Preparation of Nano-SiO_2/Silicone Color Deepening Agent for Polyester Fabric Finishing

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It is well known that there are so many advantages of polyester fiber over other fibers. But the effect of color deepening for polyester is worse than the others due to its crystallinity and smooth surface[1]. Polyester reflects most of light which shines on it and only a little is absorbed by the dyed inner fiber so that polyester fabric could not obtain better black or color deepening effect [1]. As the development of polyester microfiber, this defect turns more obviously [2]. In order to solve the problem, overabundant does of dyestuff were used although it comes to no avail [2, 3]. Moreover, polyester fabric was treated via alkali deweighting finishing to obtain rough surface and increased diffuse reflection, which would elevate color deepening. But this method has an important limitation that is loss in strength [1, 4]. Recently, more and more researchers and manufactories applied silicone to finish polyester fabric in order to form a film with low refractive index on surface [5-9]. Nowadays, much attention have been paid to nanomaterials because nanomaterials have more superior properties, such as mechanical, thermal, optical and processability [10-12]. Therefore, modified nano-SiO_2 together with silicone was used to prepare color deepening agent and the color deepening effect was studied through finishing polyester fabric.

1. EXPERIMENTAL

Material and agent

Samples of black fabric made with 100% polyester microfiber, supplied by Jishan dyeing factory were used. Aminopropyltrimethoxy silane was supplied by Jingzhou Jianghan Fine Chemical Co.,Ltd. The sample of nanometer SiO_2 powder in size 40 nm was purchased from Zibo Hina Hi-tech Material Co.,Ltd. Silicone was provided by Dalian Xinyuan Chemical Technology Co.,Ltd. Acetic acid and ethanol were obtained from Shenyang Lianbang agent factory, and were chemical grade reagents. Other chemicals were of reagent grade.

Instrument

Scanning electron microscopy JSM-6460LV was made by Japan Electron Company. Laser particle analyzer zetasize 3000HSA was produced by The British MALVERN Instrument Company. UV spectrophotometry instrument LAMBDA 35 and FTIR Spectrum One-B were provided from The American PerkinElmer Instrument Co.,Ltd. Color difference meter ADCI-60-C was produced by Beijing Chengtaike Instrument Co.,Ltd.

Modification of nano-SiO_2

Nano-SiO_2 was modified for better dispersibility. Aminopropyltrimethoxy silane (5% weight of the powder) was added into ethanol/water mixer solution (V_{water} : $V_{ethanol}$ =1 : 5) in the pH range of 3～5 (adjusted by acetic acid) and hydrolyzed 30 min at 60 ℃, then the powder was put into the solution and stirred by electric stirrer for 2 h at 60 ℃. Finally, modified nano- SiO_2 were washed and dried.

Preparation of silicone emulsion

Amino silicone (240 g), polysilicate (10 g), dimethyl silicone (60 g) and polyethoylated alkylphenol (30 g) were blended together with water(30 g) by electric stirrer and stirred till phase inversion happened. After that, more.water(630 g) was added. Uniform emulsion was obtained with further stirring.

Finishing of polyester fabric

Different dark-coloring processes were conducted to finish polyester microfiber fabric in order to study and compare the effect of the color deepening agent.

Process1—silicone emulsion

The fabric was finished through padding silicone emulsion at concentrations of 1, 3, 5, 7, 10, 15 wt%. respectively. The finishing liquor to fabric ratio was 40 : 1. The curing conditions of 140 ℃ and 3 min was used.

Process 2−nano-SiO_2/silicone

Modified nano-SiO_2 were added into silicone emulsion at the optimum concentration in process 1,

and the dosage of modified nano-SiO_2 was selected based on fabric weight 0.1, 0.3, 0.5, 0.7, 0.9, 1.1 %o.w.f. respectively. The fabric was treated by modified nano-SiO_2/silicone dispersed by ultrasonic generator for 10 min. The finishing experiment was the same as process 1.

Process 3–two step system

First, fabric was padded with acrylic resin 3 wt%. liquor blended with modified nanometer SiO_2 which was dispersed by ultrasonic generator for 10 min and the dosage of SiO_2 based on the result of process 2. The liquor to fabric was 40∶1 and the fabric was curing at 120 ℃ for 3 min. Second, the fabric was padded with silicone emulsion and curing at 140 ℃ for 3 min.

Testing

FTIR was used to characterize nanometer SiO_2. The modification of SiO_2 was checked.The grafted groups on nano-SiO_2 were studied.

Dispersibility of modified nanometer SiO_2 was measured by UV spectrophotometry. The method employed was as followed: adding 0.05 g samples into 100 mL water, ultrasonic dispersing for 10 min and standing for 48 h, taking 10 mL clear solution from up liquor. The absorbance (A) of the clear solution was measured at 604 nm. The larger value A is, the better the dispersibility is .

SEM was used to observe dispersion of powder on fabric which has been finished by color deepening agent blended with nano-SiO_2.

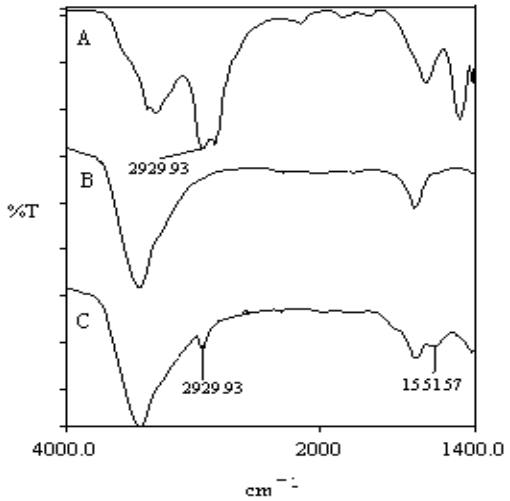
Size distribution of silicone emulsion and sioicone/ SiO_2 emulsion were measured by Laser particle analyzer, respectively. Analysis condition: temperature25.0;viscosity0.890cps;angle90.0°.

The value L^* of fabric was measured by color difference meter with illuminant D65 and it was defined as dark degree on fabric surface by CIE. The lower value L^* is , the darker the color is.

2. RESULTS AND DISCUSSION

2.1The effect of modified nanometer SiO_2

IR spectra of unmodified nano-SiO_2, modified nano-SiO_2 and hydrolyzed aminopropyltrimethoxy silane were shown in Figure 1. The spectra of unmodified nano-SiO_2, modified nano-SiO_2 were quite similar, differing mainly by the presence of peaks nearly at 1551.57 cm^{-1} and 2929.93 cm^{-1} in the spectra of A due to the symmetric deformation vibrated of —NH_3^+ and stretching vibrated of ⩾CH, They were the groups of coupling agent and appeared in IR spectra of nano-SiO_2. Thus, it is confirmed that the nano-SiO_2 powder was modified.



A: hydrolyzed aminopropyltrimethoxy silane

B: unmodified SiO_2 C: modified SiO_2

Fig. 1. IR Spectra of Modified Materials

2.2 Dispersibility of modified nanometer SiO_2

Five samples of modified and unmodified nano-SiO_2 were taken to measure absorbance respectively. The result was shown in table 1,and it indicated that the dispersibility of nano-SiO_2 had been improved remarkably after modification.The reason of this effect was that the active groups of coupling agent reacted with hydroxides were of nano-SiO_2 and formed connecting bridges so that the amino group were of coupling agent with positive charges in the acid solution outward on fabric surface. Because of the repulsion of the same charges, the nano-SiO_2 powders were not able to aggregate and dispersed well. While common nano-SiO_2 had high surface energy due to the large specific surface area and tended to agglomerate, which affected the dispersibility of the nano-SiO_2 powder.

Table 1 Absorbance of clear solution

	UNMODIFIED	MODIFIED
1	0.027	0.055
2	0.019	0.067
3	0.023	0.052
4	0.021	0.073
5	0.014	0.041
Average	0.021	0.576

SEM was taken to observe the surface of nano-SiO_2/ organic film and estimate the dispersion of modified nano-SiO_2 in the color deepening agent system. The modified nano-SiO_2 were dispersed uniformly in figure 2 due to the fact that nanometer SiO_2 were modified with aminopropyltrimethoxy silane which have NH_3^+ groups when they were in

solution pH＜7, and mutual exclusion for each other for homogeneous electric charges and uniform disperse in the emulsion. But the unmodified were aggregated as shown in figure 3 resulting from their high surface energy and large specific area.

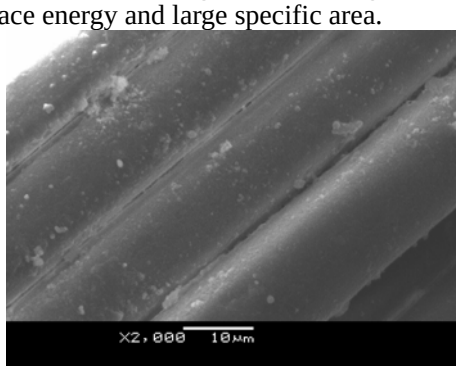


Fig. 2. SEM of modified SiO_2/silicone dark-coloring treated fabric

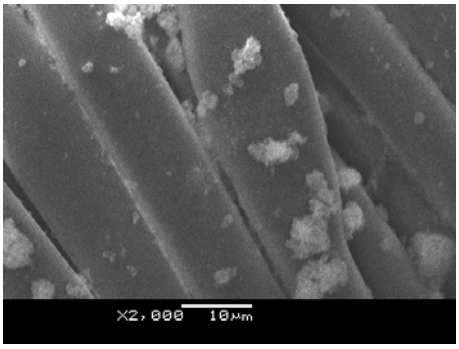


Fig. 3. SEM of unmodified SiO_2/silicone dark-coloring treated fabric

2.3 Size distribution of nano-SiO_2/silicone emulsion

The size distribution of nano-SiO_2 /silicone emulsion are shown in Fig. 4 and Fig. 5, and the data are shown in table 2 and table 3, respectively. In table 2, the peak of emulsion size was shown at 78.8 nm, and the range of size distribution was in 41.5 nm~145.9 nm. And in table 3, the peak emulsion size shown at 37.2 nm, the range of size distribution was in 20.9 nm~62.7 nm. It could be considered that modified nano-SiO_2/silicone emulsion can be increase the dispersibility in solution, and good than unmodified emulsion. It is known that the dispersibility of nano-SiO_2 had been improved remarkably after modification due to the modified nano-SiO_2 has good affinity with silicone, this affinity leads to the considerable dispersibility of nano-SiO_2 modified.

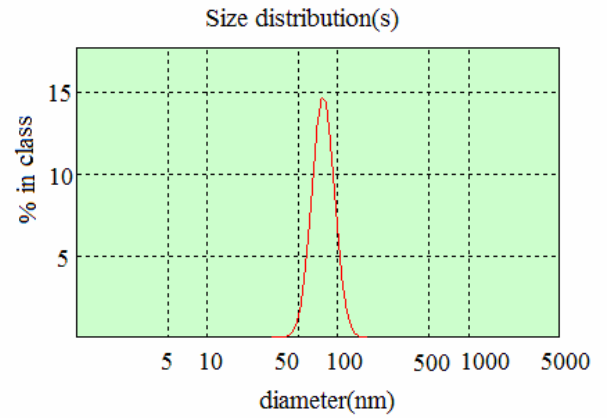


Fig. 4. Size distribution of unmodified nano-SiO_2/silicone emulsion

Table 2 Data of size distribution of unmodified nano-SiO_2/silicone emulsion

Size (nm)	% instensity	Size (nm)	% instensity	Size (nm)	% instensity
30.9	0.0	55.8	3.9	100.8	6.0
33.2	0.0	60.1	6.7	108.5	3.4
35.8	0.0	64.7	10.0	116.9	1.7
38.5	0.0	69.6	13.0	125.8	0.7
41.5	0.1	75.0	14.7	135.5	0.3
44.7	0.3	80.7	14.5	145.9	0.1
48.1	0.9	86.9	12.4	157.1	0.0
51.8	2.0	93.6	9.3	169.2	0.0

Peak: Mean 78.8 width 36.9

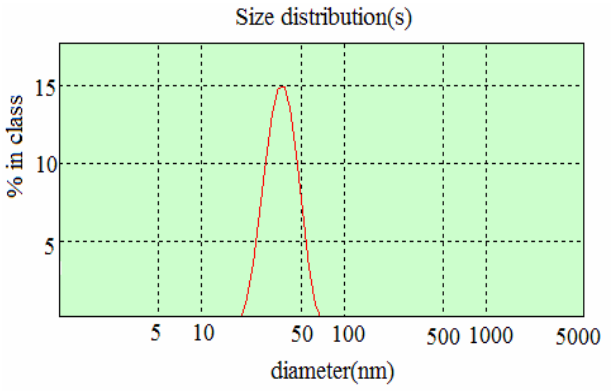


Fig. 5. Size distribution of modified nano-SiO_2/silicone emulsion

Table 3 Data of size distribution of modified nano-SiO_2/silicone emulsion

Size (nm)	% instensity	Size (nm)	% instensity	Size (nm)	% instensity
11.4	0.0	25.5	6.8	56.8	3.4
12.6	0.0	28.2	10.2	62.7	0.9
14.0	0.0	31.1	13.0	69.3	0.0
15.4	0.0	34.4	14.8	76.6	0.0
17.1	0.0	38.0	15.0	84.7	0.0
18.9	0.0	42.0	13.5	93.6	0.0
20.9	1.3	46.5	10.6	103.5	0.0
23.1	3.6	51.3	6.9	114.4	0.0

Peak: Mean 37.2 width 24.5

2.4 The effect of dark-coloring

2.4.1 Relationship between concentration of silicone emulsion and L^* of fabrics

The relationship between concentration of silicone emulsion and L^* was shown in Figure 6. The value L^* was decreased as the concentration of silicone emulsion was increased, but lose velocity at steady rate when the concentration was above 5 wt%. because the fabric was saturated and the better dark-coloring effect could not be obtained at higher concentration of silicone emulsion.

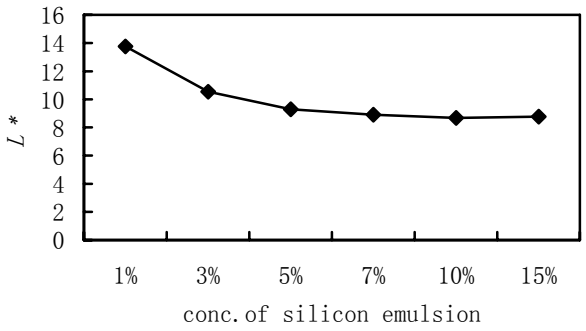


Fig. 6. Relation between concentration of silicone emulsion and L^* of fabrics

2.4.2 Relation between dosage of modified nanometer SiO_2 and L^* of fabrics

The relationship between dosage of modified nanometer SiO_2 and L^* of fabrics was indicated in figure 7. When the dosage between 0.1 %o.w.f and 0.5 %o.w.f, the L^* value was decreasing, but the value L^* increased with dosage over 0.5 %o.w.f. Because large dosage into emulsion caused blooming and the phenomenon would be serious as the dosage increased. So the optimal dosage was selected at 0.5 %o.w.f. nano-SiO_2 powder.

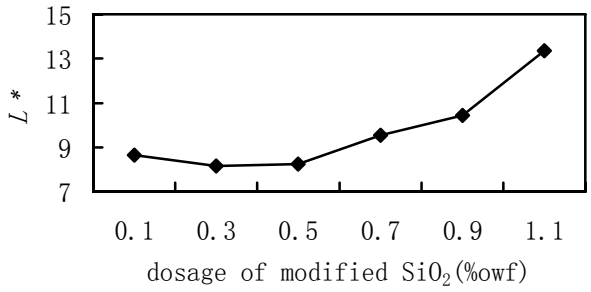


Fig. 7. Relation between dosage of modified nanometer SiO_2 and L^* of fabrics

2.4.3 Relation between process and L^* of fabrics

In figure 8, the value L^* of blank sample was larger than any other samples which were finished by process 1, 2 and 3 mentioned before. The sample finished by process 3 presented the best dark-coloring effect and achieved the lowest L^* of 7.32. While the blank sample's L^* was 14.24 which was nearly twice as large as process 3's. Two film layers which both had different low refrangibility were formed on fabrics in figure 9. Incident light was refracted twice through the two film layers on the surface of fabric to increase the absorbance of light. A rough surface on the fabric was formed by the nano-SiO_2 powder in the first layer and increased diffuse reflection. Therefore, the best dark-coloring effect was achieved.

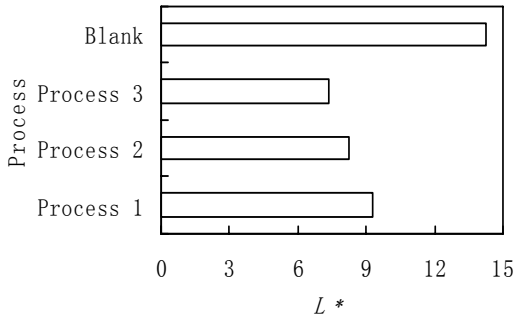


Fig. 8. Relation between process and L^* of fabrics

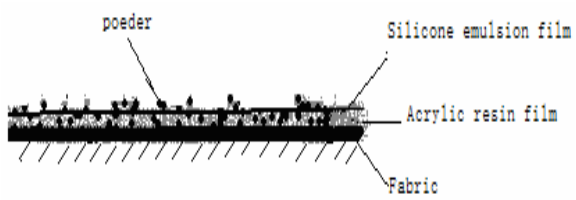


Fig. 9. Chart for mechanism of two steps double films dark-coloring effect.

3. CONCLUSIONS

The result of this study indicated that the dispersibility of nano-SiO_2 modified by aminopropyltrimethoxy silane was improved significantly, and were even able to disperse in acrylic resin uniformly and formed a roughness film on fabric. Polyester microfiber fabric was dark-coloring finished via two step process. The second low refrangible silicone emulsion film layer was formed over the first rough layer which was made of acrylic resin and modified nan-SiO_2 on fabric. This two step process showed remarkable dark-coloring effect. The optimal dark-coloring condition was found at 3wt% acrylic resin and 0.5 %o.w.f. modified nano-SiO_2 as the first finishing bath and treating fabric by padding and curing at 120 ℃ for 3 min, and then finishing the fabric with 5 wt% silicone emulsion as the second bath and curing at 140 ℃ also for 3 min.

4. REFERENCES

[1] CHEN Jiakui, YU Zhaoxiang. Review of technique about deep-dying of superfine polyester fiber [J]. *Chemical Fiber & Textile Technology*, 2005, (1): 35-37.

[2] Wang Chaoxia, Zhao Yunguo. Shade darking effect of resins on fine denier dyed polyester [J] *Journal of Qingdao University*, 1999, (1): 29-31.

[3] Xie Hongde. Preparation and application study of deep dyeing promoter [J].*Textile auxiliaries*, 2004, (1): 26-29.

[4] Mei Yujiao, Li Liping, Lv Shijing. Studied on microfiber dyeing [J]. *Shanghai textile science & technology*, 2000, (2): 42-45.

[5] Guo Zhenliang, Meng Yanfeng. Synthesis and use of built-up agent YSG for dyeing cellulosic fibers [J].*Dyeing auxiliaries,* 2001, 18 (2) : 23-24.

[6] YAMANE KOICHI, IKEDA REIKO. Darkening agent for colored solid and darking: Japan, JP 9256280 [P]. 1997-09-30

[7] ZEZU SACHIKO, OSAWA YOSHITO. Color-deepening agent for synthetic fiber: Japan, JP11081147 [P]. 1999-03-26.

[8] KATO TADAHIKO, SAITO YOSHITAKA. Deepening agent for colored fiber and method for deepening color of fiber using the agent: Japan, JP2001288683 [P].2001- 10 -19.

[9] ARIMOTO SADAO. Color deepening agent and method for color deepening processing: Japan, JP2002285475 [P]. 2002-10-03.

[10] Ji Xiaoli, Zheng Caihua, Wei Lei. Study on surface modif ication of sil icone carbide powders with aminoorganosilanes [J].*Chemistry & Bioenginee ring*, 2008, (1): 21-23.

[11] Tang Guohu, Ye Qiaoming, Lian Hongfang. Current research progress in inorganic nanosize powder surface modification [J]. *China textile leader,* 2003, (17): 33-35.

[12] Zhang Jusheng1 , Qian Juan1 , Liu Zhigang. In-situ coating process and disperse property studies of nanometer titanium dioxide prepared by hydrothermal synthesis [J].*Materials science & Technology,* 2006, (5): 495-498.

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