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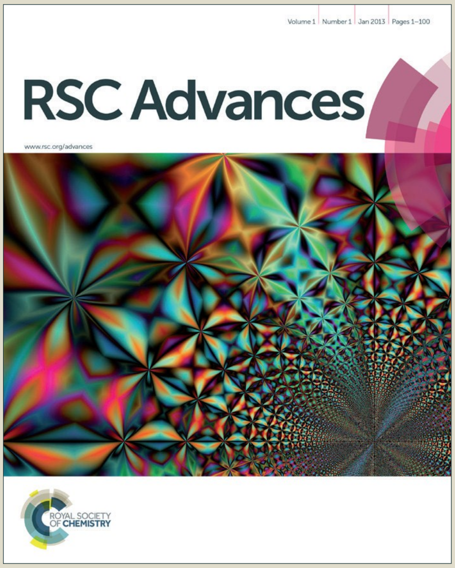

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Paper

Etherification to improve the performance of lignosulfonate as dye dispersant

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Lignosulfonates (SL) is widely used as dye dispersant. However, there are some disadvantages including poor high temperature dispersibility and sevre fiber staining resulted from the abundant of phenolic hydroxyl content in SL molecules. In this work, etherified lignosulfonate (ESLs) was obtained by using epichorohydrin to reduce the content of phenolic hydroxyl while increase the molecular weight. ESLs with lighter color can reduce 52% of fiber staining rate, which was whited by epichorohydrin process. The lower adsorption capacity of ESLs onto fiber surface can facilitate to decrease the fiber staining effect, owing to the reduction of phenolic hydroxyl content. ESLs also exhibits more excellent high temperature stability because of the higher adsorption capacity and more rigid adsorption film than that of SL.

Introduction

Lignosulfonate (SL) is a by-product in pulping and paper industry, usually recovered from sulfite or bisulfite pulping waste. It can also be obtained by the introduction of sulfonic acid groups into alkali lignin from kraft or sulfate pulping process. Lignin is commonly considered to be a three dimensional amorphous polymer composed of three phenylpropane units. They are guaiacyl (G), syringyl (S) and hydroxy-phenyl (H). Besides hydrophobic groups, SL have many hydrophilic groups, including sulfonic, phenolic hydroxyl, alcoholic hydroxyl,[1] with which have the advantage in polymer surfactant.[2] Because of its favorable wettability, adsorptivity, dispersibility and other properties of colloidal, SL is applied in various industries, such as cement water reducing agent,[3] pesticide dispersant,[4] CWS dispersant,[5] fuel cell membrane[6] and dye dispersant.[7]

Nowadays, anionic surfactants play a main role in dye dispersants, especially lignosulfonates (SL) and naphthalene sulfonates (NS) from the petroleum industry.[8] NS, derived from fossil resource, has less fiber staining and good dispersibility on dye but is expensive and toxic. However, SL which is the main component in waste liquid from paper pulping are abundant, renewable, economical and environmentally friendly. Therefore, the dosage of SL used in dye dispersant is increasing year by year. Whereas, there is a number of disadvantages in employing SL as dye dispersants such as fiber staining and poor dispersive ability[9,10]which limits its application in dye industry, especially when they are employed in the dyeing process requiring better performance. A lot of researches have revealed that the fiber staining rate is greatly dependent on the phenolic hydroxyl groups in SL,[11,12] which can form hydrogen bonds with electronegative groups in fiber.[13] Therefore, an adequate modification method is necessary for reducing the phenolic hydroxyl content of SL.

At present, the methods to reduce phenolic hydroxyl content include oxidation, chelation with divalent metal salt and other chemical reactions. Falkehag[14] treated SL with 2-chloroethanol, and the product lessened the fiber staining. A two-step process was also introduced to block the phenolic hydroxyl groups in the lignin followed by oxidation with chlorine dioxide and a light-colour lignin azo dye dispersant was abtained.[15] By reacting divalent metal salts with lignin through chelation and ester formation mechanism, the dihydroxyl groups in lignin were reduced thereby the fiber staining was weankened.[16]

Etherification by epichlorohydrin is also a useful way to block the phenolic hydroxyl group in lignin molecular. Recently, by epoxidation with epichlorohydrin and then etherification with polyethylene glycol, alkaline lignin was converted into water-soluble lignin derivates which can enhance enzymatic hydrolysis efficiency and ethanol fermentation. However, the molecular weight of the product was barely changed. [17] So in our present study, epichlorohydrin was used as cross linking agent via ring-opening reaction in aqueous solution to reduce the content of phenolic hydroxyl group as well as improve the molecular weight of SL molecular.

It has been reported that lowing the phenolic content might decrease the lignin's water solubility[18] and then cut down the dispersive ability and high temperature stability.[19] Compared with NS, SL have better high temperature stability, probably owing to the content of phenolic hydroxyl group in its molecule. Therefore, there is a contradiction between the influence of phenolic hydroxyl group on dispersive ability and

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on fiber staining. If reducing the phenolic hydroxyl content in order to lessen fiber staining, dispersive property may be deteriorate. So it is of great necessary to develop a method not only reducing the phenolic hydroxyl groups in lignin but also refraining from impairing the heat stability. It has been reported that high molecular weight of SL make great contribution to the dispersive ability and stability of particle,[20,21] so how to increase the molecular weight and reduce the phenolic hydroxyl content simultaneously become the key factor for improving the dispersive ability together with weakening the fiber staining. Fiber staining and dispersive ability of dye suspension are also related to the adsorption characteristic of SL on fiber and dye. Quartz crystal microbalance with dissipation (QCM-D) is a new technique to detect the adsorption characteristic of dispersants on solid/liquid interface by measuring the change of third overtone of the frequency shift (Δf) and dissipation shift (ΔD). The largest $|\Delta f|$ means the more the adsorption amount of dispersant on chip. ΔD is related to the viscoelastic property of film on quartz chip. The smaller ΔD indicates the stronger the density and rigidity of film.[22] The absolute value of the slope of $|\Delta D/\Delta f|$ reflects the firm level of the adsorption structure. The adsorption structure becomes solid with the increase of the $|\Delta D/\Delta f|$ value. However, the application of QCM-D in revealing the mechanism of absorption of SL in dye process is not yet reported widely. So in previous work, we had developed a method by using QCM-D and atomic force microscopy (AFM) to study the absorption characteristic of SL onto fiber and dye surface.[23]

In this paper, SL was modified with epichlorohydrin by etherification to reduce the content of phenolic hydroxyl group together with increasing the molecular weight. ESLs with different phenolic hydroxyl content are obtained by adjusting pH and adding different amount of epichlorohydrin. The influence of phenolic hydroxyl content and molecular weight on the properties of dye liquor was investigated by determining the fiber staining rate and particle size of dye. The absorption characteristics of ESLs on fiber and dye particle surface were further discussed through QCM and AFM.

Experimental

Materials

Dispersant Lignosufonates (SL) is a by-product from aspen wood sulfite pulping, supplied by Shixian Paper Making Co. Ltd., Jilin, China, which is composed of 70wt% of SL, 11wt% of reductive substances and other materials, including sugar acids, organic compounds and inorganic salts.

Sodium naphthalene sulfonic acid formaldehyde condensation (SNF) (Shangyu Wencai Co., Zhengjiang, China) is a commercial dispersant used for dye dispersion and its purity was more than 90%.

UtrazinbneNa (UNA) (Borregaard Co., Sarpsborg, Norway) is a widely used dispersant lignosulfonates which was purified by ultrafiltration and its purity was 95%, with lesser amount of inorganic salts.

C.I. disperse blue 79 is an azo dye, supplied by Runtu Co. Ltd., Zhejiang, China. Folin Ciocalteau's phenol reagent (2mol/L), vanillin and poly (diallyldimethylammonium chloride) (PDAC, Mw of 200,000–350,000, 20 % solution) are supplied by Sigma-Aldrich (Xuhui District, Shanghai, China).

Etherification of SL

30wt% of SL solution is prepared and pH is adjusted to 10.8 or 12.0 with NaOH solution. When it is heated to 90℃, epichlorohydrin is added dropwise by peristaltic pump. After 3h, the etherified SL (ESL) is obtained. Four samples with different etherification degree are selected to further study, named as ESL-15, ESL-36, ESL-45 and ESL-81 and the etherification degree are 15%, 36%, 45% and 81% respectively.

Structure characteristic of dispersant

Phenolic hydroxyl content (Ph-OH content). Ph-OH content of dispersant is determined by FC method.[24] Dispersant is prepared to a 600 mg/L aqueous solution with distilled water. 1mL of the dispersant solution is transferred into a 25mL volumetric flask, to which 1.5 mL of the FC-reagent and 15 mL of distilled water are added and mixed thoroughly. After 8 min, 5 mL of 20% (w/v) Na_2CO_3 aqueous solution and 2.5 mL distilled water are added. The mixture is stirred for 2 h at 30 °C, and the absorbance is measured at 760 nm by UV-Vis spectroscopy (UV-2450, Shimadzu Corp., Japan). The procedure was performed in duplicate, and a SL free sample is used as reference throughout the entire procedure. Vanillin is used as standard and a vanillin-free sample is used as reference.

Determination of molecular weight. The molecular weight (M_w) of dispersant is measured by aqueous gel permeation chromatography (GPC) with a Waters 2487 Dual Absorbance Detector and a Waters 1515 Isocratic HPLP pump. The chromatographic columns are consisted of UltrahydragelTM120 and UltrahydragelTM250 in series. A 0.1mol•L^{-1} $NaNO_3$ solution (pH=10.3) is used as mobile phase and the velocity is 0.50 mL•min^{-1}. Polystyrene sulfonates are used as standard for calibration. The dispersant solution is prepared with distilled water and filtered by a 0.22 μm filter.

Determination of surface charge. The dispersant is prepared to a 0.2g•L^{-1} aqueous solution and pH is adjusted to 5.2. PDAC used as standard is prepared to a 0.1mmol/L aqueous solution. The surface charge is measured by particle charge detector (PCD03, Mütek Corp., Germany).

Determination of color of dispersants. The dispersant is prepared to a 2 g•L^{-1} aqueous solution and pH is adjusted to 5.2, and the absorbance at 450 nm (A_{450}) is measured by UV-Vis spectroscopy (UV-2450, Shimadzu Corp., Japan) to represent the color of dispersant.[19]

UV spectra. The dispersant is prepared to a 2 g•L^{-1} aqueous solution and pH is adjusted to 5.2. The UV spectra is scanned in a wavelength range of 420~470 nm by UV-Vis spectroscopy (UV-2450, Shimadzu Corp., Japan).

Structure characteristic of dispersant

Preparation of dye slurry. The dispersant is mixed with C.I. disperse blue 79, distilled water and 5mm agate beads according to the mass ratio of 1:1:4.67:20 and pH is adjusted to 5.5 with acetic acid. A 30 wt% dye slurry is obtained by ball-milling at a milling rate of 400 r / min for 8 h.

Dyeing process. The dyeing process is conducted in a high-temperature program-controlled dyeing machine (GRY-12, Quanrun Machinery Co. Ltd., Wuxi, China), which starts at 30℃, increases to 130°C at the speed of 3°C •min^{-1} and keeps for 30min, and then decreases to 85°C.

Staining of dispersant on fiber. The fiber staining of dispersant is evaluated by measuring a *K/S* value of stained fiber by Datacolor colour photometer instrument (Dataclolor 110, Datacolor Corp., USA).The dispersant is prepared to a 2 g•L^{-1} aqueous solution 250mL, and pH is adjusted to 5.2. 2 g of polyester fiber is added into the solution and treated in the high-temperature program-controlled dyeing machine according to the dyeing process. After 130℃ dyeing process, the fiber is washed with running water and dried. The relation between fiber staining rate and *K/S* is as follows.

$K/S = (1-R^2)/2R$；

Then the staining rate is calculated using the follow equation.

Fiber staining rate/%=$[(R_0-R_i)]/R_0 \times 100$；

Where *K* is the absorption coefficient; *S* is the scattering coefficient; *R* is the reflectivity; and *K/S* is the apparent color depth value. R_0 is the reflectivity of the unstained fiber at 450 nm, R_i is the reflectivity of the stained fiber with dispersant at 450nm.

Dispersibility and heat stability of dye. The dye slurry is prepared to a 0.4 g•L^{-1} suspension 250 ml with distilled water. The particle size distribution is measured by a laser particle analyzer (Malvern 2000, Malvern Corp., England) to determine the dispersive ability of dye. Subsequently, the remaining suspension is placed in the high-temperature program-controlled dyeing machine and treated according to the dyeing process. The particle size distribution of the suspension treated at high temperature is measured to determine the heat stability of dye.

Adsorption of dispersants on dye and fiber

Preparation of solution. The dispersant is prepared to a 0.5g/L aqueous solution and pH is adjusted to 5.2. NaCl is added into the solution and its concentration is 0.5mol/L. Dye dissolves in acetone to prepared a 1 g•L^{-1} solution. Fiber dissolves in the mixture of chlorobenzene and phenol (the mass ratio is 1:1) to prepared a 10 g•L^{-1} solution.

Spin-coating. The dye solution and fiber solution are spin-coated on 5 MHz-AT cut sensor crystals with Au coatings by a spin coater (MSC 650Mz-23NPP/OND, MYCRO Corp., America), respectively. The spin-coating program is as follow: a speed of 3000 rmp are applied for 10 s, a speed of 5000 rmp keeps for 30s and then a speed of 1000 rmp lasts for 10s.

Adsorption characteristic measurements. The adsorption characteristic (the frequency *f* and the dissipation *D*) of dispersant on dye and fiber are detected by QCM-D (Q-Sense E1, Q-Sense Corp., Finland). In the measurements, the cell is initially washed with distilled water until a stable baseline is established and the cell are temperature-stabilized at 20°C. The dispersant solution is used as mobile phase and the velocity is 0.15 mL•min-1. The third overtone is used in the data valuation.

Atomic Force Microscopy (AFM). The dye and fiber surfaces with dispersant after being washed by distilled water for 5min are imaged with AFM ((Nanoscope V, Multimode SPM, Veeco Corp.).

Results and discussion

Effect of etherification on Ph-OH and *Mw*

It is demonstrated that the dispersive ability of surfactant is greatly affected by the molecular weight.[25] The previous study has shown that lignosufonate with medium molecular weight has favorable dispersive ability and high temperature stability. Lignosulfonate with high molecular weight display stronger steric hindrance and will prevent the dye particle aggregating while those with low molecular weight can absorb on dye particle easily but provide weaker steric hindrance.[26] The fouling of lignin onto fiber is mainly produced by the darkened colour and the hydrogen bonding force between the phenolic hydroxyl and the carboxyl of lignin and the amide bond of fiber. Meanwhile, lignosulfonate with high molecular weight contains less phenolic carboxyl and phenolic hydroxyl than those with lower molecular weight so it has less fiber staining.[5] Hence, it is necessary to improve the molecular weight of lignosulfonate together with reducing the content of phenolic hydroxyl in the sake of superior dispersive ability and weaker fiber staining.

A series of ESLs were prepared by modification with epichlorohydrin. The structure characteristics of ESLs depend on the adding amount of ECH and the value of pH. By adjusting the amount of epichlorohydrin added at pH=10.8 and 12.0, ESLs with different molecular weight were prepared. The Ph-OH content and mass average of molecular weight (M_w) are shown in Fig.1. With the increase of adding amount of epichlorohydrin and the value of pH, the Ph-OH content decreases and the M_w increases gradually. When pH=12.0, the Ph-OH content and M_w change more significantly with increasing adding amount of epichlorohydrin from 0.5 to 2.5 mmol/g. The degree of change is described by the degree of etherification and polymerization and can be calculated as follows:

$$\text{degree of etherification} = \frac{C_i - C_0}{C_0} \times 100\%$$

$$\text{degree of polymerization} = \frac{Mw(ESL)}{Mw(SL)}$$

Where C_I is the Ph-OH content of ESLs, C_0 is the Ph-OH content of SL, M_w(ESL) is the mass average of molecular weight of ESLS, M_w(SL) is the mass average of molecular weight of SL.

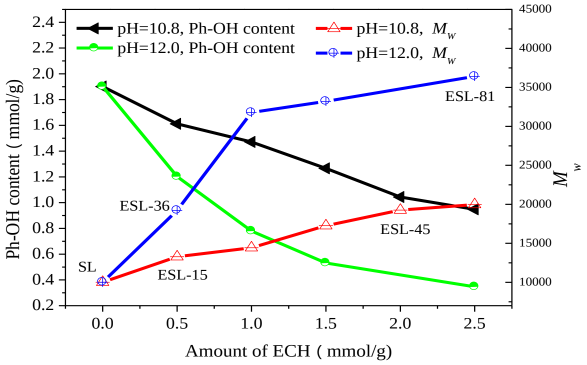

Fig.1 Ph-OH content and M_w of ESL

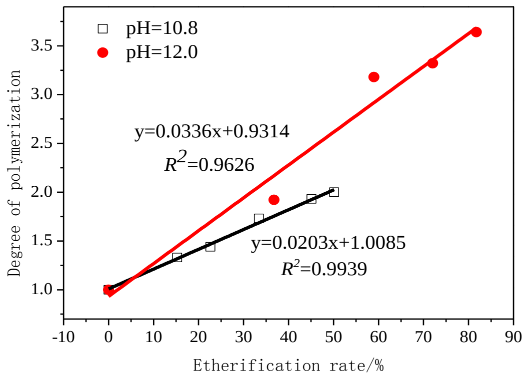

Fig.2 The relationship between phenolic hydroxyl content and Mw of ESLs

The fitting relationships between the degree of etherification and polymerization are shown in Fig.2, where *y* is degree of polymerization and *x* is etherification degree and the slope reflects the degree of change. When pH=10.8, the equation is y=0.0203x+1.0085, R^2=0.9939 and when pH=12.0, the equation is y=0.0336x+0.9314, R^2=0.9626. With the increasing etherification rate, the degree of polymerization increases more obviously at pH=12.0 than that at pH=10.8, which indicated that in high pH condition, SL molecular was easier to link together by epichorohydrin.

It is suspected that there exist two ways in the etherification reaction between lignin and epichlorohydrin, as shown in Fig. 3. Therefore, it is supposed that when a relatively small amount of epichlorohydrin is added or in lower pH, product (2) is mainly obtained and the molecular weight changes slightly after reaction; when increasing the adding amount ofepichlorohydrin or in higher pH, product (1) is predominately and the molecular weight increases obviously.

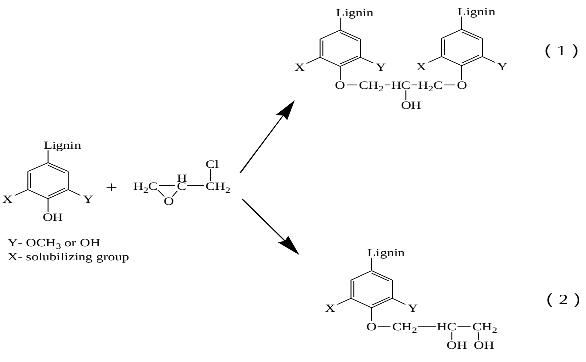

Fig.3 Reaction between lignosulfonate and epichlorohydrin

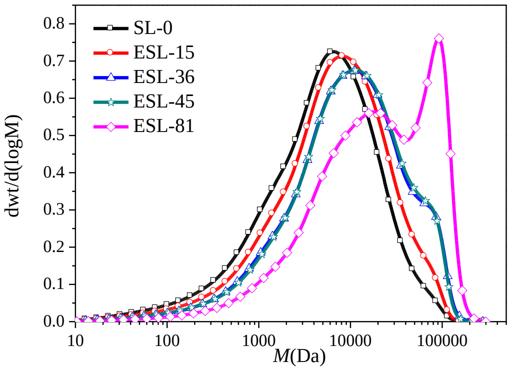

Fig.4 Molecular weight distribution of ESL

The molecular weight distributions are shown in Fig.4. The M_w, the numerical average of molecular weight (M_n), and the polydispersibility index (M_w/M_n) as well as functional group content are given in Table 1. With increasing etherification degree from 15% to 45%, the molecular weight of increased from 13,285 Da to 19,261 Da and was all much than that of SL. The polydispersibility index decreased with increasing etherification degree, indicating the smaller molecular weight lignin was linked together by epichlorohydrin. As it is known to us that the solubility and hydrophilic would be too weak to severs as dye dispersant when the molecular weight of lignosulfonate was too high,[27] so ESL-81 will not be discussed later.

UV spectra

The benzene ring structure and chromophoric groups in SL, absorbed UV light strongly are considered to be characteristic absorption peaks. The one at 210 nm are related to the unsaturated chains while that at 280 nm correspond to unconjugated Ph-OH groups and the aromatic moiety of the lignin molecule.[28] Conjugated structure and hydrogen bond of SL are regarded as the key factors to the UV absorption spectrum. The UV spectra of SL and ESL-45 are represented in Fig.5. Compared with SL, the UV absorption spectra of ESL-45 shows blue shift and the peaks appear at 204 nm and 275 nm and the absorbance decrease. This spectroscopic blue shift at 210 nm indicates that the intensity of conjugated structure in SL reduce. With regard to the absorption peak at 280nm, the spectroscopic blue shift illustrates the content of Ph-OH on the benzene ring decreases, that is, the etherification was successfully carried out.

Table. 1 Molecular weight data, functional groups and surface charge of dispersants

Samples	M_w(Da)	M_n(Da)	M_w/ M_n	Ph-OH content (mmol/g)	Surface charge (eq/Kg)
SL	10001	5264	1.90	1.90	1.07
ESL-15	13285	8252	1.61	1.61	1.02
ESL-36	19227	16023	1.20	1.20	0.95
ESL-45	19261	18520	1.04	1.04	0.89
UNA	10250	4780	2.14	0.71	-
SNF	8050	3180	2.53	0.42	-

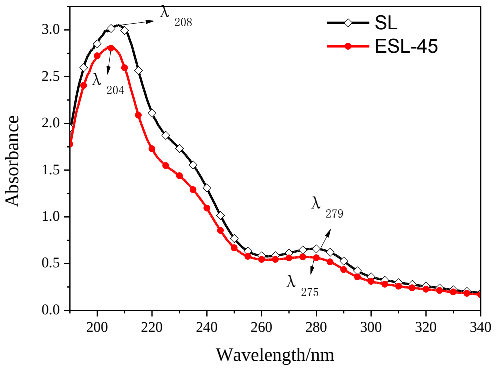

Fig.5 UV spectra of SL and ESL-45（0.1g/L，pH=5.2）

The performance of ESL in fiber staining and dispersive ability

As shown in Fig. 6(a), with increasing etherification degree, fiber staining rate decreases gradually. At 25℃, the particle sizes of dye are all less than 0.6 μ m and rarely changed. However, after 130℃ high-temperature treating, the particle size of dye decreases significantly as the etherification rate increased as Fig. 6(b) shown.

It is considerable that fiber staining of SL depends on the color of SL and the adsorption characteristic of SL on fiber surface and internal, whilst the dispersive ability and heat stability of dye is related to the adsorption characteristic of SL on dye.

Quinoid structure of SL is the key cause of colour, as well as some chromophore and auxochrome groups, such as double bond, carboxyl group, carbonyl group and hydroxyl group.[29] It is stated that the quinoid structure and chromophore groups can account for the significant UV absorption at 450 nm (A_{450}). All A_{450} of ESLs are less than SL which is believed to be the result of the reduced Ph-OH content, except ESL-36. This is because in base condition, catechol structure of SL will be oxidized to quinone structure, resulting in dark colour. With increasing etherification degree, more phenolic hydroxyl groups are blocked, which inhibits the formation of quinoid structure and leads to light colour. ESL-36 is obtained at pH=12.0, and the adding amount of ECH is 0.5mmol/g in the etherification process. Thus the quinoid structure is extremely easy to be produced, leading to dark colour consequently. The A_{450} of UNA and SNF are all less than SL, thus they exhibit lower fiber staining than SL. After etherification, on the one hand, the colour of lignin is lighter, on the other hand, the phenolic hydroxyl contents declined significantly from 1.90 mmol•g-1 to 1.04 mmol•g-1 which can distinctly lessen the hydrogen bond force between dispersants and fiber. What's more, the molecular weight also increased as the etherification degree increased. SL with low Mw was supposed to embed into the fiber interspace more easily especially during high temperature dying process because the fiber has more pores. Thus, the fiber staining rate reduce to close to UNA when the etherification degree was increased. Compared with SL, the particle size of dye with ESLs decrease essentially at 130°C, while it slightly change in the case of 25°C. According to the Table.1, with the increase of etherification degree, the molecular weight increase from 10,001 Da to 19,261 Da. It is considered that SL with high M_w provided enough steric hindrance which can break agglomeration of dye particle and maintain its stability. The M_w of ESL-45 molecular is much more than those of UNA (M_w=10250) and SNF (M_w=8050), so it exhibits much better high temperature dispersive ability and stability especially than SNF.

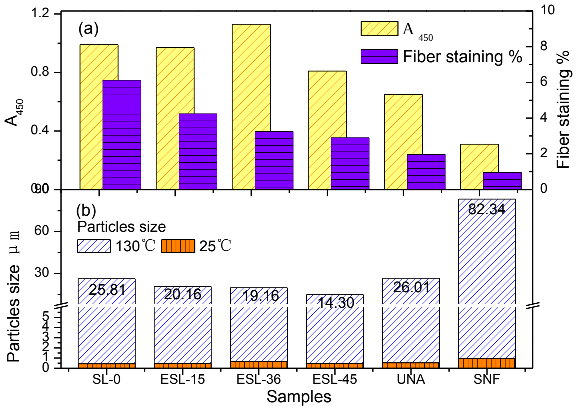

Fig.6 Effect of dispersant on fiber staining (a) and particles size of the dye bath at 25 and 130 °C (b)

In summary, ESL-45 has superior performance both in fiber staining and high temperature stability since its proper molecular weight and low amount of phenolic hydroxyl group. As what is supposed above, the performance of dispersant is mainly resulted from its adsorption characteristic on fiber and dye, so it is of great importance of finding a visual method to measure the absorption characteristic to verify the station above further more.

Adsorption characteristic of dispersants on fiber

The adsorption characteristic of dispersants on fiber surface is detected by QCM-D, but that into fiber internal still can't be measured. The higher value of $|\Delta f|$ means the larger amount of absorption, the steeper $|\Delta D/\Delta f|$ value reflects the conformation of the absorption layer is softer and more viscoelasity. On the contrary, the smaller slope value represents the absorption layer is a rigid and homogeneous structure. As it is shown in Fig. 7, for ESLs, the value of $|\Delta f|$ are of fiber surface decreases. Moreover, all the value of $|\Delta D/\Delta f|$ are slightly greater than SL, which means the adsorbed layer on fiber surface is a softer and vicous layer compared with SL, that is, the absorption layer is easier to wash out of the fiber surface. Etherification reduces the Ph-OH content, thereby lessening the hydrogen bonding, so the adsorption amount of ESLs are less than SL.

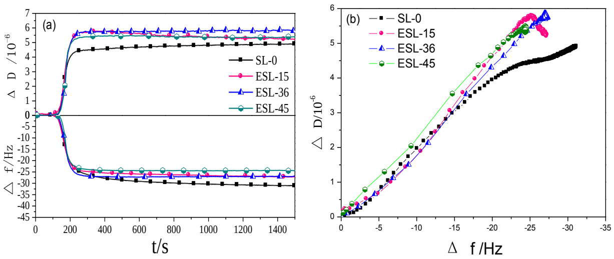

Fig.7 Adsorption characteristics of dispersant on fiber surface

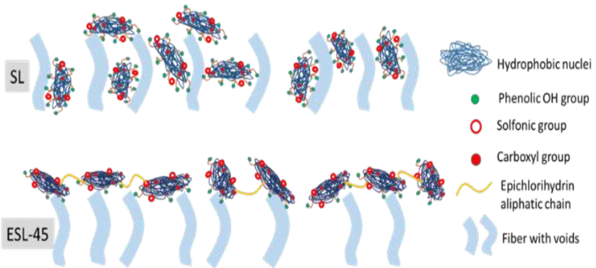

Fig.8 Adsorption models of SL and ESL-45 on fiber

The adsorption characteristic of SL on fiber internal is mainly related to M_w. During dying process, the fiber was expanded and there appeared many pores. SL with low M_w is easier to diffuse inside the fiber voids and can't be washed away easily, while that with high M_w can't easily enter the fiber due to steric hindrance.[26, 30] After etherification, the M_w of SL increases as a result of crosslink, which leads to less fiber staining. According to the description above, the adsorption model of dispersants on fiber was drawn in Fig. 8.

The adsorption characteristic of dispersant on dye

As shown in Fig. 9, with the increase of etherification degree, the value of $|\triangle f|$ increase gradually, indicating that the adsorption amount of dispersants on dye increase. Furthermore, the value of $|\varDelta D/\varDelta f|$ decreases with the increasing etherification degree, which further stated that the conformation of absorption film becomes rigid and homogenous. As the AFM image given in Fig.10, after etherification, the absorption film has lower roughness and become more homogenous. The adsorption characteristic of dispersant on dye mainly depends on steric hindrance[31] and hydrophobic interaction. After etherification, M_w of dispersant increases, leading to the significant increase of steric hindrance between dispersant and dye, so that the adsorption amount increases and a thick, viscous layer formed compared with SL.

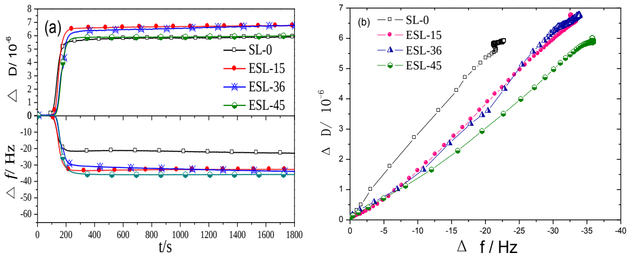

Fig.9 Adsorption charateristic of dispersant on dye

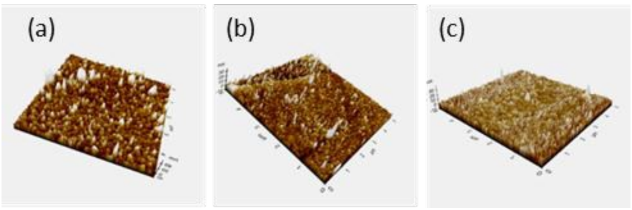

Fig. 10 AFM image of dispersant on dye (a) SL, (b) ESL-15, (c) ESL-45

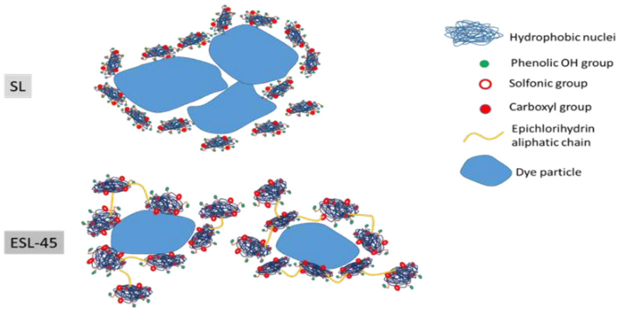

Fig.11 Adsorption models of SL and ESL-45 on dye surface

The surface charge of dispersants is shown in Table 1. The surface charge decreases from 1.07 eq/kg to 0.80 eq/kg with increasing etherification degree, which means the hydrophilic property of ESLs weakens. This is because Ph-OH content of ESL decreases after etherification. In addition, ESLs molecules conformation become curling due to the increase of M_w, making some charged groups, including sulfonic group, carboxyl group and Ph-OH wrapped in the molecule internal.[32]

Therefore, when the dye suspension is placed in a high temperature condition, the particles are easily to assemble. Hence, dispersant with optimum molecular weight has favorable performance. In accordance with the description above, the adsorption model of SL and ESL-45 on dye particles was illustrated in Fig.11. Compared with SL, ESL-45 has higher M_w and lower phenolic hydroxyl groups content, thereby it can strongly adsorb on the dye surface by hydrophobic effect. In addition, with higher M_w, the 3-D molecular of ESL-45 is more flexible and curly which can break the agglomeration of dye particles by steric hindrance.

Conclusions

A series of ESLs with different Ph-OH content and molecular weight ware prepared by adjusting the dosage of ECH and value of pH. After etherification, the ESLs samples, especially ESL-45, with proper molecular weight and content of phenolic hydroxyl group exhibit superior performance on fiber staining and high temperature property.

With the increasing of etherification degree, for one thing, the adsorption capacity of ESLs on fiber surface decreases due to the hydrogen bond force declined gradually. So, the fiber staining became weaker with the increasing in M_w of ESLs. For another thing, the adsorption amount of ESLs on dye increased and the adsorption structure became denser because of the hydrophobic interaction between ESLs and dye enhanced. Consequently, the high temperature stability improves significantly.

Acknowledgements

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Notes and references

1 X. P. Ouyang, X. Q. Qiu, and P. Chen, *Colloids. Surf., A*, 2006, **489**, 282-283.
2 M. S. Zhou, W. L. Wang, D. J. Dong and X. Q. Qiu, *RSC Adv.*, 2015, **5**, 2441-2448.
3 L. H. Grierson, J. C. Knight and R. Maharaj, *Cem. Concr. Res.* 2005, 35(4), 631-636.
4 Z. P. Li, Y. X. Pang, Y. Y. Ge and X. Q. Qiu, X, *J. Ind. Eng. Chem*., 2012, **18(1)**, 532-537.
5 D. J. Yang, X. Q. Qiu, M. S. Zhou and H. M. Lou, Energy. Convers. Manage, 2007, **48(9)**, 2433-2438.
6 X. Zhang, A. Glüsen and G. Ricard, *J. Membr. Sci.*, 2006, 276**(1-2)**, 301-307.
7 P. Dilling, G. S. Samaranayake and S. L. Waldrop, US5972047, 1999.
8 P. Dilling, US5980589. 1999.
9 P. Dilling, US4486346. 1984.
10 P. Dilling, US551151. 1985.
11 S. I. Falkehag, US3763139. 1973.
12 H. L. Hintz, US3769272. 1973.
13 G. Telysheva, T. Dizhbite, A. Kizima, A. Volpertsl and E. Lazareva, *Recent Advances in Environmentally Compatible Polymers,* England: Woodhead Publishing Ltd, 2001, 167-172.
14 S. I. Falkehag, H. H. Moorer and C. W. Bailey, US3672817, 1972.
15 P. Dilling and P. T. Sarjeant, US4454066. 1984.
16 P. Dilling, P and G. Prazak, US4355996. 1982.
17 C. Z. Chen, M. Q. Zhu, M. F. Li, Y. M. Fang and R. C. Sun, *Biothenol. Biofuels*, 2016, **9(87)**, DOI: 10.1186/s13068-016-0499-9.
18]Y. Qian, Y. H. Deng, H. Li and X. Q. Qiu, *Ind. Eng. Chem. Res.,* 2014, **53(24)**, 10024-10028.
19 S. Lin, US4184845, 1980.
20 Y. Y. Ge, Z. P. Li, Y. X. Pang and X. Q. Qiu, *Int. J. Biol. Macromol,* 2013, **52**, 300-304.
21 Y. X. Pang, W. Gao, H. M. Lou and X. Q. Qiu, *Colloids Surf. A*, 2014, **441**, 664-668.
22 M. Norgren, L. Gärdlund, S. M. Notley and L. Wågberg, *Langmuir,* 2007, **23(7)**, 3737-3743.
23 Y. L. Qin, X. Q. Qiu, W. S. Liang and D. J. Yang, *Ind. Eng. Chem. Res.*, 2015, **54(49)**, 12313-12319.
24 R. J. A. Gosselink, A. Abächerli, H. Semke, R. Malherbe, P. Käuper, A. Nadif and J. E. G. Van Dam, *Ind. Crops Prod.*, 2004, **19(3)**, 271-281.
25 X. L. Lin, M. S. Zhou, S. Y. Wang, H. M. Lou, D. J. Yang and X. Q. Qiu, *ACS Sustainable Chem. Eng.,* 2014, **2(7)**, 1902-1909.
26 Y. L. Qin, D. J. Yang and X. Q. Qiu, *ACS Sustainable Chem. Eng.,* 2015, **3(12)**, 3239-3244.
27 H. Schott, *J. Pharm. Sci.*, 1995, **84(10)**, 1215-1222.
28 C. A. Lekelefac, N. Busse, M. Herrenbauer and P. Czermak, *Int J Photoenergy*, 2014, **501**, 137634.
29 F. Imsgard, S. I. Falkehag and K. P. Kringstad, *Tappi Tech Ass Pulp Pap Indus.*, 1971, **54(10)**, 1680-1684.
30 D. J. Yang, H. J. Li, Y. L. Qin, R. S. Zhong, M. X. Bai and X. Q. Qiu, *J. Dispersion Sci. Technol.*, 2015, **36**, 532~539.
31 Y. L. Qin, W. M. Mo, L. X. Yu, D. J. Yang and X. Q. Qiu, *AHolzforschung*, 2015,DOI: 10.1515/hf-2015-0009.
32 Y. H. Deng, Y. Wu, Y. Qian, X. P. Ouyang, D. J. Yang and X. Q. Qiu*, BioResources*, 2010, **5(2)**, 1178-1196.

Graphical Abstract

After etherification, the Ph-OH content decreases and the molecular weight of ESLs samples increases which lead to high performance.