFL was purchased from Zhejiang Transfar Zhilian Co., Ltd (China). Commercial binder KG-101 was purchased from Yuxi Chemicals Co., Ltd (China). Commercial binder MP-320 was purchased from Shanghai Baote Green New Material Co., Ltd (China).

2.2. Synthesis of vinyl terminated polysiloxane (ViPDMSVi_n)

ViPDMSVi_n was synthesized with D_4 and DVMS via cationic ring opening polymerization using TfOH as catalyst, shown in Scheme 1. After reaction at 70 °C for 6 h, the product was cooled down, regulated pH 6–7 by anhydrous sodium carbonate, then filtered and purified. Controlled the mass ratios of D_4 to DVMS, vinyl terminated polysiloxanes of different molecular weights were obtained.

2.3. Synthesis of organosilicon-modified polyacrylate emulsion

PDMEMA emulsion was prepared by pre-emulsion semi-continuous mini-emulsion polymerization, shown in Scheme 2. 1.16 g SDS, 0.77 g O-10, 0.77 g V-20S and 0.8 g NMA were dissolved in 92 g deionized water. 22 g EHA, 18 g MMA, 0.6 g AA, 2.2 g of HD and a certain amount ViPDMSVi_n were mixed together in another beaker. The solutions in two beakers were mixed and emulsified for 30 min. Ultrasonic emulsification for 20 min. 1/3 mini-emulsion and APS solution were added into four-neck flask equipped with a stirrer and a condensation tube. The mini-emulsion was heated to 78 °C until the appearance of blue light, and then heated to 80 °C. The residual 2/3 mini-emulsion and APS solution were dropwise added into four-neck flask within 2 h. After reaction for another 1 h, the emulsion was cooled down and pH value was regulated to 7–8 by ammonia. When the monomer conversion reached 95%, PDMEMA was obtained.

2.4. Preparation of polymer binder film

Polymer binder emulsion was put into the polyfluortetraethylene plate to solidify into film at room temperature. Drying and then baking as selected. Finally, the film was balanced at $20 \pm 1\text{ }^\circ\text{C}$ 65 \pm 2% RH for 24 h.

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