Preparation of Modified PVA Copolymer by DAAM/ADH and Cross-Linking Mechanism for Paper

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Abstract

Herein, a novel modified polyvinyl alcohol(DA-IPVA) used as sizing agent was prepared by using diacetone acrylamide(DAAM) as graft monomer and N-(isobutoxymethyl)acrylamide(IBMA) as self-cross-linking monomer. The effect of the amount of DAAM on the properties of emulsion, film and sizing paper was discussed. The surface micro-structure of the sizing paper was characterized by SEM and AFM. The addition of DAAM/ADH and IBMA endowed DA-IPVA with cross-linked active group and increased cross-linking density and hydrophobicity after ADH was added into the emulsion and the cross-linking structure was formed. The enhancing mechanism of surface sizing agent for paper was revealed. The DA-IPVA can be cross-linked on the surface and inside of the paper to form a dense network structure, which improves the bonding force between the fibers. When the mole fraction of DAAM of the cross-linking monomer is 8%, the surface sizing performance of the paper is obviously improved compared with the base paper. The dry and wet strength is increased by 266.5% and 334.3% respectively, and the folding resistance is increased 2946.67%. This study can have a profound impact on the development of the technology of cross-linking surface sizing agent for paper.

1 Introduction

Discarded plastic packaging is white garbage and resistant to degradation. Once dumped into the soil, it will not decay and will not form organic fertilizer, accompanied by harmful substances, causing serious pollution to the environment (Ali, et al. 2021; Xu et al. 2020; Song et al. 2022). As a result, plastic governance has been a global focus. After “plastic limit order” is upgraded, the test is the ability of plastic production enterprises to produce environmental protection, but also the need for new breakthrough plastic waste treatment technology to change the status quo (Vollmer et al. 2020). If from the alternative level to understand and in the case of plastic limit being upgraded, “paper instead of plastic” as a new choice for the market (Taj et al. 2021), the paper industry will usher in a period of explosive peak. With the environmental protection being more and more important and the shortage of forest resources, paper, which is mainly made of wood, is facing technological innovation. Developing a novel surface sizing agent for paper with low cost, better comprehensive performance and environmental friendly has important research significance and application value but remains a challenge (Ni et al. 2021; Choi et al. 2019; Ni et al. 2021; Wang et al. 2019; Kansal et al. 2020; Li et al. 2021; Wang et al. 2020). Polyvinyl alcohol(PVA) aqueous dispersion has the advantages of good adhesion, film forming and weather resistance. In line with the need of environmental protection, water was used as dispersion medium of PVA. Great progress has been made in the research of coatings, adhesives and inks, especially used as surface sizing agents with high physical strength and excellent fiber adhesion. PVA has been the key research directions of paper chemicals (Zhai et al. 2021; Xiang et al. 2020; Arandhara et al. 2020; Arab et al. 2021; Zhou et al. 2021; Zhang et al. 2019; Song et al. 2020; Yun et al. 2018).

Due to that PVA aqueous dispersion has the advantages of strong film-forming ability and controllable molecular structure, it is widely used in the field of surface sizing agent for paper-making. However, water resistance of PVA is poor because it contains a lot of hydroxyl groups and its mechanical strength is low,

which limits the further application of PVA (Zhang et al. 2020; Lee et al. 2019; Li et al. 2019; Ha et al. 2019; Mansoor et al. 2021; Yang et al. 2020; Mouro et al. 2019). N-(isobutoxymethyl)acrylamide (IBMA) as a self-cross-linking monomer can improve mechanical properties, adhesion and water resistance (Liu et al. 2001; Benjamin et al. 2017). Diacetone acrylamide (DAAM) is a new type of vinyl functional monomer with unique physical and chemical properties, which is widely used in various fields such as coatings, resins and textiles (Kessel et al. 2008; Zhang et al. 2012; Wang et al. 2010; Thongnuanchan et al. 2018). As an additive for waterborne coatings, it has excellent performance and price ratio in combination with adipic dihydrazide (ADH). As a modifier for waterborne coatings, it can increase the adhesion of the coating film, prevent the coating film from cracking with the change of temperature and make the coating not lose luster for a long time. When it was used as surface sizing agent, the keto-hydrazine reaction occurred and the cross-linking structure was formed inside the paper. Generally speaking, the strength and solvent resistance of the material are improved with the increase of polymerization degree. The high polymerization degree and alcoholysis degree leads to higher viscosity of sizing agent. The high viscosity of sizing solution seriously affect the penetration ability of the sizing solution and it is difficult to improve the strength of the paper. Introducing the IBMA into the main chain can destruct the hydrogen bond strength and decrease the viscosity and further improve the penetration ability of the sizing solution. And introducing DAAM containing active groups into the side chain can react with ADH in the dry process of sizing paper. This not only ensures that the sizing liquid can penetrate into the paper well, but also makes the sizing liquid cross-linked in the later stage, which is conducive to give full play to the sizing liquid to enhance the role of paper.

In this paper, a series of cross-linked polyvinyl alcohol emulsions modified by DAAM (DA-IPVA) was prepared by graft co-polymerization using ammonium ceric nitrate as initiator, DAAM as graft monomer and IBMA as self-cross-linking monomer. Then ADH was added into the obtained emulsions to be used as surface sizing agent and the cross-linking structure was formed. The effect of DAAM/ADH on the properties of emulsion and paper was discussed.

2 Experiments

2.1 Materials

Vinyl acetate (VAc) was supplied from Shanghai Shanpu Chemical Co., Ltd.. Azodiisobutyronitrile (AIBN) was obtained by Tianjin Damao Chemical Reagent Factory. Diacetone acrylamide (DAAM) and adipic dihydrazide (ADH) were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. Ammonium ceric nitrate was supplied by Guangdong Wengjiang Chemical Reagent Co., Ltd.. N-(isobutoxymethyl)acrylamide (IBMA) was purchased from Guangzhou Sanwang Chemical Materials Co., Ltd.. Methanol was supplied from Tianjin Tianli Chemical Reagent Co., Ltd.. Sodium hydroxide was obtained from Tianjin Northern Glass Purchase and Marketing Center. Base paper (kapok mixed pulp paper, quantitative is 72g/m^2) was supplied by Chengdu Jinding Safety Printing Co., Ltd.. All the reagents were analytical pure and the water used in the experiment was deionized water.

2.2 Experimental methods

2.2.1 Preparation of D-IPVA by solution polymerization

10 g VAc, 10 g IBMA, 0.5 g Azo diisobutyronitrile (AIBN) and 20 mL methanol were added into three-necked flask equipped with a reflux condenser, agitator and nitrogen duct. The reaction lasted three hours at 70°C. Then the reaction was terminated by 1 mL thiourea-ethanol solution. The obtained transparent sticky substance was labeled as PVAc-IBMA. In this manuscript, the polyvinyl alcohol as contrast sample made from pure vinyl acetate was named PVA.

PVA-IBMA was prepared by the alcoholysis PVAc-IBMA in methanol. The specific experimental steps referred to our published literature (Li et al. 2021).

10 g PVA-IBMA and 90 g deionized water were mixed, stirring at room temperature for 3 h and gradually heated to 90°C until the solid was completely dissolved. Then PVA-IBMA aqueous solution with a mass concentration of 10% was obtained. The pH of the liquid was adjusted to 4-5 and then 0.5g 50 w.t% cerium nitrate aqueous solution, DAAM in turn were added into the liquid. The reaction lasted for five hours. The dosage of DAAM was 2%, 4%, 6%, 8% and 10% relative to the molar quantity of VAc monomer, respectively. Then series of PVA-IBMA-DAAM(D-IPVA) emulsion was obtained and the preparation reaction of D-IPVA was shown in Scheme 1.

2.2.2 Preparation of D-IPVA/ADH composite emulsion and surface sizing

The mass concentration and pH of the above D-IPVA water dispersion were adjusted to 4% and 7~8, respectively. Different dosage of ADH was added into the system and then it was stirred at room temperature to form a uniform mixture. ADH was 1.01 times relative to the molar quantity of DAAM in D-IPVA molecule. The resulted samples were named as D-IPVA/ADH1, D-IPVA/ADH2, D-IPVA/ADH3, D-IPVA/ADH4 and D-IPVA/ADH5, respectively. The sizing liquid was poured onto the paper and start the scraper, so that the sizing liquid spread on the paper evenly. The sizing paper was dried at 105 °C for 5 min.

2.2.3 Preparation of DA-IPVA film

DA-IPVA films were prepared by cast D-IPVA/ADH water dispersion into PTFE mold. It took three days for the formation of film at room temperature. Then the films were placed in 60°C vacuum drying oven overnight. The resulted film samples were named as DA-IPVA1, DA-IPVA2, DA-IPVA3, DA-IPVA4 and DA-IPVA5, respectively.

2.3 Structural characterization and performance testing

2.3.1 Structural characterization

The structure of sample was characterized by VECTOR-22 infrared spectrometer(German Bruker Company) and the scanning wave-number ranged from 4000 cm^{-1} to 400 cm^{-1} .

2.3.2 Performance test of the emulsion

Particle size of emulsion was measured at $25\text{ }^{\circ}\text{C}$ and the laser wavelength was 633 nm . Turbiscan Lab stability analyzer was used to characterize the stability of the emulsion at $40\text{ }^{\circ}\text{C}$ for 1 h . Steady state rheological performance was tested by coaxial cylinder rotating rheometer and the shear rate ranged from 0.01 s^{-1} to 100 s^{-1} .

2.3.3 Performance test of the film

According to the GB/T1040-1992 standard of China, mechanical properties test of the film was carried out by XWW-20B universal testing machine made in Chengde Jinjian Testing Instrument Co., Ltd and the tensile rate was $50\text{ mm}\cdot\text{min}^{-1}$.

The gel content was tested by Soxhlet extractor using anhydrous ethanol as extraction solvent. Each sample was tested for three times and the average value of gel content was calculated by using following formula. Herein, the mass before and after extraction was recorded as m_0 and m , respectively.

$$G=m/m_0\times 100\%$$

The film was cut into $10\text{ mm}\times 20\text{ mm}$ and was tested by X-ray diffractometer to characterize the crystallization properties. The diffraction angle ranged from 5° to 75° .

Thermogravimetric analyzer(TGAQ500, TA, U.S.A) was used to characterize the thermal stability of the samples by increasing the temperature from room temperature to 600°C at a heating rate of $10^{\circ}\text{C min}^{-1}$ in the nitrogen atmosphere.

2.3.4 Performance test and micro-structure of the sizing paper

The sizing paper with the size of $30\text{ mm}\times 30\text{ mm}$ was soaked in deionized water for 24 h . Then the surface moisture was removed quickly. The mass before test and after test was recorded as m_1 and m_2 , respectively. The value of water absorption(X) was calculated by the following formula.

$$X=(m_2-m_1)/m_1\times 100\%$$

The contact angle tester made by Germany's KRUSS company was used to characterize water contact angle of sizing paper.

According to GB/T12914-2008 test method, dry tensile strength and wet tensile strength were tested. The paper was cut into $15\text{ mm}\times 100\text{ mm}$ before test. According to GB/T1538-1979 measurement method, the folding endurance of paper with the size of $15\text{ mm}\times 150\text{ mm}$ was tested.

The surface morphology of the sizing paper was analyzed by scanning electron microscope-energy spectrum analyzer (SEM-EDS) (TESCAN, Czech republic). The paper was cut into 3mm×5mm and pasted on the conductive tape, treating by spraying gold and the acceleration voltage during the test was selected as 5kV. The surface roughness was analyzed by SPA400-SPI3800N atomic force microscope (Seiko, Japan).

3 Results And Discussions

3.1 Structural characterization

Figure 1 shows the infrared spectrum of DA-IPVA. The strong and broad absorption peak at 3500 cm^{-1} is attributed to overlapping stretching vibration peaks of N-H and O-H. The peak at $2920\text{-}2980\text{ cm}^{-1}$ can be attributed to the asymmetric stretching vibration and symmetric stretching vibration of C-H in saturated alkyl $-\text{CH}_2$ and $-\text{CH}_3$. Amide group appears at $1450\text{-}1405\text{ cm}^{-1}$. The peaks at 1734 cm^{-1} and 1451 cm^{-1} are the characteristic absorption peaks of C=O in the ester group and the flexural vibration absorption peaks of C-H bond in $-\text{CH}_2-$ connected to C-O in the ester group. The C-O-C of the ester group shows the asymmetric and symmetric stretching vibration absorption peaks at 1293 cm^{-1} and 1191 cm^{-1} . The stretching vibration absorption peak of C=N (hydrazone) appears at 1665 cm^{-1} , indicating that the cross-linking reaction between ADH and keto carbon group occurs.

3.2 The effect of DAAM on the performances of D-IPVA /ADH emulsion

3.2.1 The effect of DAAM on the particle size of D-IPVA /ADH emulsion

Compared with PVA, the particle size of PVA emulsion modified by different amount of DAAM(D-IPVA/ADH) is obviously increased. This is because the introduction of DAAM increase the polar functional groups and the interaction between latex particles is enhanced. DAAM connect more PVA molecular chain segments in the form of covalent bond and the growing chain segment of macro-molecular makes it hard for D-IPVA molecules approach, enabling the formation of inter-molecular hydrogen bond of PVA to further increase and resulting in particle size increasing. With the dosage of DAAM further increase to 10%, the average particle size of the dispersion reaches 254.2 nm. As is known to all, smaller particle size is beneficial for the D-IPVA/ADH to infiltrate into the paper fiber and further enhance the strength of the paper, so the dosage of DAAM should be controlled in a certain range.

3.2.2 The effect of DAAM dosage on the stability of D-IPVA /ADH emulsion

Figure 3 shows the influence of DAAM dosage on the stability of D-IPVA/ADH emulsion. Usually, kinetic stability index (TSI) is used to characterize the stability of the dispersion. Stability data of emulsion at different positions including global, bottom, middle and top parts is recorded and the result is basically consistent. TSI increases with the increase of the amount of DAAM, indicating that the stability of the emulsion decreases. This is because the introduction of DAAM/ADH brings the D-IPVA more cross-linking active groups, which is prone to aggregation in the storage process, resulting in a series of physical and chemical changes and the stability decreases.

Compared with PVA, the TSI of D-IPVA/ADH1 emulsion with 2% of DAAM is low, which indicates that its stability is relatively high. There are not only hydrophilic group including hydroxyl groups but also hydrophobic group including carbonyl groups and long carbon chain groups in the molecule. As it was shown in Fig. 3e, the hydrophobic groups tend to assemble internally and form a hydrophobically colloidal structure with ADH in the outer hydrophilic region. A small amount of ADH can be solubilized inside the colloid to form a stable emulsion system. However, TSI of D-IPVA/ADH3 and D-IPVA/ADH5 are higher, which is consistent with the trend of particle size change. The increase of macro-molecular chain makes it easy to appear chain winding, accompanied by reducing water solubility and the stability of the system. The kinetic stability index of the D-IPVA5 is obviously larger. Introducing too much DAAM makes the molecular chain of the whole polymer become longer and the molecular chain has a large number of hydroxyl groups, ester groups and other strong polar groups. When the active groups are close to each other, hydrogen bond and other interactions are formed. The entangle and cross-linking between chains take place to form larger particles and the stability decreases.

3.2.3 Effect of DAAM dosage on the rheological property of the emulsion

Usually, the molecular chain of PVA is linear and the regular arrangement of hydroxyl groups is easy to form intramolecular or intermolecular hydrogen bonds. And it is also easy to form hydrogen bonds with solvents, which greatly affects the rheological properties of PVA aqueous solutions (Briscoe et al. 2000). Fig. 4 shows the apparent viscosity of D-IPVA/ADH emulsion with different additions of DAAM monomer as the shear rate ranges from 0.01 to 100 s⁻¹ at 50 °C. The high viscosity of PVA is resulted from intermolecular hydrogen bond generated by the large amounts of hydroxyl group in PVA under low shear force. When the shear rate increases, the hydrogen bond is destructed and the viscosity of PVA decreases, showing the shear thinning behavior.

As it can be seen that the viscosity of series of D-IPVA/ADH emulsions is lower than PVA, which is mainly due to that the IBMA is introduced into the main chain of the molecule in the random co-polymerization phase. The distance between molecular chains increases and the hydrogen bond between D-IPVA chains decreases, so that the apparent viscosity decreases. Compared with pure PVA, D-IPVA molecule contains IBMA in the main chain and DAAM in the side chain, which increases polar groups and hydrodynamics radius. With the amount of DAAM increases from 2–8%, the viscosity increases from 4.09 Pa·s to 5.37 Pa·s. However, the increasing dependence of apparent viscosity on shear rate is not obvious. This is because the introduction of DAAM and ADH brings the D-IPVA/ADH molecular system more cross-linking active groups, which affect the fluidity of D-IPVA/ADH emulsion so that the decrease in viscosity is not obvious with the shear rate increasing.

When the dosage of DAAM reaches 10%(D-IPVA/ADH5), both DAAM and ADH increases so much that the viscosity increases significantly. D-IPVA/ADH5 shows the relatively obvious shear thinning behavior with the increase of shear rate, indicating that D-IPVA/ADH5 emulsion with high content of DAAM is more dependent on shear rate, which may be due to the increase of intramolecular and intermolecular hydrogen bond sites. As a result, it becomes more sensitive to shear and the viscosity increases more

obviously with the increase of the shear rate (Yong et al. 2008; Ma et al. 2017; Zhou et al. 2016). The decreasing viscosity is beneficial to the penetration ability of the sizing liquid.

3.3 The effect of DAAM on the properties of DA-IPVA films

3.3.1 The effect of DAAM on the crystallization and crystallinity of DA-IPVA films

Figure 5a shows the influence of DAAM dosage on the crystallization properties of the DA-IPVA film. The crystallinity of DA-IPVA films is lower than that of PVA films. This is due to the decrease of hydrogen bond between molecules and the reaction of some hydroxyl groups. While DA-IPVA is formed by random co-polymerization of vinyl acetate and IBMA and other monomers containing double bond. As a result, the original PVA molecular chain segments are disrupted, the molecular regularity and the crystallinity declines, so the intensity of diffraction peak declines. It also can be seen that the crystallinity of the film declines with the increase of the amount of DAAM, which is due to the cross-linking reaction between DAAM and ADH during film formation. The regularity of the molecular chain is damaged to a certain extent, so the crystallinity declines with the increase of the dosage of DAAM.

Figure 5b shows the gel content of DA-IPVA film, reflecting the degree of cross-linking of the DA-IPVA film. As it can be seen, the gel content of series of DA-IPVA films are above 93%. When the amount of DAAM is added up to 10% (DA-IPVA5), the gel content of DA-IPVA film is as high as 98.5%. Because DAAM molecules contain two ketone carbonyl groups and its chemical properties are active, which can form cross-linked structures by reacting with hydrazine group on the ADH molecule and improve the cross-linking degree of the film (Ha et al. 2019). With the DAAM content further increase, the increase range of gel content decreases. When the amount of DAAM is more than 8% (DA-IPVA4), the reaction between ketone carbonyl groups with hydrazine group is complete and the groups with low reaction activity of excessive chain length may remain in the film. As a result, the increasing range of gel content is low. Overall, the gel content of series of DA-IPVA films are high, which indicates that the cross-linking degree of the system is high. If used as surface sizing agent, it is beneficial to improve the mechanical properties.

3.3.2 Influence of DAAM dosage on thermal properties of DA-IPVA films

Figure 6 shows the thermogravimetric analysis of PVA film and DA-IPVA films with different dosage of DAAM. Being different from PVA film, the thermogravimetric curves of DA-IPVA films using different dosage of DAAM are similar. According to the thermogravimetric curves in Fig. 6a, the temperature at the same thermal loss rate of 10%, 30%, 50%, 70% and 90% are put together in Fig. 6b. The weight loss rate under 100 °C is mainly caused by the volatilization, desorption or decomposition of small molecules. Compared with pure PVA, the original molecular regularity is destroyed by the copolymerization among VAc, IBMA and DAAM. As a result, the molecular chain density of DA-IPVA films are impaired, which weakens the inter-molecular force. When the temperature is lower than 300 °C, the thermal stability of DA-IPVA films is inferior to pure PVA film. This phenomenon does not appear until the temperature is higher than 300°C. On the whole, with the DAAM dosage increasing, the thermogravimetric curves are moved to the high temperature direction and the temperature at the same weight loss rate is improved.

Compared with PVA film, the temperature at the thermal loss rate of 50% for DA-IPVA1, DA-IPVA3 and DA-IPVA5 are improved by 8.9°C, 39.1°C and 43.1°C, respectively. The extent of the temperature at the thermal loss rate of 70% is improved even larger. The temperature is improved by 47.1°C, 55.7°C and 69.2°C, respectively. This is mainly because the polar bond and cross-linking structure increases the cohesive energy and a dense network is formed, which contributes to improving the thermal stability.

3.3.3 Influence of DAAM dosage on mechanical properties of DA-IPVA films

The mechanical properties including tensile strength, Young's modulus and elongation at break of the DA-IPVA film with different dosage of DAAM are shown in Fig. 7. Overall, the tensile strength and Young's modulus of the DA-IPVA film are improved with the increase of DAAM dosage. Elongation at break of DA-IPVA films shows the declining trend followed by increase firstly and then decline. For DA-IPVA4, the tensile strength and elongation at break of DA-IPVA4 are maximum and the value is 30.38 MPa and 451.71%, respectively. Compared with pure PVA, the tensile strength and elongation at break of DA-IPVA4 are increased by 2.67 times and 0.40 times, respectively. This is because more DAAM and ADH in the molecular chain of DA-IPVA4 undergo cross-linking reaction, the cohesive energy and toughness are increased. When the amount of DAAM is 10% (DA-IPVA5), the modulus is significantly improved and reach the maximum. However, the tensile strength shows a slight decline and the elongation at break shows significant decline for DA-IPVA5, which is because excessive cross-linking makes the film brittle and mechanical properties is deteriorated.

The results show that the PVA modified by ketone-hydrazine cross-linking can enhance the strength of the film and the cross-linking between DAAM/ADH and PVA increases the cohesion and tensile strength of the film. However, the excessive cross-linking is disadvantageous to the comprehensive mechanical properties of the films and the elongation at break declines obviously when the DAAM amount is more than 10% (DA-IPVA5).

3.4 Influence of DAAM on performances of the sizing paper

3.4.1 Influence of DAAM on the water resistance of sizing paper

(a. contact angle and b. water absorption)

Figure 8 is the water resistance of paper with different sizing agents. As can be seen from Fig. 8a, with the increase of DAAM dosage, the contact angle of the paper shows a trend of increasing from 67.2° to 83.4°. The contact angle of the base paper without any treatment is only 19.2°. After the surface sizing by pure PVA solution, the contact angle increases obviously and can reach 66.5°. After the DA-IPVA emulsion sizing with cross-linking reaction, the compact density of the paper is further enhanced. The contact angle of the paper reaches 81.4° after DA-IPVA4 sizing, indicating that the water resistance of the paper is enhanced. This is because cross-linking reaction and dehydration takes place between ketone carbonyl group introduced into PVA molecule by DAAM and ADH at room temperature and the structure of hydrazone is formed. Relatively dense structure with paper fibers was formed and the surface of the paper became rougher. The surface of the paper becomes low-energy, which effectively prevent the water molecules from spreading inside the paper and finally the paper show better hydrophobicity. When the

dosage of DAAM is 10%, the contact angle of the paper sized by DA-IPVA5 is 83.4° , which is 3.34 times higher than that of the base paper and the water resistance of the paper is enhanced to much extent.

The results of water absorption is consistent with contact angle. With the increase of DAAM dosage, the water absorption of the paper shows a trend of decreasing from 145.5–91.3%. Compared with the base paper, the water absorption rate of DA-IPVA5 is decreased by 70%, which is further proved that the cross-linking structure is beneficial to the improvement of water resistance property.

3.4.2 Effect of DAAM dosage on the mechanical strength of the sizing paper

Figure 9a shows the folding endurance of DA-IPVA sizing paper. Compared with base paper, the folding endurance of PVA sizing paper increases from 15 times to 40 times. Pure PVA contained more hydroxyl group can penetrate into the gap of paper fiber to enhance the bonding force between fiber through hydrogen bonding (Li et al. 2019). The folding resistance of the paper after sizing by series of DA-IPVA emulsions are significantly increased. Compared with base paper, the folding resistance of the paper sized by DA-IPVA4 reaches 457 times and increases by 2946.67%. When the amount of DAAM is more than 8%, the folding resistance decreases slightly because of excessive cross-linking between ketone carbonyl group on DAAM and ADH, which reduces the toughness of the sizing paper and increases the brittleness, thus reducing the folding resistance times of the paper.

(a. folding resistance, b. dry and wet strength)

Figure 9b shows the dry strength and wet strength of DA-IPVA sizing paper. Compared with base paper, the dry tensile index of pure PVA sizing paper increase from $32.42 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ to $74.33 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ and wet tensile index increase from $4.31 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ to $12.49 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$. This is because the pure PVA solution is permeated into the paper and hydrogen bonding is formed between PVA and hydroxyl group of the paper fiber, which also weakens the erosion action of water on the paper and the wet strength is improved. The dry strength and wet strength of the paper after sizing by series of DA-IPVA emulsions are significantly increased. The maximum dry strength and maximum wet strength can reach $111.82 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$ and $18.72 \text{ N}\cdot\text{m}\cdot\text{g}^{-1}$, respectively, which are increased by 266.5% and 334.3% compared with the base paper, respectively. This is because the cross-linking reaction occurs between ketone carbonyl group in DAAM and ADH at room temperature, which improves the bonding strength between paper fibers and the mechanical strength. As the amount of DAAM continues to increase, the dry and wet strength of paper decreases. This is because the excessive introduction of DAAM leads to the increasing brittleness of material, which is not conducive to the increase of paper strength.

3.4.3 Influence of DAAM dosage on surface roughness of DA-IPVA sizing paper

The surface morphology of the samples including base paper, DA-IPVA1, DA-IPVA3 and DA-IPVA5 by AFM is shown in Fig. 10. Compared with base paper, the average roughness (R_a) of DA-IPVA sizing paper increases from 85.6 nm to 162.5 nm and increase by 1.02 times and 2.83 times, respectively. The root mean roughness (RMS) increases from 107.8 nm to 228.6 nm and improves by 0.67 times and 2.53 times, respectively. On one hand, the strong hydrogen bond is formed between fibers, which is due to a lot of hydroxyl groups are retained in the modification process of sizing agent. On the other hand, the

introduction of DAAM and ADH increase the polar bond, which also makes the system further cross-linked and forms a complex secondary structure on the surface of the paper and between fibers. The bright bulge is mainly produced by the cross-linking structures by the reaction between DAAM and ADH (Zhang et al. 2019). What's more, the IBMA segment also contributes to the formation of the cross-linking structure. This effect becomes more obvious with the increase of DAAM dosage, especially when DAAM dosage reaches 10%, the surface roughness of which increases to much extent. For DA-IPVA5, the 10 points height (R_z) and the difference between the maximum peak height and the lowest peak valley (P-V) increase by 1.82 times and 1.91 times.

3.4.4 Micro-morphology, elemental composition and enhancing mechanism of sizing paper

Figure 11 shows the micro-morphology of the sizing paper by SEM images. As can be seen from Fig. 11, the surface of the base paper without sizing is loose and porous. The fibers are mechanically intertwined and there are obvious pores between the paper fibers (Fig. 11a). After surface sizing by DA-IPVA, the pore spacing and voids are reduced (Fig. 11b, Fig. 11c and Fig. 11d). This is because DA-IPVA sizing liquids penetrate into the paper and the adhesion strength of the paper fibers is improved. The cross-linking reaction between IBMA and paper fiber and the distance between the fibers is reduced to form more hydrogen bond (Yang et al. 2019). The macromolecular chains of sizing liquids approach and ketone carbonyl of DA-IPVA reacts with ADH accompanied by dehydration to form hydrazone. Cross-linking and three-dimensional network structure on the surface or internal of the paper are formed and tiny fibers are bonded for each other, enhancing the bonding strength between paper fibers and form a compact structure, which greatly improves water resistance, folding resistance, tensile strength and other performances mentioned above of the paper.

(a.Base paper, b.DA-IPVA1 sizing paper, c.DA-IPVA3 sizing paper, d.DA-IPVA5 sizing paper)

To further make clear the cross-linking mechanism of the paper, energy spectrum of paper sized by DA-IPVA1 (a), DA-IPVA3 (b) and DA-IPVA5 (c) (2K $\times$) are examined and shown in Fig.S1. Fig. 11e shows the element and content including C, O and N at cross-linking point. The content of N element increases and O element decreases slightly at the cross-linking point. The result confirms the dehydration reaction between DAAM and ADH groups in DA-IPVA molecules and cross-linking is formed, which contributes to improving the mechanical properties and water resistance of the paper.

DA-IPVA1 and DA-IPVA3 and DA-IPVA5

The chemical composition for paper sized by DA-IPVA1, DA-IPVA3 and DA-IPVA5 was examined by XPS. The XPS wide scanning spectrum was shown in Fig. 12. The types and contents of elements on the paper surface obtained by XPS wide scanning spectrum were shown in Table 1. According to the position of strong signal spectrum peak and element characteristic binding energy in XPS wide scanning spectrum in Fig. 12, it can be determined that the surface of DA-IPVA1, DA-IPVA3 and DA-IPVA5 sizing paper contains C element (about 284~288 eV), O element (about 530 eV) and N element (about 397 eV). Table 1 shows the variation of atomic content of C, O and N. The content of N element is 2.08%, 2.82% and 4.24% respectively, indicating that the content of nitrogen element in sizing paper is very low. The content of N

element on the surface of DA-IPVA3 and DA-IPVA5 sizing paper is about 1.35 times and 2.03 times than that of DA-IPVA1 sizing paper. This shows that there are more N element on the surface of DA-IPVA3 and DA-IPVA5 sizing paper, while the content of C element is decreasing. Fig. 12 also presents the high resolution C1s spectra for DA-IPVA sizing paper with different amount of DAAM/ADH. The peaks at 284.6 eV, 286.1 eV and 287.5 eV are attributed to the functional groups of C-C/C-H, C-O/C-N and C=O/C=N, respectively. The composition and chemical state of different C components are listed in Table 2. The content of both C-O, C-N and C=O, C=N shows a trend of increasing first and then decreasing with increasing DAAM/ADH. The value of O/C and N/C shows the trend of increasing gradually. It can be ascribed to the reaction between carbonyl group and hydrazine to produce hydrazone and the incorporation of nitrogen compound ADH into DA-IPVA. This result suggests that DA-IPVA displays better penetrability into the paper and cross-linking occurs between DA-IPVA molecules and between fibers.

Table 1 Carbon, nitrogen, and oxygen contents for sizing paper

Sample	C/%	O/%	N/%	O/C	N/C
DA-IPVA1	25.26	71.81	2.08	2.84	0.08
DA-IPVA3	26.05	70.37	2.82	2.70	0.11
DA-IPVA5	20.57	74.63	4.24	3.63	0.21

Table 2 Qualitative and quantitative XPS analysis for sizing paper

Binding energy	284.6 eV	286.1 eV	287.5 eV
Bonding mode	C-C,C-H	C-O,C-N	C=O,C=N
DA-IPVA1	46.07	36.15	17.78
DA-IPVA3	38.81	42.14	19.06
DA-IPVA5	50.29	38.51	11.21

In order to further explain the enhancing mechanism of paper after surface sizing, the cross sections of base paper and sizing paper are analyzed by SEM in Scheme 2. It turns out the section of ordinary paper is relatively flat, indicating that the base paper is brittle fracture. While the section of DA-IPVA sizing paper is relatively rough, indicating that the DA-IPVA3 sizing paper is ductile fracture, which further shows that the folding resistance and tensile strength of the paper are enhanced. We try to explain this phenomenon and the paper strengthening mechanism is put forward combined with the change of paper strength. The hydrophilic colloid protective layer of cross-linked DA-IPVA sizing particles forms a uniform network system with the fiber under the action of hydrogen bond. In drying stage 1, with the evaporation of water,

the cross-linked DA-IPVA shrinks in the vertical direction (Z direction). In drying stage 2, the further evaporation of water causes the cross-linked DA-IPVA to shrink in the horizontal direction (X-Y plane). The combination of cross-linked DA-IPVA with fiber forms a continuous sizing layer and a cross-linked network structure, which plays a role in buffering the external tensile force, so as to require greater tensile force when the paper is destructed.

4 Conclusions

DA-IPVA is prepared by using DAAM as graft monomer and IBMA as self-cross-linking monomer. The addition of DAAM and IBMA endow DA-IPVA with cross-linked active group and increase cross-linking density and hydrophobicity after ADH is added into the emulsion. The DA-IPVA can be cross-linked on the surface and inside of the paper to form a dense network structure, which improves the bonding force between the fibers. The tensile strength and elongation at break of DA-IPVA4 are increased by 2.67 times and 0.40 times than pure PVA, respectively. When the mole fraction of DAAM of the cross-linking monomer is 10%, the surface sizing performance of the paper is obviously improved compared with the base paper. The maximum dry and wet strength is increased by 266.5% and 334.3%, respectively. The folding resistance is increased 2946.67%. This study can have a positive impact on developing a novel effective cross-linking surface sizing agent for paper.

Declarations

Conflict of interest

The authors declare that there is no conflict of interest regarding publication of this paper.

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Scheme

Please see the Supplementary Files for the Scheme 1 and 2.

Figures

Figure 1

Infrared spectrum of DA-IPVA

Figure 2

The effect of DAAM dosage on particle size of D-IPVA/ADH emulsion

Figure 3

The effect of DAAM dosage on the stability of D-IPVA/ADH emulsion(a,b,c,d) and mechanism of stability(e)

Figure 4

The effect of DAAM dosage on viscosity of D-IPVA/ADH sizing solution

Figure 5

The effect of DAAM dosage on crystallinity(a) and gel content(b) of DA-IPVA films

Figure 6

Effect of DAAM dosage on thermal properties of DA-IPVA films

Figure 7

The effect of DAAM dosage on the mechanical properties of DA-IPVA films:(a) Stress-strain curve; (b) Tensile strength; (c) Young's modulus; (d) Elongation at break.

Figure 8

Effect of DAAM dosage on the water resistance of sizing paper

Figure 9

The effect of DAAM dosage on the mechanical strength of the sizing paper

Figure 10

Surface morphology(a, base paper; b, DA-IPVA1; c, DA-IPVA3; d, DA-IPVA5) and roughness parameters(e) of paper by AFM

Figure 11

Surface morphology by SEM (2Kx) and element composition by EDS

Figure 12

High resolution C1s XPS spectra for paper sized with DA-IPVA1 and DA-IPVA3 and DA-IPVA5

Supplementary Files

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