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Effects of the Molecular Structure of Polyvinyl Alcohol on the Adhesion to Fibre Substrates

Abstract

The influence of the molecular structure of polyvinyl alcohol, including the degree of polymerisation and the degree of alcoholysis, on the adhesion of PVA to pure polyester, pure cotton, and polyester/cotton-blend fibres were investigated by using a method on impregnated roving. The adhesion is evaluated in terms of the maximum strength and work-to-break of the rovings. It was found that the molecular structure has evident influence on the adhesion. No matter what type of tested fibre was used as substrates, the adhesion increased with the increase in the degree of polymerisation. However, it seems that the greatest effect on enhancing the adhesion is reached when the degree of polymerisation exceeds 1700. The degree of alcoholysis of PVA shows less effect on the adhesion than the degree of polymerisation does. The influence of the molecular structures of PVA on the adhesion of PVA-starch blends to fibres is less than that of PVA alone. We also discuss and analyse the experimental results from the point of view of the adhesion theory, especially from the type of failure, dispersion forces and internal stress on interfaces, and cohesive forces of the adhesive layer.

Key words: *fibres, polyvinyl alcohols, warp sizes, adhesion, determination.*

◼ Introduction

Polyvinyl alcohols (PVA) possess such unique characteristics as excellent film-forming ability, good water-solubility, appropriate compatibility with starch, superior resistance to solvent and grease, and excellent film properties such as remarkable abrasion resistance, flexing resistance, breaking strength and elongation. They have been widely used as adhesives and sizing agents both in warp sizing and making nonwoven fabrics. Warp sizing practices demonstrate that, by using PVA as sizing agents, many difficulties in warp sizing operation can be overcome since PVA was introduced to the textile industry as warp sizes in 1940s. Currently, PVA is a necessary ingredient for the warp yarns of fine number, high density, and synthetic fibres in determining a sizing formulation.

It is as well to emphasise that sufficient adhesion to fibres is one of the essential demands for a sizing agent used in warp sizing [1] as well as for an adhesive used in manufactures of non-woven fabrics. The main function of adhesion is to adhere to the fibres in warp yarns and non-woven fabrics in order to increase their strength. Moreover, as the contact area of sizing film and fibres is constrained by adhesion, the adhesion functions by increasing the connection between the fi-

bres and the films around the yarns to the yarn body. It has been elucidated that the adhesion of a sizing agent influences the physical and mechanical properties of the sized yarns, and determines how heavily a warp yarn must be sized [2]. For this reason, its behaviour has received more and more attention recently, and a great deal of research work has been done [3-6].

It is evident that the molecular structure of PVA plays an important role in adhesion to fibres. For warp sizing operations, the degree of polymerisation (DP) and degree of alcoholysis (DA) are the only two indexes that must be considered for the use of commercial PVA. If the adhesion dependence of the indexes on adhesion were known quantitatively, it would be very helpful in choosing which PVA is to be used as the sizing agent. Unfortunately, none of the investigations has taken this problem into quantitative consideration, and no reference book or handbook gives figures to allow us to quantitatively evaluate the adhesion dependence, even though the size ingredients have been applied to sizing operations for many years. For this reason, the object of this investigation is to build the connection between DP and adhesion, and between DA and adhesion. Furthermore, the investigation is also beneficial to the choice of PVA in non-woven fabrics.

◼ Experimental

Materials

PVA 1799 (DP = 1700; DA > 99% mole), PVA 2499 (DP = 2400; DA > 99% mole),

and PVA 1792 (DP = 1700; DA = 92% mole) were supplied by the Hunan Vinylon Co. from Hunan Province, China. PVA 1788 (DP = 1700; DA = 88% mole) and PVA 0599 (DP = 500; DA > 99% mole) were obtained from the Sichuan Vinylon Co. in Sichuan Province, China. Commercial natural cornstarch with a paste viscosity of 160 mPa·s was supplied from the Jincheng Starch Ltd Co. in Zaozuang, China. Prior to use, the starch was refined in a methanol-distilled water medium according to the method found in references [7, 8].

The pure polyester roving (300 tex, twist factor: 53.8) and polyester/cotton blend roving (460 tex, twist factor: 62.0, and 65/35 in blending ratio of polyester to cotton) were obtained from Textile Factory 3509 (Hanchuang, Hubei Province). Pure cotton roving (485 tex, twist factor: 116) was supplied by the Yudahua Textile Co. (Wuhan, Hubei Province, China). The polyester fibres in the pure polyester and polyester/cotton blend rovings were PET staple fibres, and their parameters were 38 mm × 1.56 dtex. The cotton fibres were 30 mm × 1.72 - 1.78 dtex in the blend roving and 29.5 mm × 1.77 dtex in pure cotton roving. Both cotton fibres were supplied by Yudahua Textile Co., China.

Starch acidification

To use starch on warp yarns satisfactorily, the paste viscosity of native starch must be reduced so as to raise the impregnation extent of sizing paste into warp yarns. It was discovered long ago that steeping or

Table 1. *Characterisation of the PVA used.*

Samples	Degree of polymerisation	Degree of hydrolysis, %	Volatile content, %	Viscosity, mPa·s
PVA-2499	2400	>99%	6.70	43
PVA-1799	1700	>99%	6.85	27
PVA-0599	500	>99%	8.35	7
PVA-1792	1700	92%	9.64	22
PVA-1788	1700	88%	7.42	26

Table 2. *Influence of the PVA molecular structure on the strength properties related to adhesion of pure polyester fibres.*

PVA molecular structure		Maximum strength		Work to break	
Degree of polymerisation	Degree of hydrolysis, %	S_m, N	Coefficient of variations, %	W_b, J	Coefficient of variations, %
500	>99	101.0	8.79	0.847	14.72
1700	>99	108.4	3.39	0.941	6.47
2400	>99	108.8	3.45	0.961	6.01
1700	92	107.9	4.55	0.925	8.33
1700	88	105.4	4.07	0.905	6.70

Table 3. *Influence of the PVA molecular structure on the strength properties related to adhesion of pure cotton fibres.*

PVA molecular structure		Maximum strength		Work to break	
Degree of polymerisation	Degree of hydrolysis, %	S_m, N	Coefficient of variations, %	W_b, J	Coefficient of variations, %
500	>99	67.4	5.69	0.284	8.77
1700	>99	90.0	4.85	0.391	7.80
2400	>99	92.0	5.07	0.398	7.91
1700	92	85.0	4.86	0.359	7.48
1700	88	82.9	4.50	0.355	9.84

soaking granular starch in acidic suspension at temperatures below the gelatinisation points would produce a starch size which would display a reduced paste viscosity when cooked. Therefore, the native starch refined was acidified before application in our experiments.

Starch acidification was carried out in an aqueous suspension. 300 g (dry weight) of the refined starch were suspended in 500 g of distilled water at room temperature. The suspension was transferred into a flask and heated during mechanical stirring. When the temperature of the suspension raised to 50 °C, 27 ml of 2 mole/l HCl solution was added. The acidification was carried out during continuous stirring at 50 °C for 4 h. Then, the product was neutralised with 1% NaOH solution, filtered, washed carefully with distilled water, dried at 60 °C, pulverised and sieved to pass through a 100 mesh-sieve.

Characterisation of samples

The apparent viscosities of PVA were measured by a rotary viscometer (NDJ-79) with a shear rate of 2028 s^{-1}. The PVA samples were cooked individually with distilled water under stirring and condensing to obtain PVA solutions with a concentration of 4%, and the apparent viscosities of the solutions were determined at room temperature.

The volatile contents of PVA and the moisture content of acidified starch were determined by the weight method in an oven at 105 °C by eliminating the water and volatile ingredients contained in the samples.

The apparent viscosity of acidified starch was measured by the method reported previously [9] only with an exception of shear rate at 2028 s^{-1}. The viscosity instability of the starch pastes was expressed as a percentage of apparent viscosity fluctuation over a period of 2.0 hours at 95 °C. The determination was conducted over a period from 1 to 3.0 hours after starch gelatinisation, during which the viscosity readings were taken every 30 min. The instability was calculated according to reference [10].

The moisture content, apparent viscosity and viscosity instability of the acidified starch prepared are 8.50%, 10.0 mPa·s, and 9.52% respectively. The various PVA samples employed in our experiment are characterised in Table 1.

Measurement of adhesion

22.0 g (dry weight) of PVA was cooked with 2178 ml of distilled water in a flask under mechanical stirring and condensing at 95 °C for 3h to form a 1% PVA solution. For the PVA-starch blend paste, PVA and starch were cooked in separate flasks with mechanical stirring and condensing at 95 °C. The blend paste was prepared by combining PVA solution and starch paste in the required proportions. The PVA solution or PVA-starch paste were poured into a metal pan which was placed on a water bath at 95 °C. The roving, which was carefully wound onto a special frame [11], was impregnated with the solution or paste for 5 minutes. Then the frame was hung on a rope and the roving samples were dried by air. Finally, the roving was cut and collected for mechanical measurement.

The failure loads of the roving samples were measured when the samples had been kept at 65% relative humidity and 20 °C for 24h. The loads were determined on a Zwick Material Tester (BZ2.5/TNIS) with an initial chuck-distance of 100 mm and a drawing speed of 50 mm/min. For every sample, more than 20 replicates were taken and the data was taken for calculating the mean value of the behaviours only after the abnormal values had been rejected by statistical analysis [10, 12].

The **maximum strength** (S_m) and **work-to-break** (W_b) of a slightly sized roving have often been used to **evaluate the adhesion** of a sizing agent, which is a common practice in most laboratories all over the world. Generally, S_m indicates the adhesive strength of the sizing agents on fibres, and W_b expresses the ability of the roving to resist the drawing break by bonding [3, 4]. By using these two strength property indexes, the adhesion capacity of PVA to fibres can be easily and accurately evaluated. The greater the values, the better the adhesion is.

■ Results and discussions

Effect of the molecular structure on adhesion

The correlations between the PVA's molecular structure and the adhesive strength of PVA to polyester, cotton and polyester/cotton fibres are shown in Table 2-4. It can be clearly seen that the adhesion apparently depends on the molecular structure of the PVA. No matter

what type of fibre is used, the adhesion increases with the increase in the degree of polymerisation. However, it seems that a maximum effect in the adhesion is reached when the degree of polymerisation exceeds 1700. Moreover, the adhesion slowly reduces as the degree of alcoholysis is decreased.

As an adhesive joint will fracture at its weakest position, the bonding strength of an adhesive joint is determined not only by interfacial attraction, but also by the mechanical properties of the adhesive layer. Generally, a strong bonding is obtained only when neither cohesive failure nor interfacial failure occurs at low applied loads. It is as well to emphasise that the adhesion of a sizing agent to fibres is achieved only through intermolecular forces, and cannot allow interfacial chemical bonding. It is also well known that intermolecular forces increase as molecular weights increase. Apparently, increased intermolecular forces not only enhance the interfacial forces between the PVA and fibres, but also increase the cohesive strength of the adhesive layer among fibres. With a rise in the PVA's molecular weight, the increased interfacial forces evidently cause the interfacial failure to happen only at higher loads. Also, the enhanced cohesive strength certainly raises the loads when the cohesive failure occurs. Consequently, the increase in the molecular weights of PVA enhances the adhesion to the three kinds of fibres. On the contrary, however, the increase in molecular weight will increase the viscosity of PVA paste, and tends to retard the wetting of PVA paste to fibres. Incomplete wetting will produce interfacial defects, and induces stress concentration around an unwetted interfacial defect as an adhesive bond is stressed. When the local stress exceeds the local strength, the adhesive bond will fracture [13]. It is evident that the favourable effect in increasing the molecular weights on adhesion is offset by the deleterious effect of the paste solution when the degree of polymerisation exceeds 1700.

Partially alcoholised PVA incorporates a certain amount of acetyl groups into their macromolecules. The presence of the groups will induce three changes to an adhesive bonding: (1) cohesive forces are reduced; (2) internal stresses on the interfaces between adhesive layers and fibres are decreased; (3) dispersion forces of the interfaces between the adhesive layer and polyester fibres are enhanced, due to the similarity of the molecular structures.

Table 4. *Influence of the PVA molecular structure on the strength properties related to adhesion of polyester/cotton blend fibres; blending ratio of polyester to cotton fibres is 65:35.*

PVA molecular structure		Maximum strength		Work to break	
Degree of polymerisation	Degree of hydrolysis, %	S_m, N	Coefficient of variations, %	W_b, J	Coefficient of variations, %
500	>99	80.1	7.87	0.601	12.11
1700	>99	98.1	4.27	0.789	8.00
2400	>99	100.7	3.98	0.818	7.35
1700	92	94.2	5.77	0.742	9.18
1700	88	93.5	5.99	0.754	10.06

Obviously, reduced cohesive forces will result in cohesive failure and are deleterious to adhesion, while decreased internal stresses and enhanced dispersion forces are favourable to adhesion. The experimental results presented demonstrate that the influence of the factor (1) is greater than the sum of factors (2) and (3). It should be noted, however, that PVA and polyester or cotton is dissimilar and incompatible, and their diffusion coefficients are quite small. Thus, a sharp interface between the fibre and adhesive layer may exist. The dispersion forces between polymers (1-5 kcal/mole) are too weak to prevent molecular slippage at a sharp interface [13]. Furthermore, fully alcoholised PVA is polar substance that can be elasticised through absorbing water. This suggests that fully alcoholised PVA will show a certain elasticity, and their internal stresses on the interfaces may not be too heavy. For this reason, the degree of alcoholysis of PVA shows little effect on the adhesion.

Effect of PVA-starch blends on the adhesion

The influences of the PVA's molecular structure on the adhesion of PVA-starch blends to all-polyester, pure cotton and

Table 5. *Effect of the PVA structure on the strength properties related to adhesion of pure polyester fibre glued with PVA-starch blends; the ratio of PVA to starch is 65:35 (wt/wt).*

PVA molecular structure		Maximum strength		Work to break	
Degree of polymerisation	Degree of hydrolysis, %	S_m, N	Coefficient of variations, %	W_b, J	Coefficient of variations, %
500	>99	100.8	3.73	0.839	7.60
1700	>99	106.3	2.76	0.913	5.59
2400	>99	107.0	3.55	0.923	5.73
1700	92	105.3	2.85	0.909	4.59
1700	88	104.5	3.96	0.906	8.02

Table 6. *Effect of the PVA structure on the strength properties related to adhesion of pure cotton fibre glued with PVA-starch blends; the ratio of PVA to starch is 65:35 (wt/wt).*

PVA molecular structure		Maximum strength		Work to break	
Degree of polymerisation	Degree of hydrolysis, %	S_m, N	Coefficient of variations, %	W_b, J	Coefficient of variations, %
500	>99	70.2	5.23	0.291	8.65
1700	>99	81.5	5.31	0.343	9.48
2400	>99	82.4	4.37	0.355	6.15
1700	92	82.3	4.87	0.351	7.15
1700	88	83.5	7.06	0.348	11.21

Table 7. *Effect of the PVA structure on the strength properties related to adhesion of polyester/cotton fibres glued with PVA-starch blends; the ratio of PVA to starch is 65:35 (wt/wt), blending ratio of polyesterto cotton fibres is 65:35 (wt/wt).*

PVA molecular structure		Maximum strength		Work to break	
Degree of polymerisation	Degree of hydrolysis, %	S_m, N	Coefficient of variations, %	W_b, J	Coefficient of variations, %
500	>99	86.2	4.32	0.663	6.84
1700	>99	97.0	4.84	0.797	7.65
2400	>99	99.6	2.56	0.816	5.07
1700	92	94.5	5.58	0.752	8.15
1700	88	92.2	6.20	0.740	8.46

polyester/cotton fibres are shown in Tables 5, 6 and 7 respectively. No matter what type of the three types of fibres is used as the bound substrate, the adhesion of the blends to fibre substrates increases also with the increase in the molecular weight of PVA. However, the increment in adhesion of the blends with the molecular weight is less than that of PVA alone. This is mainly attributed to the presence of the starch ingredient, which does not vary in molecular structure as PVA samples do, and is constant in adhesion. The bonding strengths of the blends to fibres evidently do not further increase if the degree of polymerisation of PVA exceeds 1700. On the other hand, the degree of alcoholysis of PVA shows little effect on the adhesion of the blends to fibres.

By further contrasting the data listed in Table 6 with those in Table 3, it can be found that the maximum strength and work-to-break of cotton rovings sized with PVA-starch blends decreases when the degrees of polymerisation of PVA are 1700 and 2400, and increases when the degree of polymerisation equals 500. This can be interpreted as the adhesion of the blends to cotton fibres reducing upon the higher molecular weight of PVA and rising upon the lower molecular weight, compared with the single PVA ingredient. When the cohesive force of an adhesive layer is sufficient, which is often true in the case of higher PVA molecular weights, the interfacial situation should be considered, since interfacial failure often occurs in this case and causes the reduction of the bound strength. It has been elucidated that pure starch pastes can be described as a suspension of swollen particles of broken starch granules dispersed in a continuous phase [14, 15], whereas aqueous PVA solution is only a simple homogenous system of PVA macromolecules dissolved in water. Incorporating starch paste into PVA solution also results in a suspension in which the swollen particles are dispersed in a continuous medium comprising the soluble starch fraction and dissolved PVA [9]. It is obvious that the swollen particles have less effect on the adhesion than the soluble fractions in the continuous phase, due to their uneven spreading on the surfaces of fibres. Incomplete spreading also produces interfacial defects and results in stress concentration around the defects when an adhesive bond is stressed. Moreover, starch is more brittle than PVA, and the internal stresses of starch layers must be greater as compared with those of PVA

layers. For this reason, the adhesive bond will fracture under lower applied loads. It might be the swollen particles and brittleness of starch that make the bonding strength decrease in the case of higher molecular weight of PVA. On the other hand, the viscosity of the starch used is greater than that of PVA 0599. Increase in paste viscosity favours the adsorption of sizing agents onto the surfaces of fibres, and benefits the enhancing of the adhesion. With the increased viscosity of the paste, the amount of the sizing agents adsorbed rises, and the adhesion can be expected to increase in the situation of incorporating starch into the PVA ingredient if the degree of polymerisation is as low as 500.

The optimum condition for adhesion based on wettability is that the polarities of the adhesive and the adherent are equal [16]. This means that a strong bond may be obtained when the adhesive and adherent are either polar or nonpolar; in addition, polar/nonpolar pairs never form strong adhesion. PVA, starch and cotton are all polar polymers, whereas polyester is a nonpolar material. Undoubtedly, according to the adhesion evaluation on wettability alone, strong adhesion would be achieved between cotton fibres and PVA or PVA-starch blends. As for polyester/PVA or PVA-starch blends, weak bonding should be logical. However, the experimental data is contradictory. This is mainly due to the length of fibres used as substrates. The length of polyester fibres is much longer than that of cotton ones. The loads transferred through a boundary between fibres and adhesive layer are enhanced with the increase of the fibre length [16]. For this reason, the maximum strength and the work-to-break increase.

■ Summary

1) The molecular structures of PVA influence the adhesion of both PVA and PVA-starch blends to polyester, cotton, and polyester/cotton fibres.

2) For a pure PVA sizing agent, the adhesion increases with the increase of molecular weights of PVA, and a maximum effect in adhesion is nearly reached when the degree of polymerisation equals 1700. The degree of alcoholysis of PVA shows much less effect on adhesion than the degree of polymerisation does.

3) When PVA-starch blends are used, the variation in the adhesion caused by the molecular structures of the PVA ingredient is less than that of PVA alone. The adhesions of the blends to fibres increase initially with increasing the degree of polymerisation of PVA. However, the adhesion does not obviously increase further if the degree of polymerisation exceeds 1700. Compared with the pure PVA ingredient, the adhesion of PVA-starch blends decreases when the degrees of polymerisation of PVA equal 1700 and 2400, and rises if the degree of polymerisation is as low as 500. Therefore, incorporation of starch into PVA damages the adhesion of the blends for the PVA ingredient with the higher molecular weight, but favours the adhesion with the lower molecular weight. The degree of alcoholysis does not show any marked influence on the adhesion of the blends to the fibres.

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