

Effect of Acrylate Constituent Units on the Adhesion of Polyacrylate Sizes to Fiber Substrates

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ABSTRACT: The influences of chemical structure of (meth)acrylate monomers, including the carbon atom number of alkyl ester groups and the α -methyl group, on the adhesion of polyacrylate sizes to all-polyester, pure cotton, and polyester/cotton blend fiber substrates are investigated by using an impregnated roving method for warp sizing. The adhesion is evaluated in terms of the bonding strength, breaking extension, and work of break of a slightly sized roving. The polyacrylate sizes are prepared through free radical copolymerization of (meth)acrylates with acrylic acid in ethanol. It was found that the adhesion is strongly affected by the structure of acrylate monomers. The adhesion enhances with increasing the carbon atom number of alkyl

ester side chains of acrylates, whether or not it is an acrylate or a methacrylate. The α -methyl does not favor the adhesion to polyester fibers, but favor to polyester/cotton blend fibers. Moreover, the molar ratio of butyl acrylate to acrylic acid is also considered. Excessively lowering the amount of acrylate or acrylic acid damages the adhesion. A favorable molar ratio of butyl acrylate to acrylic acid is found to be about 60 : 40. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3016–3022, 2004

Key words: acrylic copolymer; warp sizes; constituent unit; adhesion; bonding strength

INTRODUCTION

Warp sizes are the polymeric substances that are applied to warp yarns for the improvement of their weavability. By means of impregnating with size paste, the warp yarns are penetrated and coated. The operation brings about the increment of breaking strength and abrasive resistance of sized yarns, while the hairiness of warp yarns is decreased. Consequently, the incidence of warp breaking during weaving operation is reduced.

Sufficient adhesion to fiber substrates is one of the essential demands for a sizing agent.^{1,2} The main function of the adhesion can be classified into two aspects. One is the adhesion of the fibers in warp yarn for increasing the yarn strength. Another is the adhesion of hairiness onto the body of warp yarns by forming a sizing film around the yarns. Therefore, the adhesion behavior of sizing agent influences the physical and mechanical properties of sized yarns and determines how heavily a warp yarn must be sized.³ For this reason, the behavior has received more and more attention recently. A great deal of research has and is being done concerning this field.^{1–7}

Polyacrylate sizes are one of the most important and useful ingredients in warp sizing. They possess excellent adhesion capacity to synthetic fibers compared with starches and polyvinyl alcohol. The excellent adhesion makes them suitable for enhancing the adhesion behavior of blended sizing pastes. Consequently, they are often used with other sizing agents for sizing a large variety of synthetic yarns, filaments, and synthetic/cellulose blend spun yarns. Polyacrylate sizes are the copolymers of various acrylates with unsaturated acids mainly through solvent⁸ or emulsion polymerizations.^{9,10} The most commonly used acrylate monomers include methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate, and butyl methacrylate. Although the reactivity ratios of the above monomers with acrylic acid are known to be influenced by reaction solvents^{11–13} to some extent in free radical copolymerization, solvent copolymerization is also one of the most commonly used methods for the preparation of polyacrylate sizes.

It is as well to emphasize that the structure of acrylate constituent units in polyacrylate copolymers appears to play a very important role on the adhesion to fiber substrates. If the adhesion dependence of structure of these most commonly used acrylate monomers were known, it would be very helpful in the choice of the aforementioned monomers in the design and production of polyacrylate sizes. Unfortunately, no inves-

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tigation has taken this problem into serious consideration, even though the sizing agents have been applied to warp sizing for many years. For this reason, the object of this investigation is to study the contribution of each aforementioned monomer to adhesion. Furthermore, the effects of chemical structure of acrylate monomers on the adhesion of polyacrylate sizes are obtained.

EXPERIMENTAL

Materials

Methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), methyl methacrylate (MMA), butyl methacrylate (BMA), and acrylic acid (AA) were all chemically pure reagent grades and were used directly without further purification. Benzoyl peroxide (BPO), analytical reagent grade, was obtained from the Chemical Plant of Hubei University (Hubei, China) and was stored in a refrigerator until use. Ethanol, acetone, ammonia liquor, and sodium hydroxide were all analytical reagent grades and were used as received.

Roving materials such as pure cotton roving (623 Tex, twist factor: 65.0), all-polyester roving (300 Tex, twist factor: 53.8), and polyester/cotton blend roving (460 Tex, blending ratio of polyester to cotton: 65/35, twist factor: 62.0) were obtained from 3509 Textile Factory (Hanchuang, Hubei Province, China). The parameters of polyester fibers in above roving were 38 mm \times 1.55 dtex and 30 mm \times 1.72–1.78 dtex for the cotton fiber.

Synthesis of acrylic copolymers

The copolymerization of the acrylates with acrylic acid was carried out in ethanol solution in a 500-mL four-necked flask. The flask was equipped with a mechanical stirrer, a thermometer, a condenser, and a dropping funnel and was immersed in a thermostatically controlled oil bath. BPO (0.6 g) was dissolved in 100 g of acrylate–acrylic acid blend monomer solution at room temperature. The molar ratio of acrylate to acrylic acid was varied over a range of 80 : 20 to 40 : 60. Ethanol (160 mL) was added into the flask and heated to slightly refluxing. The initiator containing monomer solution (40 mL) was then charged. Forty minutes later, the remaining initiator–monomer solution was added continuously through the dropping funnel at such a feed rate that the addition was completed uniformly in about 2 h. The initiator (0.2 g) was charged 1 h after the monomer addition was completed. The copolymerization was carried out under continuous stirring and under reflux for 6 h. About 30 mL of reaction products was then taken for the subsequent analysis of residual monomer and copolymer compo-

sitions. The remaining products were neutralized with 10% ammonia liquor when the temperature was decreased to about 60°C. After 200 mL of distilled water was added into the flask, the product was evacuated with a water aspirator to eliminate ethanol solvent from the product. Finally, the product was diluted with distilled water to about 360 mL.

Determination of acrylic copolymers

Conversion of monomer

Conversion of monomer (%) expresses a weight percentage of the synthetic copolymer to the monomers charged.^{14–16} The amounts of residual monomers in aqueous polyacrylate sizes can be titrated by a bromination method. The method for the determination of residual monomers in the sizes was regulated by the Professional Association for Cotton Spinning and Weaving. The principle of this method is that double bonds of the monomers react with Br₂, which is derived from the oxidation of HBr with KBrO₃, the residual bromine then acts with iodine, and finally the excessive iodine is titrated with sodium thiosulfate. Since the residual monomers are dissolved in aqueous sizes, the method has been practically used for the determination. The conversion of monomer was calculated as follows:

Conversion of monomer (%)

$$= (1 - W_r/W_0) \times 100\%$$

where W_r and W_0 are the weights of the residual monomer and the monomer charged, respectively. The weight of the residual monomer was titrated^{16,17} when the copolymerization was just completed.

Glass transition temperature of acrylic copolymers

The glass transition temperature (T_g) of the copolymers was calculated according to following equation:

$$T_g = T_{g1} \beta_1 + T_{g2} \beta_2$$

where T_{g1} and T_{g2} are the glass transition temperatures of corresponding homopolymers of polyacrylate and polyacrylic acid. β_1 and β_2 are the weight fractions of the corresponding constituent units measured in the copolymers, respectively.

Titration of carboxyl groups

About 10 g of the copolymers (before neutralization) was dried under vacuum at 80°C to dryness, washed with distilled water, and dried again under the same conditions. Dried copolymer (0.5 g) was then taken, exactly weighed, and dissolved in 50 mL of ethanol

(the methacrylate-containing copolymers were dissolved in the same volume of acetone). The solutions were titrated¹⁸ using a 0.1 M sodium hydroxide by adding two drops of 0.1% phenolphthalein solution as indicator. The titration was carried to the first pink color that persisted for 10 s.¹⁹ The amounts of (meth)acrylate constituent units were calculated by deducting the amounts of acrylic acid unit from the corresponding copolymers.

Apparent viscosity

The apparent viscosity of the polyacrylates was measured by a rotary viscometer (NDJ-79) with a shear rate of $1,850 \text{ s}^{-1}$. The polyacrylate products were diluted with distilled water to a concentration of 4%, and the apparent viscosity of the diluted polyacrylates was determined at room temperature.

Solid content

Solid content of the polyacrylate products was determined by a weight method. Exactly weighed sample (15–20 g) in weighing bottle was placed in an oven, dried to a constant weight, and exactly weighed again. The weight percentage of the residual sample to the total one was expressed as solid content of the products.

Measurement of adhesion

Preparation of sized roving samples

A definite amount of the product containing 20 g (dry weight) of polyacrylate sizes was diluted with distilled water to 1,000 mL. The dilute solution was transferred into a flask and heated with mechanical stirring to 95°C. The heated solution was poured into a metal pan, which was kept on a water bath of 95°C. The roving that was carefully wound onto a special frame^{1,2} was impregnated with the solution for 3–5 min. The impregnated roving then was cut with scissors, clamped with spring clips, hung on a rope, and dried by air. Finally, the roving samples were collected for the measurement of mechanical behaviors.

Mechanical behaviors of sized roving

The sized roving samples were determined after they had been kept at 65% relative humidity and 20°C for 48 h. The mechanical behaviors of the roving were measured on INSTRON 5566 with an initial chuck-distance of 200 mm. For every sample, more than 20 replicates were measured, and the data were collected for calculating the mean value of the behaviors only after the abnormal values had been rejected by statistical analysis.

RESULTS AND DISCUSSION

The composition of a copolymer is generally different in quantity from the composition of monomer feed from which it is produced, because it rarely happens that both reactivity ratios of monomers equal unity. The reactivity ratios, r_1 and r_2 , of the copolymer pairs of (meth)acrylates and acrylic acid are shown as follows: for MA (M_1) and AA (M_2) in methanol,¹¹ $r_1 = 2.2$ and $r_2 = 0.1$; for BA (M_1) and AA (M_2) in ethanol,²⁰ $r_1 = 1.07$ and $r_2 = 0.58$; for MMA (M_1) and AA (M_2) in *tert*-butyl alcohol,¹³ $r_1 = 4.32$ and $r_2 = 0.27$; and for BMA (M_1) and AA (M_2) in ethanol,²⁰ $r_1 = 3.67$ and $r_2 = 0.29$. The two monomer reactivity ratios are different, that is $r_1 > 1$ and $r_2 < 1$, hence the (meth)acrylates are more reactive than acrylic acid toward propagating species. Moreover, the products of the reactivity ratios of methacrylates and acrylic acid tend to be unity, which means that the copolymerizations are nearly ideal, and for the monomer pairs of acrylates and acrylic acid, the products is $r_1 r_2 < 1$. As the product of $r_1 r_2$ decreases from unity toward zero, there is an increasing tendency toward alternation.²¹ The independent homopolymerizations of the two monomers should not occur since neither r_1 nor r_2 tends to infinity.

Warp sizing requires that sizes must be soluble or dispersible in water. It is no doubt that the solubility depends on the molar ratio of the hydrophobic/hydrophilic units. Based on the values of reactivity ratios, (meth)acrylates tend to be incorporated into the copolymer chains, whereas acrylic acid is incorporated individually if a single-step approach is employed. This causes a preferential depletion of (meth)acrylates and results in a formation of the initial copolymers with a large proportion of (meth)acrylate units. To produce the copolymers with relatively narrow composition range from their corresponding monomers, therefore, a stepwise approach was used for the synthesis of the copolymers. It means that the feed monomers are in the same ratio as in the copolymer being produced and at the same rate the copolymer is formed. This is the simplest way to maintain the concentrations of each monomer and the initiator constant when the copolymerizations enter a steady state. This technique has been used for the industrial production of polyacrylate sizes for many years. In this way, the acrylic comonomers we prepared are water soluble except the poly(MMA-*co*-AA), which is steadily water dispersible.

To measure the composition ranges of a MMA-AA copolymer, Askill and Gilding¹⁸ withdraw, in time intervals, the samples in the process of copolymerization until the reaction is terminated. They determined the molar percentages of carboxyl in the acrylic acid units and gave the composition ranges of the copolymers formed at different conversions. The method

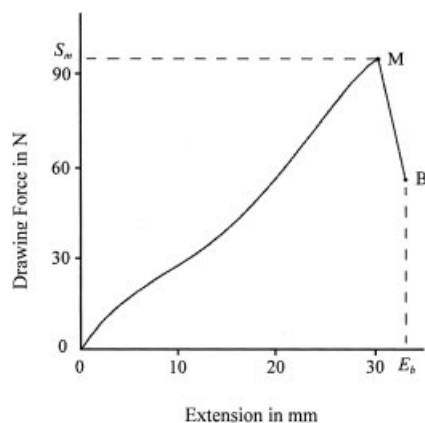


Figure 1 A typical drawing curve of slightly sized roving

was adequate for the analysis of early samples, but became less useful as polymer content increased¹⁸. For this reason, this method is also not adequate for analyzing the composition ranges of the copolymers we prepared through a single-step approach. Furthermore, the composition range is never the same as the distribution of constituent units. On the other hand, however, after the copolymerizations were completed, the main difficulties in experiments for determining the distribution of constituent units in (meth)acrylate-acrylic acid copolymers is how to choose the solvents that are used to grade the composition fractions of the acrylic copolymers. It is difficult to search two solvents, one used as solvent for (meth)acrylate constituent units and as precipitant for acrylic acid unit, another used as solvent for acrylic acid unit and as precipitant for (meth)acrylate units, and at same time have the two solvents be miscible. Furthermore, it is less adequate to use gel permeation chromatography for the determination, because the (meth)acrylate and acrylic acid units do not have appropriate ultraviolet absorbance, hence the changes of the refraction index include the variation of concentration and the distribution of the constituent units. It is difficult to distinguish the influences of the two factors.

It should be noted that warp sizes are a kind of temporary adhesive in textile operation. Easy flow is a necessary behavior since it must penetrate into the body of warps to increase the breaking strength and abrasion resistance of sized yarns. It is generally preferable that the sizes have relatively low molecular weights. Consequently, the usual measures for eliminating the oxygen from the reactants are not frequently taken both in laboratory and in industrial preparations of polyacrylate sizes.

A typical tensile curve of the sized roving is shown in Figure 1. Points B and M are the breaking point and maximal drawing force point. S_m and E_b are corresponding to the maximal force and breaking extension of the roving. The S_m values of the sized roving indicate the bonding strength of sizing agents and are used to represent the adhesion capacity of sizes to fiber substrates. The index has been used in many studies.^{1,2,4,5,7} The larger the S_m the better is the adhesion. Work of break (W_b) of the roving expresses an ability of the roving to resist drawing break by bonding. Consequently, it is also a measurement of the adhesion. The E_b could be used to evaluate the extension ability^{1,2} or toughness of the agents at room temperature. The higher the E_b value, the better the extensile ability. The measured values of the polyacrylate sizes are given in Table I.

Effect of acrylate structure on adhesion

The effects of acrylate monomers on the adhesion of polyacrylate sizes to fiber substrates are shown in Tables II–IV. It could be clearly seen that the molecular structure of (meth)acrylate units does play an important role on the adhesion and on the material toughness. No matter what type of these fiber substrates is used, the maximal strength, breaking extension, and work of break are increased with increasing the carbon atom number of alkyl ester groups in acrylate constituent units. This suggests that the bonding strength and material toughness are raised with the increase of the carbon atom number. Moreover, the

TABLE I
Characterization of Polyacrylate Sizes Prepared

Polyacrylate sizes	Molar ratios of acrylate to acrylic acid in copolymers		Conversion of monomer (%)	Solid content (%)	Apparent viscosity (mPa/s)
	Monomer Fed	Measured			
P(MA/AA)	60 : 40	66.4 : 33.6	98.53	30.67	5.5
P(EA/AA)	60 : 40	63.7 : 36.3	95.62	32.87	4.2
P(BA/AA)	40 : 60	41.2 : 58.8	97.28	29.84	3.8
P(BA/AA)	60 : 40	63.0 : 37.0	97.26	26.25	4.8
P(BA/AA)	80 : 20	82.9 : 17.1	97.67	27.50	2.6
P(MMA/AA)	60 : 40	65.5 : 34.5	91.57	25.83	14.4
P(BMA/AA)	60 : 40	61.8 : 38.2	92.57	30.91	3.8

TABLE II
Influence of Acrylate Constituent Units on the Adhesion to All-polyester Fiber

Type of acrylate unit	Maximum strength		Breaking extension		Work of break	
	S_m (N)	CV (%)	E_b (mm)	CV (%)	W_b (J)	CV (%)
MA	84.96	6.58	26.20	4.66	1.056	11.26
EA	104.55	4.59	30.59	3.08	1.477	7.95
BA	104.75	4.48	30.65	2.64	1.488	7.19
MMA	68.19	7.14	23.93	4.07	0.846	13.02
BMA	92.42	5.07	28.42	3.92	1.222	8.76

The molar ratio of feed (meth)acrylates to acrylic acid was 60 : 40, CV, coefficient of variation.

α -methyl also has much effect on the adhesion and on the toughness of the sizing agents. The presence of the α -methyl did not favor the enhancement of the adhesion to polyester fibers, but it favored the adhesion to polyester/cotton blend fibers. In the case of pure cotton fibers as bound substrate, neither of these opposite observations could be found. The contribution of (meth)acrylate constituent units for raising the adhesion to pure cotton follows the order: BA > BMA > EA > MMA > MA. The type of fibers or bound substrates showed a dominant effect on the adhesion. Among the three types of fibers considered, all-polyester fibers achieve the highest adhesion whereas pure cotton achieves the lowest. Therefore, the polyacrylate sizes containing a large amount of acrylate constituent units are especially suitable for sizing all-polyester yarns from the viewpoint of adhesion. It is unfavorable for these polyacrylates to be applied to pure cotton yarns or to the blend yarns containing a great quantity of cotton fibers.

To elucidate the experimental results, the diffusion theory of adhesion and the characteristics of both polyacrylate sizes and fibers should be taken into consideration. The diffusion theory of adhesion pertains in particular to the adhesive bonding of polymer to polymer. In essence, the theory states that, during the adhesive bonding process, segments or portions of the polymer in the adhesive diffuse into the polymeric substrates and *vice versa*.²² The bonding strength strongly depends on the nature and movability of segments or portions of polymeric adhesives. As it is well known, with the increase of carbon atom number

of alkyl ester groups in (meth)acrylate units, the T_g of polyacrylates decreases, and the flexibility and movability of the copolymer backbone or segment increases. Furthermore, the length of the alkyl ester side chains rises with the increase of the carbon atom number. Enough length would be favorable for the relatively short side chains to diffuse into the amorphous regions of bound fibers, especially when the sizes and fibers have same polarity. Consequently, the diffusion is promoted and the bonding strength would be enhanced with increasing the carbon atom number, whether or not the α -methyl is involved. Acrylate polymers have a lower T_g than methacrylates for a given ester group. The increased movability makes the diffusion easy, which induces enhanced bonding strength. For this reason, the acrylate copolymers show higher bonding strength to all-polyester fiber than the methacrylate ones. However, the change in T_g caused by α -methyl cannot explain the situations in which pure cotton or polyester/cotton blend fibers were used as bonding substrates.

Another viewpoint of diffusion theory is²³ that the bonding strength between two polymers is closely related with their mutual solubility, which is determined by the polar resemblance of adhesives and substrates. If the two polymers are all polar or nonpolar, relatively high bonding strength can be achieved. Otherwise, it is usually impossible to achieve substantially high bond strength. It should be noted that, although there is a certain amount of hydrophilic groups along the macromolecules, the majority of the copolymers is composed of nonpolar acrylate units.

TABLE III
Influence of Acrylate Constituent Units on the Adhesion to Polyester/Cotton Blend Fibers

Type of acrylate unit	Maximum strength		Breaking extension		Work of break	
	S_m (N)	CV (%)	E_b (mm)	CV (%)	W_b (J)	CV (%)
MA	52.02	7.21	20.31	7.91	0.609	12.17
EA	76.35	8.95	25.41	7.68	1.045	15.60
BA	84.00	8.26	27.39	5.07	1.151	12.60
MMA	69.62	7.21	24.15	5.63	1.020	11.08
BMA	86.95	3.50	27.95	2.93	1.282	5.23

The molar ratio of feed (meth)acrylates to acrylic acid was 60 : 40. CV, coefficient of variation.

TABLE IV
Influence of Acrylate Constituent Units on the Adhesion to Pure Cotton Fiber

Type of acrylate unit	Maximum strength		Breaking extension		Work of break	
	S_m (N)	CV (%)	E_b (mm)	CV (%)	W_b (J)	CV (%)
MA	8.71	17.01	12.53	6.03	0.066	16.67
EA	21.71	15.86	13.33	11.14	0.155	27.10
BA	27.80	14.33	12.41	7.96	0.156	21.15
MMA	19.36	20.82	13.31	9.12	0.126	29.37
BMA	26.17	8.22	14.88	6.91	0.176	17.05

The molar ratio of feed (meth)acrylates to acrylic acid was 60 : 40. CV, coefficient of variation.

Therefore, the highest bonding strength was obtained for all-polyester substrate, while the lowest one was found for pure cotton.

Effect of BA amount on adhesion

Table V demonstrates the influences of the amount of BA unit on the adhesion to all-polyester, pure cotton, and polyester/cotton blend fibers, respectively. The molar ratio of BA to AA is varied over a range from 40 : 60 to 80 : 20. No matter what type of these fibers is used as bound substrates, the molar ratio also plays an important role on the adhesion. The maximal drawing force enhances with increasing the molar ratio from 40 : 60 to 60 : 40. A sharp decrease in S_m is observed when the molar ratio is further raised to 80 : 20. It seems that a maximal effect on enhancing the bonding strength was reached at nearly 60 : 40. The tendency of their variations follows the same as that of S_m . Consequently, the adhesion of polyacrylate sizes is directly correlated with the molar ratio. The adhesion reached a maximum at the molar ratio of about 60 : 40 for the aforementioned three types of fiber substrates.

Undoubtedly, the T_g of the copolymeric sizes decreases with the increase of BA unit. The enhanced movability promotes the access and diffusion of the copolymer molecules to or into fiber substrates. The access and diffusion to polyester or cotton substrates

are possible because the macromolecules contain both polar and nonpolar constituent units. For this reason, the bonding strength would be increased. But at a still higher molar ratio of BA to AA, the number of carboxylic groups is greatly decreased and the solubility of the acrylic copolymer is abruptly reduced. It is as well to emphasize that solubility is also important for water-based sizes, because a badly dissolved paste is poor for the adsorption, spreading, and access, which supply a base for the diffusion between the two polymers. It is more likely that such an abrupt decrease in bonding strength is caused by the decreased solubility of polyacrylate sizes.

CONCLUSION

The present investigation shows that the adhesion of polyacrylate sizes to fibers are strongly dependent on the molecular structure of acrylate constituent units, the molar ratio of (meth)acrylates to acrylic acid, and the nature of fiber substrates. The adhesion is significantly raised by increasing the carbon atom number of the alkyl ester groups in acrylate and/or methacrylate units, no matter what types of fibers are used as bound substrates. α -Methyl in the constituent units does not favor the enhancement of the adhesion to polyester fiber, but it favors it to polyester/cotton blend fibers. Among the three types of fibers, polyacrylate sizes

TABLE V
Effect of BA Amount on the Adhesion to All-polyester, Pure Cotton, and Polyester/Cotton Blend Fibers

Types of fiber substrates	Molar ratios of BA to AA in copolymers		Maximum strength		Breaking extension		Work of break	
	Fed	Measured	S_m (N)	CV (%)	E_b (mm)	CV (%)	W_b (J)	CV (%)
All Polyester	40 : 60	41.2 : 58.8	95.27	10.54	29.69	8.04	1.256	19.51
	60 : 40	63.0 : 37.0	104.26	4.48	30.15	2.64	1.418	7.19
	80 : 20	82.9 : 17.1	37.98	14.87	24.90	6.00	0.725	22.20
Polyester/Cotton	40 : 60	41.2 : 58.8	67.31	10.91	24.33	7.93	0.791	17.83
	60 : 40	63.0 : 37.0	84.00	8.26	27.39	5.07	1.151	12.60
	80 : 20	82.9 : 17.1	27.40	14.58	20.70	15.20	0.863	23.17
Pure Cotton	40 : 60	41.2 : 58.8	22.18	15.61	13.38	11.12	0.148	23.56
	60 : 40	63.0 : 37.0	27.80	14.33	12.41	7.96	0.156	21.15
	80 : 20	82.9 : 17.1	5.38	19.31	12.59	17.14	0.130	38.19

CV, coefficient of variation.

show the highest adhesion to polyester fibers and the lowest to cotton. Excessively lower amounts of acrylate or acrylic acid damage the adhesion capacity. A favorable molar ratio of BA to AA for achieving higher adhesion is found to be about 60 : 40. The results obtained will greatly increase the ability of size engineers to tailor-make polyacrylate sizes with desired adhesion capacity to fibers.

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