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Effects of alkyl chain length of acrylates on sizing properties of grafted feather keratin

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In this study, sizing properties of grafted feather keratin for high polyester content warp yarns have been improved by preparing a series of feather keratin-*g*-poly(acrylic acid-co-acrylate) through grafting acrylate monomers with various alkyl chain lengths and hydrophilic monomer [acrylic acid (AA)] onto molecular chains of native feather keratin. The feed molar ratio of AA/acrylate is kept constant during the preparation. Effects of alkyl chain length of acrylate monomers on sizing properties of feather keratin-*g*-poly(acrylic acid-co-acrylate) to polyester/cotton(65/35) blended warp yarns has been studied in terms of tensile strength & elongation, abrasion resistance, and hairiness. The grafting of acrylates onto the molecular chains of feather keratin significantly improves the sizing properties of grafted feather keratin. With the increase in alkyl chain length, the tensile strength, tensile elongation, and abrasion resistance of the sized yarns are improved, while the hairiness amount is increased. Acrylate monomers with different alkyl chain lengths during the preparation of grafted feather keratin sizes can be selected according to various requirements for high polyester content warp yarns.

Keywords: Acrylic acid, Alkyl chain length, Cotton, Feather keratin, Graft copolymerization, Polyester, Sizing properties

1 Introduction

Three to four billion pounds of feather by-products are generated from poultry industry in USA alone every year[1], which are often regarded as solid wastes and simply disposed by incineration or deep burial. Keratin is the main component of feather by-products and is wasted idly in the common disposition. It is estimated that about 2.2 billion pounds of sizing agents are consumed annually in textile industry globally[2]. It is important for textile scientists to develop more kinds of cheap, reproducible and environment-friendly sizing agents from agricultural by-products, such as chicken feathers, soybean meals and cotton linters, after appropriate physical or chemical modifications.

Native feather keratin contains many cysteine residues and exhibits poor water-solubility due to large amounts of disulfide bonds. Sizing operation is based on an aqueous paste nowadays[3] and the poor water-solubility prevents native feather keratin from becoming a qualified sizing agent. In 2016, Li *et al.*[4] prepared a new kind of water-soluble chemically-modified feather keratin through grafting of hydrophilic monomer [acrylic acid (AA)] onto molecular chains of native feather keratin. As compared to the traditional method of adding alkaline liquor to dissolve feather keratin[5], the graft modification endows the keratin with good water-solubility under neutral condition, avoids many usage problems, and provides a good base to the use of feather keratin as a sizing agent for natural fibre yarns.

Polyester fabric exhibits many good mechanical and wearable properties and is one of the most important materials for textile and clothing industry. However, polyester fibre lacks polar groups, has high hydrophobicity & crystallinity, contains many ester groups, and belongs to non-polar polymer. Such characteristics lead to the difficulty in sizing operation for polyester yarns. As a result, textile mills do not have many choices from existing sizing agents for high polyester content warp yarns. Only a few traditional sizes, such as esterified starch and partially alcoholysized PVA, are used for polyester yarns. Like many sizing agents having strong polarity, feather keratin-graft-polyacrylic acid (feather keratin-*g*-PAA) shows poor sizing performance for polyester yarns also due to large difference in molecular polarity of polyester fibre and feather keratin-*g*-PAA.

Considering the molecular structure of sizing object (e.g. polyester fibres), in the present study, acrylate monomers have been grafted with various

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alkyl chain lengths [i.e. methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA) and ethylhexyl acrylate (EHA)] onto native feather keratin, in order to introduce a number of ester groups onto molecular chains of the keratin, decrease molecular polarity of the keratin and increase the affinity of grafted keratin sizes to polyester fibres. In order to maintain good water-solubility of the feather keratin, AA monomers are also graft copolymerized onto the keratin. Feed molar ratio of AA/acrylate is kept constant to get rid of influence of the amount of AA and acrylate on sizing properties of feather keratin-*g*-poly(acrylic acid-co-acrylate). In our previous study, MA and AA monomers with various molar ratios in the range of 10:90 - 30:70 were grafted onto the molecular chains of native feather keratin under the same monomer concentration so as to obtain the optimum feed molar ratio. A series of feather keratins-*g*-P(AA-co-MA) is prepared to size polyester/cotton(65/35) warp yarns. Finally, influence rule of alkyl chain length of the acrylates on sizing properties of the grafted feather keratin for high polyester content warp yarns has been proved up in terms of apparent viscosity, viscosity stability of sizing paste, mechanical properties of sizing film, tensile properties, abrasion resistance and hairiness amount of sized polyester/cotton(65/35) blended yarns.

2 Materials and Methods

2.1 Materials

Native feather keratin was extracted from chicken feathers through alkaline hydrolysis in lab, freeze dried, pulverized and stored in desiccator. Acrylic acid (AA), methyl acrylate (MA), ethyl acrylate (EA), butyl acrylate (BA), ethylhexyl acrylate (EHA), potassium peroxodisulfate ($K_2S_2O_8$), sodium bisulfite ($NaHSO_3$) and paradioxybenzene purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) were used as monomers, oxidant, reductant and terminator in the graft copolymerization respectively. All the reagents used were chemically pure. The polyester/cotton(65/35) warp yarns (13.0 tex) used for sizing experiment were obtained from Weifang Guanjie Textile Co. Ltd (Weifang, China).

2.2 Graft Copolymerization

The native feather keratin hydrolysates were dispersed in distilled water initially. Then, the dispersion was transferred into a four-neck flask. Acetic acid was added to adjust the keratin dispersion to *p*H 4.0. The flask was maintained at 60°C in a water bath. The mixture was then deoxygenated by passing N_2 for at least 30 min before adding reactants. The initiators including $K_2S_2O_8$ and $NaHSO_3$ were dissolved in distilled water respectively. The oxidant solution, reductant solution, AA and acrylates with different alkyl chain lengths (MA/EA/BA/EHA) were added into the flask simultaneously. In order to obtain similar grafting ratios of feather keratin-*g*-poly(AA-co-acrylate), the monomer concentrations (w/w, the sum of AA and acrylate monomers/feather keratin) were not equal; the values were 40, 46, 52 and 52% for the acrylates MA, EA, BA and EHA respectively. Our previous study showed that the yarns sized by the feather keratin-*g*-P(AA-co-MA), of which feed molar ratio of MA/AA monomers was 1:4, exhibited better mechanical properties and hairiness-elimination capacity. Therefore, feed molar ratio of AA/acrylate was kept constant at 1:4 in the study. The addition was completed in 10-20 min and final bath ratio of feather keratin to water was 1:7. The concentration of $K_2S_2O_8$ was 0.078 mol/L and the molar ratio of $K_2S_2O_8/NaHSO_3$ was 2:3. The graft copolymerization was carried out under vigorous stirring using a mechanical stirrer at 1000 rpm under nitrogen atmosphere for 3.5 h. About 2% of paradioxybenzene solution was added to terminate the copolymerization. The product was filtered and then washed thoroughly with distilled water. Finally, the product was freeze dried and stored in desiccator.

2.3 Measurement of Grafting Parameters

The amount of residual AA and acrylates with different alkyl chain lengths after grafting was determined by titrating the double bonds of the monomer in the filtrate after the graft copolymerization. Monomer conversion (MC) is the weight percentage of the polymers formed (i.e. grafted branches and homopolymers) to the total monomers (AA and acrylate) added. Grafting ratio (GR) is the weight percentage of PAA and polyacrylate (PA) branches grafted onto feather keratin to the keratin. The detailed titration process and calculation of MC and GR were the same as per the Jin's report[6].

2.4 ^{1}H-NMR Characterization

Proton nuclear magnetic resonance (^{1}H-NMR) was used to verify the grafting of PAA and PA onto the feather keratin. Native feather keratin, feather keratin-*g*-PAA, feather keratin-*g*-P(AA-co-MA) and feather keratin-*g*-P(AA-co-EA) were characterized by ^{1}H-

NMR in DMSO solvent using an AVAMCE III 400MHz digital NMR spectrometer (Bruker Co. Ltd. Switzerland). The concentration of feather keratin solution was about 1% (w/w). The grafted feather keratins were purified thoroughly and the homopolymers (PAA and PA) which adhered on the grafted keratins were removed completely.

2.5 Measurement of Apparent Viscosity

Apparent viscosity of the grafted feather keratin paste was measured using an NDJ-79 viscometer purchased from Electrical Machinery Plant of Tongji University (Shanghai, China). The grafted feather keratin was suspended into neutral distilled water to form 6% (w/w) dispersion. The dispersion was heated and maintained at 60°C under mechanical stirring for 1 h. Apparent viscosity of the keratin sizing paste was then measured with a shear rate of 3500 s^{-1}. Viscosity stability of sizing paste denotes the percentage of viscosity invariability over a period of 3 h. The viscosity was measured after every 0.5 h and the stability was calculated in accordance with the following equation[7]:

$$\text{Viscosity stability (\%)} = (1-\frac{V_{\max}-V_{\min}}{V})\times 100 \quad \ldots(1)$$

where V is the apparent viscosity of paste (the value at 1.0 h); and V_{max} and V_{min}, the maximum and minimum viscosity values at 1.0, 1.5, 2.0, 2.5 and 3.0 h respectively.

2.6 Preparation of Sizing Film and Measurement on Its Tensile Properties

A rectangular glass board was put on a triangular shelf and adjusted to level. Then a piece of PET plastic film of the same size was spread on the glass board. An epoxy resin frame was put on the PET film substrate. The paste preparation process for casting sizing film of the grafted feather keratin was the same as used for the measurement of apparent viscosity. The feather keratin paste prepared was decanted onto the PET film substrate. The paste was dried to form a film at room temperature and then the dried feather keratin film was peeled carefully from the PET substrate. The films thus prepared were cut into strips (220mm×10mm) and then conditioned at 65% relative humidity and 20°C for 24 h before evaluation. Tensile strength and elongation of the films were measured on a BZ2.5/TNIS Zwick Material Tester[8]. Twenty samples were measured to obtain the mean value for each parameter.

2.7 Sizing Experiment

Cooking process of the grafted feather keratin sizing paste was the same as described for the measurement of apparent viscosity, except that the concentration of sizing paste was 12% (w/w). The sizing experiment for polyester/cotton(65/35) warp yarns was carried out using a GA392 laboratory single-yarn sizing machine purchased from Jiangyin Tongyuan Textile Machinery Co. Ltd (Jiangyin, China). Sizing style of the machine was single-dip-single-nip. The warp yarns were wound in the machine and the cooked sizing paste was poured into a size box, where it was adjusted to 60°C. Sizing tension was 1.0 N and the running speed of sizing machine was 30 m/min. Hot air and cylinder allied drying style was employed in drying chamber at 110°C. The sized yarns were dried in the chamber for 3 min and finally conditioned at 65% relative humidity & 20°C for at least 48 h before performance tests.

2.8 Measurement of Size Add-on

The measurement was carried out through the alkali-desizing method to estimate size add-on of each series of the sized polyester/cotton(65/35) blended yarns. Ten grams (10 g) of the sized yarns were taken and dried at 105°C for 4 h and exact weight was recorded. The sized yarns were boiled in 400 mL of 2% NaOH solution for 20 min and then taken out to be washed by distilled water thoroughly. Kjeldahl determination was used to ensure that the feather keratin was completely desized from the yarns[9]. Finally, the yarns were dried again at 105°C for 4 h and exactly weighed. The size add-on was calculated according to the following equation:

$$\text{Size add-on (\%)}=\frac{x_1-[x_2/(1-s)]}{x_2/(1-s)}\times 100\% \quad \ldots(2)$$

where s is the damage ratio of fibres of raw yarns, measured through blank test; and x_1 and x_2, the dry weights of the sized and desized yarns respectively.

2.9 Measurement of Tensile Properties

Tensile strength and elongation of the yarns were determined on a model YG023A electric strength tester purchased from Laizhou Electronic Instrument Factory (Laizhou, China). The initial chuck-distance and drawing speed were 500 mm and 500 mm/min respectively. For every sample, fifty replications were taken and their mean values were obtained.

2.10 Measurement of Abrasion Resistance

The yarns were abraded reciprocatively on an LFY109B electric yarn abrader purchased from Textile Science Research Institute of Shandong Province (Qingdao, China). The yarn abrader has a grinding roller wrapped by a piece of abrasive paper. Before test, the yarn was tensioned by the pull of a 10 g weight tied to one end of the yarn and hanging freely and crossed the roller under constant pressure produced by the weight gravity. Ten yarns can be placed on the grinding roller once in the test. In the abrasion measurement, the grinding roller did reciprocal motion and rotated on its own axis simultaneously. The resistance to reciprocating friction of the sized yarns was evaluated in the reciprocal motion times of the grinding roller until yarn breaking. The values reported were mean of 50 tests for each case. The abrasive material used was W5(06) abrasive paper manufactured by Shanghai Emery Wheel Company (Shanghai, China).

2.11 Measurement of Hairiness Amount

Dense and long hairiness on surface of warp yarns frequently causes unclear shed and high breakage rate. The hairiness (≥ 3 mm) has adverse impact on weaving and is regarded generally as “harmful hairiness”. The amount of yarn hairiness (length 3-9 mm) was evaluated by YG171B-2 hairiness tester purchased from Nantong Sansi Electronic Instrument Factory (Nantong, China). The values reported were mean value of 10 tests for each case. Each test requires a 10 m long yarn with a drawing speed of 30 m/min.

2.12 Statistical Analysis

The data were analyzed using SAS software (SAS Institute Inc., Cary, NC). Tukey’s HSD test was utilized to compare the multiple means in this study. The confidence interval was set at 95% and a ‘p’ value smaller than 0.05 was considered to have a statistically significant difference by Tukey’s HSD test. According to the operation results of the analysis software, small letters (a, b, c) were inserted above or below the data points in Fig. 1. The data points with different small letters were statistically significantly different from each other.

3 Results and Discussion

3.1 Evidence of Grafting

^{1}H-NMR spectra of native feather keratin, feather keratin-*g*-PAA and feather keratin-*g*-P(AA-co-MA), and feather keratin-*g*-P(AA-co-EA) are shown in Fig. 2. Besides characteristic peaks of DMSO (2.5 ppm), residue water (3.3 ppm) in DMSO and native feather keratin (e.g. proton peak of peptide link at 6.5-8.0 ppm) in Fig. 2(a), a new chemical linkage is found in feather keratin-*g*-PAA as compared to that in native keratin. As shown in Fig. 2(b), a new chemical shift peak appearing at 12.2 ppm can be correspondent to the proton peak of carboxyl (-COOH)[10]. As for feather keratin-*g*-P(AA-co-MA) and feather keratin-*g*-P(AA-co-EA), in addition to all the chemical linkages of feather keratin-*g*-PAA, the new chemical shift peaks at 3.5 and 4.0 ppm [Figs 2(c) and (d)] can be attributed to the proton peaks of methyl of methyl ester ($-COOCH_3$)[11] and methylene of ethyl ester ($-COOCH_2CH_3$)[12]. The chemical shift peaks at 12.2, 3.5 and 4.0 ppm indicate the presence of PAA and PA branches on the grafted feather keratins. In addition, the increase in the intensity of alkyl proton peaks ($–CH_2$- and >CH-) appeared in range of 0.9-2.3 ppm [Figs 2(b), (c) and (d)] indicates the presence of PAA and PA branches[11] on the grafted keratins as compared to native keratin.

3.2 Effects of Alkyl Chain Length on Grafting Parameters

Effects of alkyl chain length of acrylates on monomer conversion and grafting ratio of the grafted feather keratin are shown in Table 1. The feather keratin-*g*-PAA has higher grafting ratio than the feather keratin-*g*-P(AA-co-MA). Both the grafted feather keratins have similar monomer conversions when the feed monomer concentration is equal. In order to get rid of influence of grafting ratio and to make fair comparison of application performance of the feather keratin grafted with various acrylates, all

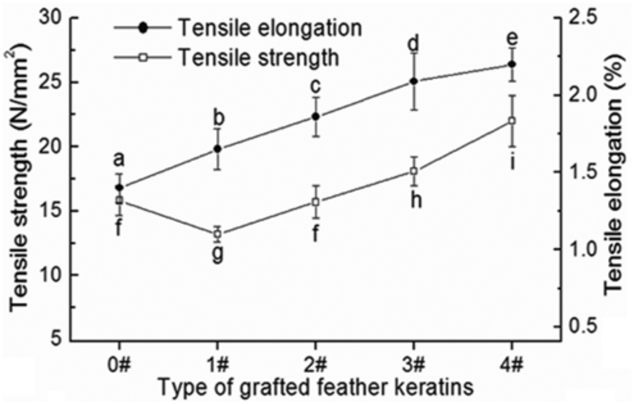

Fig. 1 — Effects of alkyl chain length of acrylates on tensile properties of sizing film [0# - feather keratin-*g*-PAA, 1# - feather keratin-*g*-P(AA-co-MA), 2# - feather keratin-*g*-P(AA-co-EA), 3# - feather keratin-*g*-P(AA-co-BA), and 4# - feather keratin-*g*-P(AA-co-EHA)]

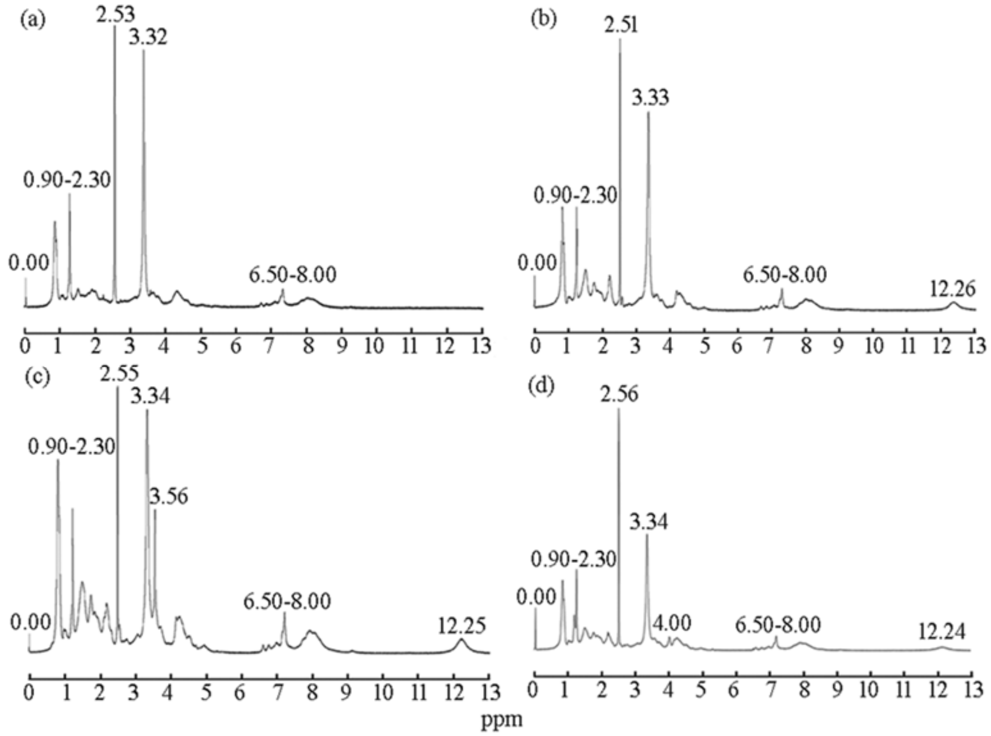

Fig. 2 — ^{1}H-NMR spectra of (a) purified native feather keratin, (b) feather keratin-*g*-PAA, (c) feather keratin-*g*-P(AA-co-MA), and (d) feather keratin-*g*-P(AA-co-EA)

the feather keratin-*g*-poly(AA-co-acrylate) prepared for the tests have similar grafting ratios at 27±1.5%. For acrylates with longer alkyl chain, the higher feed monomer concentration is required so as to obtain similar grafting ratios. In addition, the alkyl chain length has no marked effects on monomer conversions, which are 95±1%.

Among the optimum graft polymerization conditions, enough polymerization time is considered as a sufficient condition for monomer conversion in free radical polymerization to reach a high value. In Li *et al.*[4] study, the optimum graft polymerization conditions for feather keratin substrate and acrylate monomers using $K_2S_2O_8/NaHSO_3$ as redox initiator, such as initiator concentration, molar ratio of $K_2S_2O_8/NaHSO_3$, polymerization temperature and time, have been clearly mentioned. Three and a half hours (3.5 h) is long enough for most acrylate monomers to convert into polyacrylates[13]. Therefore, all the monomer conversions arrive at about 95%, no matter how long the alkyl chain is.

As for grafting ratio, alkyl (methyl or ethyl) of ester group of acrylate obviously occupies much larger space than H atom of carboxyl group of AA. Consequently, when the grafting monomers are in the vicinity of feather keratin radicals, the acrylates are more difficult to be grafted onto the keratin than AA. It is the great steric hindrance that inhibits the grafting of the acrylates. Therefore, the feather keratin-*g*-PAA has higher grafting ratio than the keratins grafted with acrylates when feed monomer concentration is equal. Similarly, the longer the alkyl chains of acrylates, the larger is the space occupied by the alkyl group. The acrylates with longer alkyl chain show more marked steric hindrance effect and are more difficult to be grafted onto feather keratin. Thus, in order to obtain similar grafting ratios of the feather keratin-*g*-poly(AA-co-acrylate), the longer the alkyl chains of acrylates, the higher is the monomer concentration required.

3.3 Effects of Alkyl Chain Length on Paste Viscosity

Effects of alkyl chain length of the acrylates on apparent viscosity and viscosity stability of the grafted feather keratin are also described in Table 1. The feather keratin-*g*-PAA paste possesses higher apparent viscosity and is more stable than all the feather keratin-*g*-poly(AA-co-acrylate) ones. In addition, both the viscosity and its stability of the feather keratin-*g*-poly(AA-co-acrylate) sizing paste decrease with increasing the alkyl chain length.

Feather keratin-*g*-poly(AA-co-acrylate) has fewer PAA branches than the feather keratin-*g*-PAA with

Table 1 — Effects of alkyl chain length of acrylates on grafting parameters and paste viscosity

Grafted FK	Feed monomer concentration, %	Monomer conversion, %	Grafting ratio %	Apparent viscosity mPa·s	Viscosity stability %
FK-g-PAA	40	94.66	29.72	3.25	93.8
FK-g-P(AA-co-MA)	40	95.34	27.47	2.85	91.2
FK-g-P(AA-co-EA)	46	95.10	27.38	2.65	90.6
FK-g-P(AA-co-BA)	52	94.98	26.39	2.40	89.6
FK-g-P(AA-co-EHA)	52	94.38	25.87	2.10	88.1

FK- Feather keratin

similar grafting ratio. PAA branches of the grafted feather keratin contain a number of carboxyl groups, which are hydrophilic and endow the keratin with good water solubility. The fewer the PAA branches, the less is the carboxyl on the molecular chains of the grafted keratin. As a result, the decrease in the amount of PAA branches reduces polarity of the grafted feather keratin and interaction between the keratin and the water molecules. As is well known, apparent viscosity of a polymer solution closely relates to interaction between the polymer and the water molecules. The weaker the interaction, the lower is the apparent viscosity; the feather keratin water solution is not an exception. In addition, it is more probable to form light physical crosslinking between the grafted feather keratin macromolecules when more carboxyl groups are introduced into the keratin[4]. The physical crosslinking can play a positive role in stabilizing the paste viscosity. The decrease in the number of carboxyl groups can reduce the number of the physical cross-links and favor the fluctuation of apparent viscosity of the sizing paste under vigorous shear stirring. Consequently, The feather keratin-*g*-poly(AA-co-acrylate) pastes have lower apparent viscosity and viscosity stability than the feather keratin-*g*-PAA one. It should be noted that viscosity stability is very important for a sizing agent because high stability is the base of a stable size add-on[14].

The experimental results show that increasing alkyl chain length of the acrylates causes decrease in the apparent viscosity and stability of the feather keratin-*g*-poly(AA-co-acrylate) paste. There are two main reasons for the decrease, viz (i) with an increase in the alkyl chain length, side chains of the grafted keratin shrink and their hydrophobicity increases[15], and (ii) longer hydrophobic side chains tend to aggregate in water. The hydrophobicity decreases the intermolecular forces between the grafted keratin and water. Moreover, the longer the alkyl chains of the acrylates, the higher is the molecular weight of constitutional unit of the polyacrylates. All the feather keratins-*g*-poly(AA-co-acrylate) prepared in this study have similar grafting ratios (about 27%), which means that the total weight of the grafted branches (PA & PAA) is nearly the same. Thus, the mole number of the acrylates with longer alkyl chain is smaller. Accordingly, the mole number of AA compatible with the acrylate is smaller due to the constant feed molar ratio of acrylate/AA. It has been interpreted above that decreasing the molar number of AA, i.e. carboxyl groups weakens the interaction between the grafted keratin and the water, and reduces light physical cross-links between the grafted keratin macromolecules. Therefore, both apparent viscosity and viscosity stability of the sizing paste decrease with the increase in alkyl chain length of the acrylates.

3.4 Effects of Alkyl Chain Length on Tensile Properties of Sizing Film

Film coating on sized yarns provides a layer of protection for the yarns and is required to possess good tensile properties, such as high strength and elongation. Therefore, effects of alkyl chain length of the acrylates on tensile properties of the grafted feather keratin film are studied. As shown in Fig. 1, tensile strength of the feather keratin-*g*-PAA film stands in between the feather keratin-*g*-P(AA-co-EA) and feather keratin-*g*-P(AA-co-BA) films, while the elongation is lower than that of all the feather keratin-*g*-poly(AA-co-acrylate) films. With the increase in the carbon chain length of the acrylate, tensile strength and elongation of the feather keratin-*g*-poly(AA-co-acrylate) film keep increasing.

In order to endow feather keratin sizes with water-solubility under neutral condition, it is necessary to graft a number of PAA branches onto the molecular chains of the keratin. However, the grafting of PAA increases polarity of the keratin and probability of the formation of hydrogen bonds simultaneously. The change in property of the keratin can increase tensile strength of the film at the expense of the extension. As a result, the feather keratin-*g*-PAA film has the lowest tensile elongation in all the grafted feather keratin ones. In addition, tensile properties of the film highly depend on film-forming property of the feather keratin water solution. In general, film-forming process of a polymer watersolution can be divided into three stages, namely (i) evaporation of water, (ii) deformation of particles, and (iii) inter-diffusion of polymer macromolecules. The grafting of long and flexible side chains, such as PEHA and PBA branches, can improve film-forming property of feather keratin. There are two main reasons for the improvement. Firstly, the graft copolymer containing long side chains often have good chain flexibility, which favors the inter-diffusion of the macromolecules and helps the 3rd stage to go on smoothly. Secondly, the macromolecules of graft copolymer containing long side chains tend to have orientation arrangement and form a more uniform and integrated film. Therefore, the longer the alkyl chains of acrylates, the better is the film-forming property of the grafted keratin. As a result, tensile properties of the grafted keratin film are improved therewith.

3.5 Effects of Alkyl Chain Length on Mechanical Properties of Sized Yarns

Effects of alkyl chain length of the acrylates on mechanical properties of the polyester/cotton(65/35) blended yarns sized by grafted feather keratins are shown in Table 2. All the mechanical properties of the yarns sized by feather keratin-*g*-PAA, such as tensile strength, elongation and abrasion resistance, are lower than those sized by feather keratin-*g*-poly(AA-co-acrylate). With the increase in alkyl chain length of the acrylates, the mechanical properties of the sized yarns are gradually improved.

As described above, feather keratin-*g*-PAA has strong polarity but polyester fibre belongs to non-polar polymer. The former has low affinity to the latter due to the impossibility of formation of strong adhesion between a polar–nonpolar pair[14]. As a result, the polyester/cotton(65/35) blended yarns sized by feather keratin-*g*-PAA show poor properties. Introduction of PA branches onto the molecular chains of feather keratin can decrease polarity of the grafted keratin. Furthermore, PA and polyester both contain many ester groups. Sizing agents usually have high compatibility with fibres in the case that the former possess a great number of the same functional groups to the latter. Thus, the grafting of acrylates is able to improve sizing properties of the modified feather keratin for high polyester content warp yarns effectively.

Besides the affinity of sizing agents to fibres, the mechanical properties of sizing film should be taken into consideration. Warp yarns are subjected to stretching & bending, are abraded by reed, heddle & shuttle, and keep rubbing against each other during the weaving process. Therefore, as a layer of protection for warp yarns, it is required for sizing film to have good mechanical properties. Figure 1 shows that both tenacity and extension of sizing film of the feather keratin-*g*-poly(AA-co-acrylate) are improved with increasing alkyl chain length of the acrylates. The results of the mechanical tests for the yarns sized by feather keratin-*g*-poly(AA-co-acrylate) are in good agreement with the changes of tenacity and extension of the sizing film. As a result, the longer the alkyl chains of the acrylates, the better are the mechanical properties of the sized yarns.

3.6 Effects of Alkyl Chain Length on Hairiness Amount of Sized Yarns

Effects of alkyl chain length of the acrylates on the hairiness amount of the yarns sized by grafted feather keratins are shown in Table 3. The hairiness amount of the yarns sized by feather keratin-*g*-PAA falls in between that of the yarns sized by feather keratin-*g*-P(AA-co-EA) and feather keratin-*g*-P(AA-co-BA). With the increase in alkyl chain length of the acrylates, the hairiness amount of the yarns sized by keratin-*g*-poly(AA-co-acrylate) continues to increase.

Table 2 — Effects of alkyl chain length of acrylates on mechanical properties of sized yarns

Sizing agents	Size add-on %	Tensile strength N	CV, %	Tensile elongation, %	CV, %	Abrasion resistance, cycles	CV, %
Raw yarns	0	2.36	6.28	8.94	8.55	44	9.98
FK-g-PAA	10.02	2.54	4.54	7.47	7.76	132	8.31
FK-g-P(AA-co-MA)	9.97	2.77	5.72	7.89	8.79	139	8.50
FK-g-P(AA-co-EA)	9.50	2.91	3.75	8.13	5.56	152	9.76
FK-g-P(AA-co-BA)	9.85	2.97	4.10	8.28	6.68	155	9.85
FK-g-P(AA-co-EHA)	9.60	3.36	5.27	8.66	5.86	173	9.00

Table 3 — Effects of alkyl chain length of acrylates on the hairiness amount of sized yarns

Sizing agents	3-4 mm	4-5 mm	5-6 mm	6-7 mm	7-8 mm	8-9 mm
Raw yarns	40.3	22.1	10.8	2.1	1.2	0.7
FK-g-PAA	18.2	6.5	3.0	1.5	0.6	0.1
FK-g-P (AA-co-MA)	8.5	3.2	1.0	0.3	0.2	0
FK-g-P (AA-co-EA)	17.7	6.0	2.7	1.3	0.7	0.1
FK-g-P (AA-co-BA)	22.8	9.7	5.0	1.8	0.7	0.2
FK-g-P (AA-co-EHA)	27.5	13.1	7.7	2.7	1.0	0.5

The hairiness amount of the sized yarns is closely related to apparent viscosity of sizing paste. Sizing paste with low apparent viscosity can easily permeate through the yarns and increase inter-fibre cohesive force. However, excessively low viscosity reduces resistance that the hairiness encounters when warp yarns are going through sizing paste and thus causes less hairiness cling to yarn body. As shown in Table 1, the longer the alkyl chain, the lower is the apparent viscosity of the feather keratin-*g*-poly(AA-co-acrylate) paste. As a result, the sizing pastes of the feather keratins grafted with BA and EHA, which have excessively low viscosity (≤ 2.5 mPa·s), possess low ability to eliminate the hairiness. Besides paste viscosity, the hairiness of the sized yarns is determined by the adhesion of sizes to fibres. Enhancing the adhesion is an effective way to decrease the hairiness amount. As is mentioned above, in the case of similar grafting ratios of the modified keratins and constant molar ratio of acrylate/AA, the total weight of the grafted branches is nearly the same with each other and thus the mole number of the acrylate (ester) with shorter alkyl chain is larger. Thus, the grafted feather keratin using the acrylate monomers with shorter alkyl chains has better affinity to polyester fibres, which are the main component of polyester/cotton(65/35) yarns. The adhesion of the corresponding modified feather keratin sizes, such as the ones grafted with MA and EA, to polyester fibres is relatively high. Thus, after taking both paste viscosity and adhesive capacity into consideration, we find that the shortening of alkyl chains of acrylates is efficient to decrease the amount of polyester/cotton yarn hairiness.

As far as feather keratin-*g*-PAA is concerned, it has poor affinity to polyester fibres due to the stronger molecular polarity and the lack of ester groups of the grafted branches. The feather keratin-*g*-PAA has lower adhesion to polyester fibres than feather keratin-*g*-poly(AA-co-acrylate), though its sizing paste has the highest viscosity in all the samples. When alkyl chain of the acrylates is short enough (e.g. EA and MA), the beneficial effect of high adhesive capacity of the feather keratin-*g*-poly(AA-co-acrylate) to polyester fibres may outweigh the adverse effect of decrease in apparent viscosity of the sizing paste on the ability to eliminate the yarn hairiness. Therefore, the hairiness of the yarns sized by feather keratin-*g*-PAA falls in between that of the yarns sized by feather keratin-*g*-P(AA-co-EA) and feather keratin-*g*-P(AA-co-BA).

4 Conclusion

4.1 The grafting of acrylate monomers onto the molecular chain of feather keratin is an effective way to improve sizing properties of the grafted feather keratin for high polyester content warp yarns. The alkyl chain length of acrylate monomers has remarkable influence on the grafting parameters and sizing performance of feather keratin-*g*-poly(AA-co-acrylate). Grafting ratio, apparent viscosity and its stability, tensile properties of sizing film, tensile strength & elongation, abrasion resistance and the hairiness amount of the polyester/cotton(65/35) blended yarns sized by feather keratin-*g*-poly(AA-co-acrylate) are all closely related to the alkyl chain length. The modified feather keratins exhibit various sizing properties after grafting with acrylates with different alkyl chain lengths.

4.2 With the increase in alkyl chain length of the acrylate, all the monomer conversions are around 95%, and higher feed monomer concentration is required in order to obtain similar grafting ratios of the modified keratin.

4.3 The preferred feather keratin-*g*-poly(AA-co-acrylate) used as sizing agents with better properties for high polyester content yarns can be prepared by choosing native feather keratin as substrate, AA and acrylate as grafting monomers, $K_2S_2O_8$ and $NaHSO_3$ as oxidant and reductant in redox system respectively. Feed molar ratio of AA/acrylate is kept constant as 1:4. The graft copolymerization should be carried out at 60°C and *p*H 4.0 under the protection of N_2.

4.4 The modified feather keratin grafted with acrylates with different alkyl chain lengths thus produced has different favorable sizing properties.

The feather keratin-*g*-P(AA-co-EHA) possesses higher parameters of 22 N/mm^2, 2.20%, 3.36 N, 8.66% and 173 cycles in tensile strength and elongation of sizing film, tensile strength, elongation and abrasion resistance of the sized polyester/cotton yarns respectively.

4.5 Meanwhile, the feather keratin-*g*-P(AA-co-MA) has higher parameters of 2.85 mPa·s, and 91.2% in apparent viscosity and its stability respectively. Moreover, the yarns sized by feather keratin-*g*-P(AA-co-MA) have the least harmful hairiness in all the sized yarns.

4.6 The two types of modified feather keratins, which are grafted with EHA and MA respectively, are expected to well meet various requirements in sizing process.

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