

Effect of Poly (Sodium P-Styrenesulfonate) on Anti-Sedimentation of Wollastonite and its Application in Textile Coating

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Abstract. Aiming at the problems of the low stability and easy deposition of the coating slurry when wollastonite was used as a filler in the wet coating of polyamide. Effect of poly (sodium p-styrene sulfonate) (PSS) on the static stability and rheological properties of coating slurry was studied. The surface structure of the coating film, the mechanical properties, the antistatic properties of the coated fabric and ink absorption and color fastness to water after printing were analyzed. The results show that, the stability of the coating slurry is remarkably improved when the amount of PSS added is 10%, and the sedimentation does not occur within 12 hours; the rheological property is better and the surface of coating film has more microporous, and the distribution is more uniform inducing the improvement of ink absorption. The adverse effect of PSS on mechanical properties is not significant, the antistatic property of the coated fabric is greatly improved, and the grade of colour fastness to washing of the printing textiles is 4 or more.

1. Introduction

In early 1980s, the trademark fabric began to be produced by polyamide wet coating technology. The wet coating of the polyamide is a novel process that covers the surface of fabric with polymer membrane, which transfers and agglutinates in solidification process from slurry that generates by dissolving the waste polyamide with calcium chloride and methanol solvent and adds some fillers. The formation of a layer of polymer coating film on fabric gives the fabric pretty printing performance[1], excellent wear resistance[2,3], elasticity and handle[4,5]. In textile coating, the most common fillers, including water talc, mica, kaolin, calcium carbonate, aluminium silicate and wollastonite etc, have a great influence on the stability, viscosity and rheological properties of the coating slurry and fabric style[6,7]. The study found that the rheological properties of coating slurry is excellent, the coating film is smooth and flat with uniform microporous distributing, ink absorption is good, whiteness and colour fastness to washing of coated fabric is good as well when wollastonite was used as a filler in the wet coating of polyamide. However, it has greatly influence on the product quality because of the low stability and easy deposition of the coating slurry.

Poly (sodium p-styrenesulfonate) (PSS) is a water-based polymer with pale amber liquid, odourless and soluble in water. It has high stability and is not easy to be used for the settlement of slurry made of PSS [8-10]. So it often is used to make reactive emulsifier, coagulant, semiconductor, heat conduction products, etc. It should be used in coating slurry that not only can improve the static stability of slurry,



and the rheological properties of the antistatic properties because the PSS molecule contains a hydrophilic anionic sulfonic acid groups that increases the prepared solution conductivity [11, 12]. So, this paper focuses on the static stability and rheological properties of the coating slurry, the surface structure and the mechanical properties of the coating film, the antistatic properties and the colour fastness to washing of the coated fabric when wollastonite was used as a filler in the wet coating of polyamide, and discusses the effect of PSS on wollastonite anti-settling performance and the properties of the wet coating of polyamide.

2. Experimental

2.1. Materials and Drugs

Absolute methanol (analytical grade) and poly(sodium p-styrenesulfonate) (technical grade) were purchased from Hangzhou Jing Jing Fine Chemical Co., Ltd. Anhydrous calcium chloride (analytical grade) and recycled polyamide 6 (technical grade) were supplied by Huzhou Xinli label belt Co., Ltd. Wollastonite (5 μ m) was purchased from Shanggao County Huagui science and Technology Co., Ltd.

2.2. Experimental Method

2.2.1. Coating slurry formula

Drugs	Waste polyamide 6	Anhydrous calcium chloride	Absolute methanol	Wollastonite	Poly(sodium p-styrenesulfonate)
Weight(g)	16	35	100	22	X

2.2.2. *Preparation of Polyamide Coated Slurry.* Mixing 22 g wollastonite with PSS solution at 250 mL three flasks at room temperature in methanol as solvent, stirring at high speed. After 30 min, the mixed solution was heated to 65 °C, slowly adding calcium chloride until the reaction was complete. Taking 16 g polyamide 6 waste silk, and cut into pieces, slowly added to the mixed liquor to dissolve. Starting to mix high-speed when waste nylon was dissolved completed. After 1 hour, the water bath decreased from 65 °C to room temperature, then removed the spare.

2.2.3. *Preparation of Coating Film.* According to the preparation method of coating film in the [4] literature, the specifications of glass plate fixed on the level is 10 cm * 10 cm. The 4 layer (0.16 mm of the total thickness) parallel transparent tape were pasted on the glass plate on both sides of the fixed spacing as the top coating slurry take a certain amount of 7 cm. A certain amount of polyamide coated slurry is uniformly applied to the top of the glass plate and the glass plate is tilted 30 degrees slowly into the water bath. After waiting for 5 min, the completely solidified coating film was taken out and solidified and set at 100 °C in the electro-thermal constant temperature blower drying box.

2.2.4. *Preparation of Coated Fabric.* The polyamide 6 fabrics were coated in both sides. Then putting the coated fabric slowly into 25 °C water bath to solidify. Taking out after 3 min, it was put into a continuous stretch setting machine and solidified at 160 °C for 90 s.

3. Results and Discussion

3.1. Properties of Coating Slurry

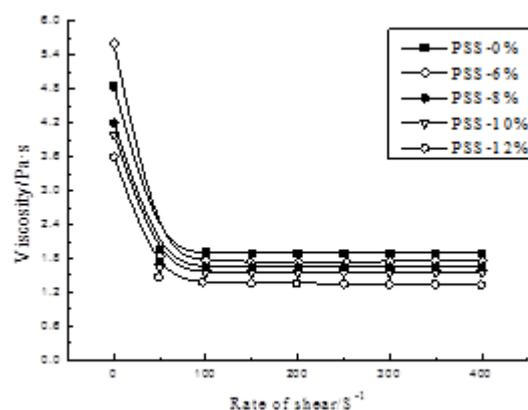
3.1.1. *The static Stability of Coated Slurry.* The compatibility evaluation method is rod drop, and the standard is the bottom precipitate height of the samples of coating slurry in a certain time. After a lot of experiments found that the amount of PSS accounted for 6-12% of wollastonite weight on the static stability of coating paste effect is obvious. Considering the actual production cost, the final selection of 0%, 6%, 8%, 10%, 12% and numbering respectively sample 1, sample 2, sample 3, sample 4 and sample 5. The results are shown in table 1 with the effects of PSS dosage on the static stability of polyamide coating slurry.

Table 1. Effect of PSS on the static stability of coating slurry

Coating-slurry placement time /h	Paste settlement height /mm				
	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
12	6	4	3	0	0
24	12	7	5	3	0
48	18	10	8	5	8
72	25	14	12	9	7

As can be seen from table 1, PSS can significantly improve the static stability of polyamide 6 coating slurry. With increasing PSS content in the coating slurry, the static stability of the coating slurry was increased gradually. When the content of wollastonite quality accounted for 10%, coating slurry did not occur within 12 hours and sedimentation height was 3 mm after 24 h. Compared with no adding, coating slurry sedimentation height was 12 mm after 24 h. The static stability of coating slurry was improved, which can ensure the coating processing better and the stability of product quality. Its anti-settling mechanism: on the one hand, PSS was easily adsorbed on the inorganic filler surface. The structure of the network was cross-linked with each other, so that the thickness of the adsorbed film on the inorganic filler surface was increased, and the steric hindrance was increased. Therefore, the particles did not agglomerate easily. On the other hand, PSS molecule chain contains many sulfonate groups, which can improve the surface potential of inorganic filler particles. The particles were uniformly dispersed in the system to avoid agglomeration between particles, thereby improving the compatibility of the inorganic filler in the coating slurry.

3.1.2. Rheological Properties of Coating Slurry. The viscosity of the coating slurry was measured by MCR52 type rotational rheometer at the shear rate range of 0-400 S^{-1} , at a temperature of 25 $^{\circ}C$. The rheological curve of coating slurry under different dosage of PSS was determined. The result was shown in figure 1.

**Figure 1.** Effect of PSS on the rheological behavior of slurry

It can be seen from the figure 1, the viscosity of polyamide 6 coating slurry decreases with the increase of shear rate in different amount of PSS. The viscosity decreases drastically at low shear rate. At a higher shear rate, the decrease of the size of the polyamide coating slurry is small, and it shows a steady trend, which is manifested as a plastic fluid. When the shear rate is constant, coating slurry viscosity gradually decreases with the increase of PSS dosage. It indicates that an increase of the amount of PSS is beneficial to the improvement of coating slurry rheological properties. When the amount of PSS in the range of 12%, the adsorption of wollastonite on the surface of PSS is more easily

cross-linked and forms a stable network structure with the increase of the amount of PSS. When coating slurry is sheared cut by other forces, network structure between wollastonite particles can be destroyed, wrapped in the internal of methanol will be released. So the apparent viscosity of the slurry decreases with the resistance movement of particles. The rheological properties of the slurry are improved.

3.2. Analysis of Pss Dosage and Viscosity of Coating Slurry

The viscosity of polyamide coated slurry was tested by MCR52 rotational rheometer. In the process of coating, the coating slurry viscosity is too small, will make the slurry infiltration and casting etc. When the viscosity of coating slurry is too large, it spreads unevenly and the amount of coating is less. So the viscosity of coating slurry is one of the key factors to prepare polyamide coated fabrics with excellent properties. This paper tested the viscosity of coating slurry after preparation for 2 hours, and analysed the influence of the amount of PSS on the viscosity of coating slurry. The results were shown in Figure 2.

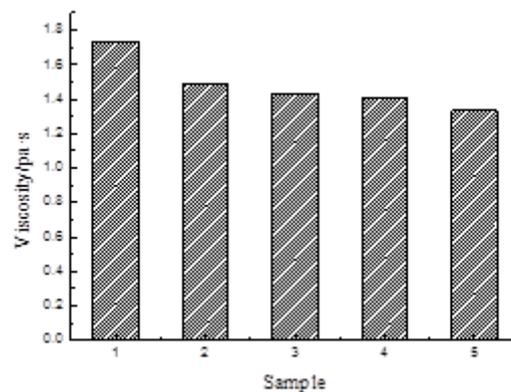


Figure 2. Effect of PSS additive on viscosity of slurry

We can see from Figure 2 that the coating slurry viscosity gradually decreased with the increase of PSS contents, which is due to many hydrophilic groups of PSS. When it is adsorbed on the surface of wollastonite particles, PSS can increase the hydrophilicity of the particle surface, so that the surface tension of the particles was significantly improved. On the other hand, when PSS adsorb on the surface of wollastonite particles, adsorption film will form a certain thickness. When subjected to an external force, the resistance between the particles became smaller, so that the apparent viscosity of coating slurry is reduced. From the figure it can be seen that, when PSS was added to the sample 5, the coating slurry viscosity is 1.34 Pa s. When the viscosity is low, the coating is easy to permeate, and the coated fabric is thin. Therefore, it is recommended that the amount of PSS be added no more than sample No.5.

In conclusion, when the content of PSS was sample No.4, the static stability of polyamide coating slurry and the rheological properties are good. It is not easy to settle, and the viscosity was more suitable for wet coating. It can better ensure the stability of the quality of coating products. Therefore, the amount of PSS is determinate to sample No. 4 and further studies the wet coating film and polyamide fabric performance

3.3. Properties of Polyamide Coating Films

3.3.1. Mechanical Properties of Coating Film. In accordance with the GB/T 1040.3--2006<The Determination of Tensile Properties>of Plastic film and sheeting of "by the HF-9007s type universal material testing machine. According to the experiment, the polyamide coating film was prepared and

the stress-strain curve of polyamide 6 coating film was tested. The influence of PSS on the mechanical properties of the coating film was investigated. The results are shown in Table 2 and Figure 3

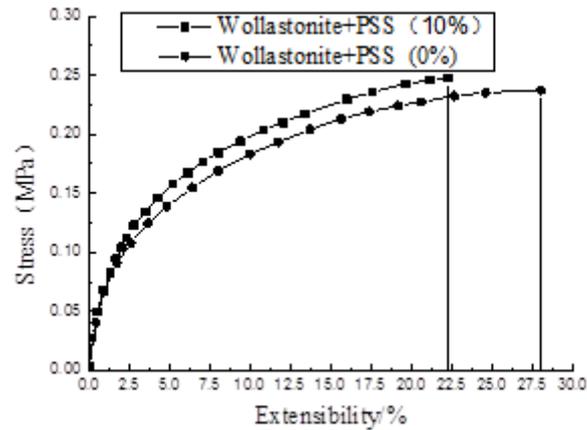


Figure 3. Effect of PSS on the mechanical properties of coating film

Table 2. Effect of PSS on the mechanical properties of coating film

PSS/%	Breaking stress /MPa	Elongation at break /%	Initial elastic modulus/ MPa
0	0.23	28.6	0.059
10	0.24	22.2	0.065

It can be seen from table 2 and figure 3: the elongation at break of the coating film without PSS reached 28.5% and the fracture stress was 0.23 MPa. The elongation at break of the coating film with PSS addition was 22.2%, which decreased slightly compared with that without addition. But the fracture stress had little difference, which was 0.24 MPa. This showed that PSS would slightly reduce the flexibility of the coating film. It was possible that the addition of PSS results in a decrease in the degree of entanglement between the flexible chains of polyamide 6 and the molecules in the coating. There, the elongation at break of the coating film is slightly decreased. As can be seen from the diagram, the initial elastic modulus of the two coating films were relatively small. The coating film was soft. Therefore, the wear of the trademark fabric is very small in the subsequent cutting process, and it is more suitable for enterprise production.

3.3.2. Surface Structure of Coating Film. The contact angle of polyamide 6 coating film was tested by DSA-20 video contact angle tension tester. The surface structure of PA6 coating was observed by scanning electron microscope (SEM), and the influence of PSS on the surface structure of the coating film was investigated. The result was shown in Figure 4.

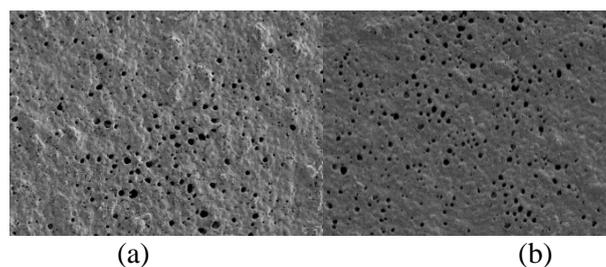


Figure 4. SEM surface structure of polyamide coating film (a) f wollastonite coating without PSS ($\times 1000$) (b) wollastonite coating film containing PSS-10% ($\times 1000$)

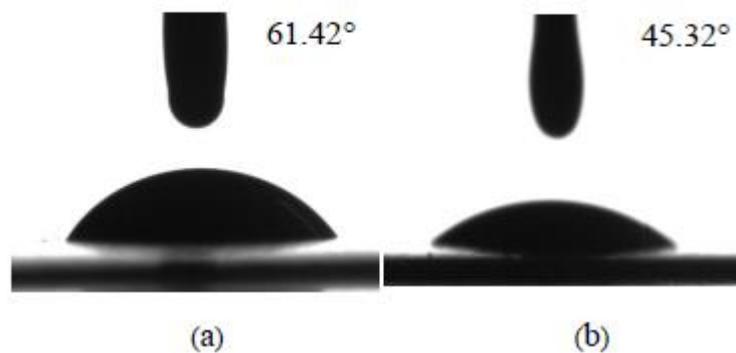


Figure 5. Contact angle of coating film (a) Coating film without PSS (b) Coating film without PSS-10%

It can be found from figure 4 and figure 5: the wollastonite coating film has more microporous structure on the surface than without PSS. The distribution was uniform and the pore size was larger. The average size of the contact angle was decreased from 61.42 ° to 45.32 °. It is indicated that adding PSS in the polyamide coating slurry is beneficial to increase the microporous structure of the coating film surface. The formation of a large number of microporous structure led to the increase of the specific surface area of the coating film. Therefore, it was advantageous to adsorb and fix the ink on the surface during flexography. The ink absorption rate of the coating film was improved, and the ink can be quickly fixed to prevent seepage. It is indicated that the addition of PSS in the coating slurry is beneficial to improve the ink absorption of the coating film.

3.4. Antistatic Properties and Color Fastness of Coated Fabrics

The colour fastness to washing of coated fabrics was tested in accordance with GB/T 3920 - 2008< Textiles - Tests for colour fastness - Colour fastness to soaping>. And the antistatic property was investigated by this method. In the constant temperature and humidity room (at the temperature of 20 °C, relative humidity of 35%), the coated fabric was set 4 h, and then tested electrostatic voltage peak and half-life. Each sample was tested three times, and took its average value. The results were shown in Table 3.

Table 3. Effect of PSS on antistatic properties and color fastness of coated fabrics

PSS /%	Peak electrostatic voltage /V	half-life period /s	The colour fastness to washing/grade		
			Staining (Original sample)	Staining (Polyester)	Staining (Nylon)
0	1030	1206	4-5	5	4-5
10	684	1.93	4-5	5	4-5

Table 3 shows: The electrostatic voltage and half-life of the fabrics coated with PSS were significantly decreased than coated fabric without PSS added. It showed that PSS can obviously improve the antistatic property of polyamide coated fabric and reduce the static electricity produced when the trademark fabric is cut. The reason is that PSS belongs to hydrophilic polymers with better moisture absorption and electrical conductivity. And it has good compatibility with polyamide coating slurry. When the coated fabric is prepared by blending PSS with the coating slurry, a continuous film with a three-dimensional network structure can be formed on the surface of the coated fabric. It is easy to absorb moisture in air and increase the conductivity of coated fabrics. At the same time, PSS

macromolecular chains penetrate through the polymer to form conductive channels, which can improve the antistatic properties of coated fabrics. It also can be seen from table 3, PSS has no effect on the colour fastness to water washing of printed fabrics. All of them can reach 4 or more, and meet the requirements of trademark products.

4. Conclusion

(1) By studying the effect of PSS on the properties of polyamide coating slurry, it was found that PSS can improve the compatibility of wollastonite filler in coating slurry. When the dosage of PSS is 10% of the quality of wollastonite, the stability and rheological properties of the coating slurry were better, and the viscosity was more suitable for wet coating.

(2) The study of stress-strain of coating film showed that the elongation at break of the coating film was decreased when PSS was added. The elongation at break of coating film reached 28.5% without adding PSS, and the elongation at break of coating film decreased to 22.2%. But it could meet the requirements of trademark fabric coating process. Meanwhile, the surface of the coating film containing PSS had a large number of microporous structure. The distribution was uniform and contact angle decrease to 45.32°, which was beneficial to the improvement of ink absorption.

(3) By studying the effect of PSS on the properties of polyamide coated fabrics, it was found that PSS can improve the antistatic properties of coated fabrics. It did not affect the colour fastness to washing of printing coated fabrics, and achieved grade 4 and above.

5. Acknowledgements

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6. References

- [1] Nobuyuki Tanaka. Possibility of porosity control in nylon-6 membranes [J], *Polymer*, 1995, 36(13): 2597-2601.
- [2] Y Y Chen, J H Zheng and Y Guo. Preparation of nylon 6 waste silk coating slurry and properties of its coating film [J]. *Journal of Zhejiang Sci-Tech University*, 2013, 30(6):830-833.
- [3] T Li, Y L Du and H Y Li. Effect of inorganic fillers on properties of polyamide wet-coating trademark fabrics [J]. *Textile journals*, 2017, 38(3):119-125
- [4] H H Zhi, J H Zheng and Y H Pan. Study on the application of black colorant in wet coating [J]. *Journal of Zhejiang Sci-Tech University*, 2015, 33(1):20-25
- [5] Y L Du, H H Zhi and L Zhang. Study on the preparation of black wet coating trademark cloth [J]. *Modern textile technology*, 2015, (3):21-25
- [6] X Y Zou. Study on the property of PA6/kaolin composite[D]. Qingdao University of Science & Technology, 2010:3-30
- [7] L LYu. Effect of fillers, heat stabilizers and carbon black on properties of PVC paste [J]. *Modern Plastics Processing and Applications*, 2006, 18(5):31-34
- [8] Y J Ding, F Gao and Y X Li. Influence of polymer molecular weight sodium p-styrene sulfonate additive on the properties of coal water slurry [J]. *Journal of fuel chemistry*, 2006, 34(3):298-302
- [9] Z Y Miao, G G Wu and L Y Zhang. Study on the effect of sulfonation degree of sodium polystyrene sulfonate on the performance of coal water slurry [J]. *Coal Engineering*, 2010, 1(12):101-103
- [10] X C Wang, G G Wu and G Y Wang. Additives of coal water slurry and its research progress [J]. *Coal Chemical Industry*, 2004, 32(6):15-18
- [11] X R Wang, S Z Wu and J Q Zhao. Effect of sodium polystyrene sulfonate on the performance of electrostatic PET resin [J]. *Plastics Industry*, 2008, 36(4):20-22
- [12] X P Ouyang, C M Tan and X Q Qiu. Synthesis of water-soluble styrene styrene sulfonate copolymer and dispersion stability research [J]. *Journal of Chemical Engineering*, 2010, 24(4):681-687